

Abstract

Interaction of oxygen and nitrogen impurities with dislocations in silicon single-crystals

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An experimental technique based on the immobilisation of dislocations by segregation of impurity atoms to the dislocation core (dislocation locking) has been developed and used to investigate the critical conditions for slip occurrence in Czochralski-grown and nitrogen-doped floating-zone-grown silicon crystals.

The accumulation of nitrogen and oxygen impurities along a dislocation and the resulting dislocation locking effect has been investigated in silicon samples subjected to different annealing conditions. In particular, the stress needed to unlock the dislocations after their decoration by impurities has been measured as a function of annealing duration and temperature.

The approach used in this study has allowed the determination of new diffusivity data for oxygen and nitrogen in silicon in the technologically important range of temperatures 350-850°C. No other data covering such wide temperature range are available in the literature.

In addition to transport properties, the binding energy of an impurity atom to a dislocation in silicon has been deduced from the experimental data in the case of oxygen and nitrogen impurities. A discussion in terms of the impurity species responsible for transport (monomers or dimers) and dislocation locking is also presented.

The role of oxide precipitates in the generation of glide dislocation loops and the parameters affecting the occurrence of slip have been investigated in silicon samples containing precipitates of different sizes and different morphologies.

The fundamental parameters deduced in this work have been used to develop a numerical model to investigate the effect of different heat treatments on the mechanical properties of silicon wafers containing a controlled distribution of impurities. This model has then been used to simulate real wafer processing conditions during device fabrication to show how they may be modified to increase dislocation locking. It is hoped that these results will have relevance to how wafers are processed in order to minimise or eliminate dislocation multiplication and consequent warpage.

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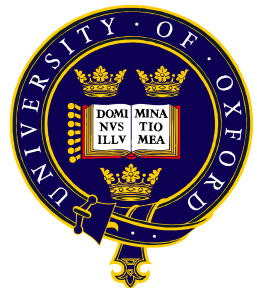
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Supervised by Dr. P. R. Wilshaw

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OxfordMaterials



*To my father, my mother and my wife
for their continuous love and support.*

Preface

This thesis is an account of the work carried out by the author in the Department of Materials, University of Oxford, under the supervision of Dr. P. R. Wilshaw.

No part of this thesis has been previously submitted for a degree at this or any other university. The work of other authors has been freely drawn upon and is duly acknowledged in the text. A list of cited references is given at the end of each chapter.

Some of the work described in the thesis has been presented by the author in three international conferences (EDS-2002, CMS-2002, ICDS-2003) and published in the following papers:

- 1) A. Giannattasio, S. Senkader, R. J. Falster, and P. R. Wilshaw, "Dislocation locking by nitrogen impurities in FZ-silicon", *Physica B*, **340-342**, 996 (2003)
- 2) S. Senkader, A. Giannattasio, R. J. Falster, and P. R. Wilshaw, "Dislocation locking in silicon by oxygen and oxygen transport at low temperatures", *Solid State Phenomena*, **95/96**, 43 (2003).
- 3) A. Giannattasio, S. Senkader, S. Azam, R. J. Falster, and P. R. Wilshaw, "The use of numerical simulation to predict the unlocking stress of dislocations in Cz-silicon wafers", *Microelectronic Engineering*, **70**, 125 (2003).
- 4) S. Senkader, A. Giannattasio, R. J. Falster, and P. R. Wilshaw, "Dislocation locking by oxygen in silicon: new insights to oxygen diffusion at low temperatures", *proceedings of the 202nd Meeting of The Electrochemical Society*, Salt Lake City, Utah (October 2002). Volume: PV 2002-20 High Purity Silicon VII (published by The Electrochemical Society Inc., 2002), p.171.
- 5) A. Giannattasio, S. Senkader, R. J. Falster, and P. R. Wilshaw, "Generation of dislocation glide loops in Czochralski silicon", *J. Phys.: Condens. Matter*, **14**, 12981 (2002).
- 6) S. Senkader, A. Giannattasio, R. J. Falster, and P. R. Wilshaw, "On the dislocation-oxygen interactions in Cz-Si: Oxygen diffusion and binding at low temperatures", *J. Phys.: Condens. Matter*, **14**, 13141 (2002).
- 7) A. Giannattasio, S. Senkader, R. J. Falster, and P. R. Wilshaw, "The role of prismatic dislocation loops in the generation of glide dislocations in Cz-silicon", *Computational Materials Science*, **30**, 131 (2004).
- 8) A. Giannattasio, J.D. Murphy, S. Senkader, R.J. Falster, P.R. Wilshaw, "Impurity locking of dislocations in silicon", *High Purity Silicon VIII*, ed. C. Claeys, M. Watanabe, R. Falster, and P. Stallhofer, (The Electrochemical Society Inc., Pennington, 2004).

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Chapter 1: Introduction and literature survey

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1. Background

The worldwide semiconductor industry has an enormous importance in modern society and in the economy. It is worth reminding the reader that its annual turnover reaches 200 billion dollars and the average annual growth rate over the last 30 years is 14%¹. The reason for this success, particularly in the last ten years, is found in the rapid development of information technology and everyday communication, especially the internet and mobile phones.

Pure single-crystal silicon is the basic material for most electronic devices. However, silicon crystals used in microelectronics contain oxygen and other impurities whose effects, in many cases, have not been investigated or fully understood. In spite of the strong impact on society and the economy, the volume of academic research into silicon processing technology has been very small compared to studies on compound semiconductors. On the other hand, it is well known that defects and impurities in silicon play an important role in industrial productivity² and more coordination between academic university based and industrial research could lead to better quality silicon products.

Today, the main challenge in the development of silicon crystal growth is the transition from 200 to 300 mm diameter wafers³. The reasons for this conversion are mainly economic since it is necessary to reduce the production cost per unit area of wafer. In commercial silicon wafers, however, thermal and gravitational stresses^{4,5} undergone during the fabrication process induce the generation and movement of dislocations, which in turn lead to wafer warpage. Since these stresses are considerably higher in larger diameter wafers, the study of the interaction between dislocations and impurities in silicon crystals is

becoming rather important and the possibility of dislocation immobilisation by impurities, resulting in a reduction of wafer warpage, makes this field of investigation very attractive. Experimental data concerning impurity-dislocation interactions in silicon are rare and most of the information contained in the literature is related to the sole effect of oxygen impurities. Thus, there is a need to investigate more extensively the effect of oxygen and/or other impurities on the mechanical properties of wafers and, more particularly, on dislocation behaviour in silicon crystals.

Recently, nitrogen-doped silicon wafers have become technologically interesting because nitrogen suppresses vacancy related defects, can be used in the formation of oxynitrides as dielectric layers in metal oxide semiconductors (MOS) and has a strong immobilisation effect on dislocations.

In this thesis, the onset of dislocation movement and the interaction of oxygen and nitrogen impurities with stationary dislocations in silicon is investigated from the experimental point of view. The evidence that the mechanical properties of silicon wafers during device processing can be significantly improved after dislocation decoration with impurities will be shown in the following chapters. Although the original motivation for this research was to investigate the mechanical effects of impurities on silicon wafers during processing, equally important information has been gained about the transport properties of oxygen and nitrogen in silicon.

2. Silicon growth techniques

Silicon single-crystals used for device fabrication are grown either by the Czochralski (Cz)⁶ or the floating-zone (FZ)⁷ technique. Cz-grown silicon crystals are preferred as basic material to fabricate very large-scale integration (VLSI) devices. The reason for this is their

lower cost compared to the FZ-grown wafers and also the differences in their mechanical strength at high temperatures, as Cz-grown silicon wafers are less susceptible to slip in comparison with FZ-grown silicon wafers^{8,9}. In addition, Cz wafers are favourite because their diameter can be larger (up to 300 mm) than that of FZ wafers.

In 1958, Dash¹⁰ developed a special pulling technique to obtain dislocation free crystals using the Cz method with the introduction of a crystal neck. The experimental set-up for the pulling of single crystals by this method is illustrated in Fig. 1-1. Polycrystalline silicon is held in a silica (SiO_2) crucible and is heated up to the melting point. A single crystal seed is first dipped into the melt and is slowly withdrawn vertically, whereby the liquid silicon crystallises around the seed. During this process, oxygen atoms can diffuse from the silica crucible to the melt. For that reason, in Cz-silicon crystals oxygen is always present as an interstitial impurity in concentrations of about $10^{17} - 10^{18} \text{ cm}^{-3}$, whereas the concentration of carbon ($<10^{15} \text{ cm}^{-3}$) or other non-intentionally introduced impurities is usually below the detection limit.

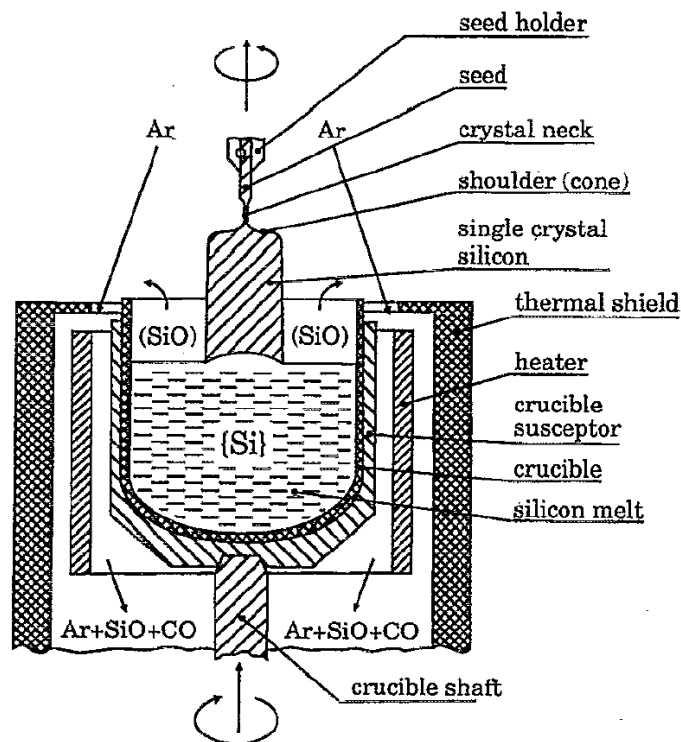


Figure 1-1: Czochralski method for pulling silicon single-crystals (after Borghesi⁹).

At temperatures typical to device processing (less than 1200°C), oxygen in Cz-silicon is a supersaturated solid solution. In fact, as is shown in Fig. 1-2, at temperatures lower than 1400°C the equilibrium state of the Si-O system is reached by means of oxygen precipitation, i.e., formation of SiO₂ particles (oxide precipitates) in the silicon crystal. The processing temperature, together with other parameters such as thermal history and initial oxygen concentration, plays an essential role in determining the formation and the morphology of oxide precipitates.

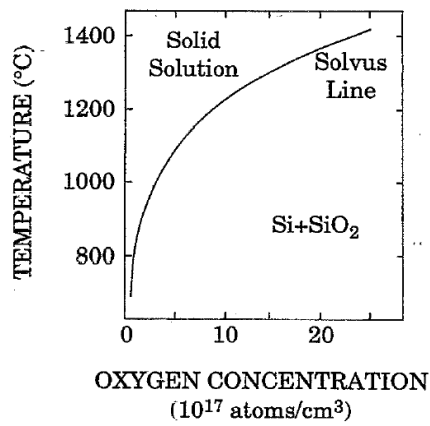


Figure 1-2: Partial phase diagram of the Si-O system (after Borghesi⁹).

The presence of oxygen and associated precipitates in Cz-silicon wafers induces both beneficial and detrimental effects on wafer yield. For example, it is known that under certain conditions, dislocation decoration with oxygen atoms can improve the mechanical properties of wafers at high temperatures¹¹. On the other hand, while oxide precipitates in silicon bulk act like gettering centres for metallic impurities (*intrinsic* or *internal* gettering) and hence are required to fabricate high-purity active regions for the integrated circuits, the same precipitates behave as dislocation sources under an applied stress. In turn, this can lead to wafer warpage and a reduction in device yield¹².

Zone refining of crystals has been known for more than 50 years as a method to increase the purity of the crystals. The purification method is based on the segregation of most impurities to the liquid phase during the liquid/solid transition. Many different purification techniques exist, but the most interesting is the FZ refining method, where the floating zone is suspended between the melting and the freezing interfaces (Fig. 1-3). FZ technology has been improved especially for the growth of silicon single-crystals. During the FZ purification process, most of the impurities initially present in a silicon crystal segregate to the end of the ingot and remain confined in that area. Since the zone is free to float with no contact with crucibles and other possible contaminant sources, it is possible to grow monocrystalline silicon with the highest purity. This is important for a number of electronic and optoelectronic applications such as high efficiency solar cells¹³, photodetectors¹⁴, high resistivity silicon for radio frequency devices and micro-electro-mechanical systems (MEMS)¹⁵.

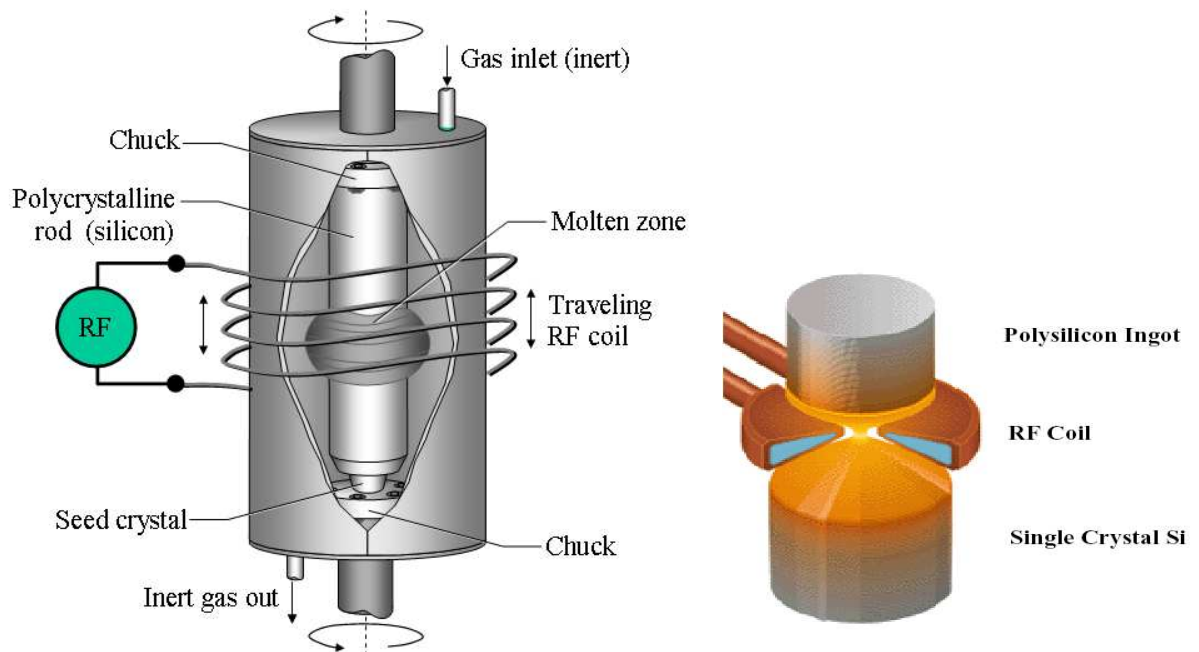


Figure 1-3. Schematic representations of Float-Zone growth technique (source: www.usna.edu).

FZ technology represents the best method for high-purity crystal growth and silicon ingots obtained with this technique have unique properties which cannot be found in silicon materials grown with other methods. For example, FZ-silicon can be grown with resistivity exceeding $10^5 \Omega \cdot \text{cm}$ because of the intrinsic process purity. The concentrations of oxygen and carbon in FZ wafers can be well below the detection limit ($<10^{15} \text{ cm}^{-3}$) with Fourier-Transform Infra-Red spectroscopy (FT-IR). However, the main drawback for FZ-grown silicon is represented by the elevated production cost, which is much larger than that of Cz-grown materials. Moreover, the absence of oxygen precipitation in bulk FZ-silicon imposes the application of other methods for impurity gettering (*extrinsic* gettering) during device processing. The important disadvantage is the tendency of FZ wafers to warp during thermal processing. As mentioned before, FZ-silicon crystals are generally more susceptible to plastic deformation than Cz-silicon crystals when subjected to high temperature treatments and this is attributed to the low oxygen concentration in FZ materials¹⁶.

3. Oxygen impurities in silicon

3.1 Different species and anomalous diffusion of oxygen

Since the 1950s, many studies have been performed on the behaviour of oxygen in silicon, but many aspects remain unclear. It is widely accepted that isolated oxygen atoms dissolved in silicon are most stable at interstitial sites and are covalently bonded to two neighbouring silicon atoms¹⁷ as shown in Fig. 1-4. However, there is strong evidence for oxygen-oxygen interaction at $T < 500^\circ\text{C}$ with the formation of fast diffusing O_2 dimers¹⁸. These observations have led to significant advances in understanding the growth and structure of small oxygen

clusters, identified with the so-called thermal donor defects. It is known that electrical and transport properties of oxygen dimers are rather different from those of oxygen monomers, therefore it is important to determine which species is dominant in the particular temperature range investigated. Theoretical studies showed that at low temperatures oxygen dimers can also form complexes. For example, a proposed structure for an interstitial- O_2 complex¹⁹ is shown in Fig. 1-5.

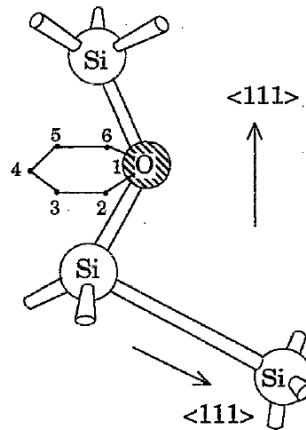


Figure 1-4: Interstitial position of an oxygen atom in silicon lattice covalently bonded with two neighbouring silicon atoms. The equivalent interstitial positions are indicated (*after Borghesi*⁹).

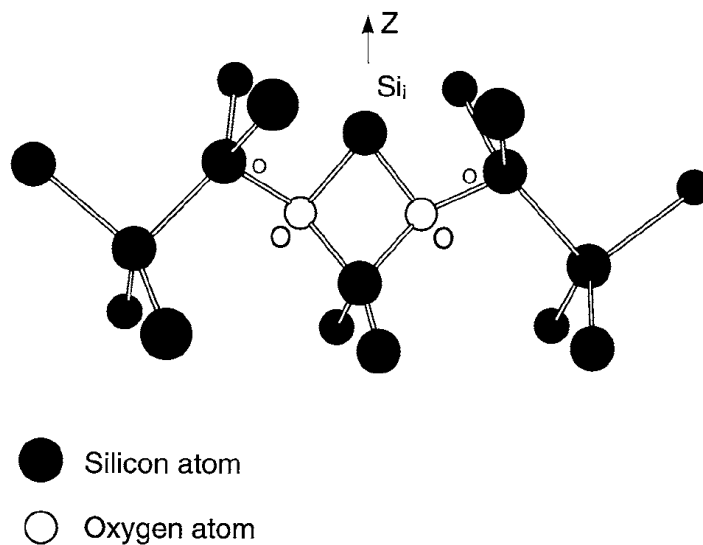


Figure 1-5. Proposed structure of the I- O_2 complex for the core of thermal donor centres, with unperturbed lattice positions marked by small open circles (*after Corbett*¹⁹).

The magnitude of oxygen diffusivity affects the general behaviour of oxygen in silicon at different temperatures. For example, the diffusion coefficient largely controls the kinetics of oxygen precipitation. For this reason, it is important to study and understand the mechanism of oxygen diffusion at different temperatures and/or in presence of other defects in silicon crystals. In general, the temperature dependence of the diffusion coefficient D of an impurity in silicon is expected to have the form²⁰

$$D = D_0 \exp\left(-\frac{E_D}{kT}\right) \quad (1.1)$$

where D_0 is the pre-factor, E_D is the activation energy of the diffusion process, k is Boltzmann's constant and T is the absolute temperature. Several techniques such as secondary-ion-mass-spectrometry (SIMS), charged particle activation analysis (CPAA) and X-ray diffraction have been used to study oxygen diffusivity in the high-temperature range (700-1200°C), whereas infrared (IR) spectroscopy has been used to measure the oxygen diffusivity in the low-temperature range (220-360°C) by means of stress-induced dichroism data. For temperatures lower than 400°C it was found that oxygen mass transport is by single atomic hops with an activation energy of about 2.5 eV (Fig. 1-6). The same activation energy was measured at temperatures higher than 700°C.⁹ However, the oxygen diffusivity at temperatures in the range 400-700°C is not easy to measure and therefore data in the literature are scarce and deduced from indirect observation. At these temperatures, several experiments indicate that the rate of oxygen transport is anomalous (Fig. 1-7) and deviates from expected behaviour of single atomic jumps^{21,22,23,24}.

It has been observed that the high nucleation rate of oxygen precipitates and unexpected long range out-diffusion of oxygen from wafer surfaces at lower temperatures cannot be explained with normal oxygen diffusivity data extrapolated from high temperature measurements. One of the earliest indications of this behaviour was thermal donor formation.

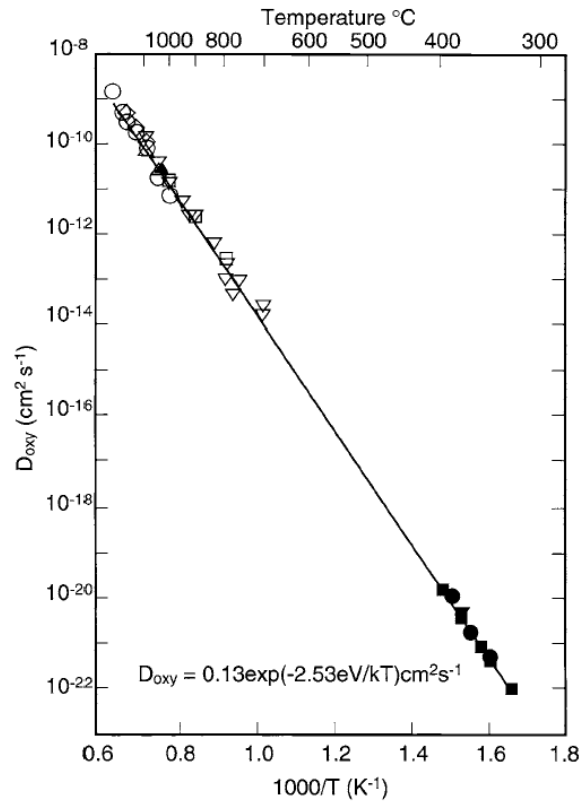


Figure 1-6. Measured values of 'normal' oxygen diffusion together with a line fitted to the data by $D_{\text{ox}} = 0.13 \exp(-2.53 \text{ eV}/kT) \text{ cm}^2 \text{s}^{-1}$. The data points for the high temperatures relate to measurements of SIMS profiles, except for one point (black triangle) that is obtained from internal friction measurements. The low temperature data refer to the relaxation of stress-induced dichroism (single atomic jump). Further details are given in references [18, 25] (after Newman).

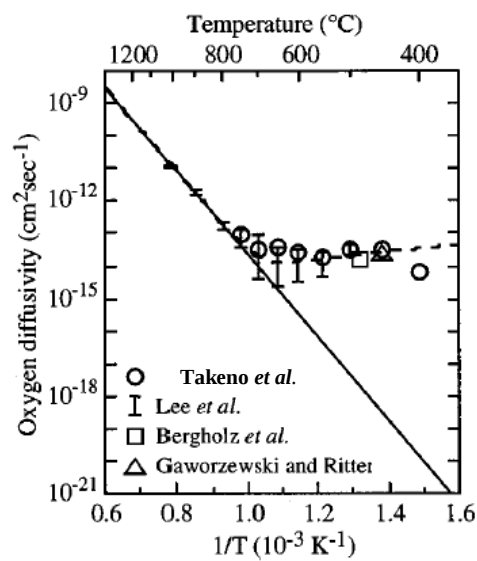


Figure 1-7. Anomalous diffusion between 400°C and 700°C deduced from oxygen precipitation experiments by different authors (after Takeno²¹).

Thermal donors are oxygen-containing electrically active clusters formed in the temperature range of about 350-550°C. The rates of thermal donor formation, corresponding to an activation energy of about 1.7-1.8 eV, are much larger than those expected from diffusion by single atomic jumps²⁶. Therefore it is necessary to invoke mechanisms assuming fast diffusing oxygen containing species to explain the kinetics of thermal donors. Enhanced oxygen diffusivity in the middle range 400-650°C has been attributed to different species such as interactions of oxygen atoms with self-interstitials (I atoms), lattice vacancies (V “atoms”), a second oxygen atom (to form O₂ dimers), fast diffusing metallic contaminants, carbon, nitrogen or hydrogen impurities²⁷. Although the techniques used to determine the oxygen diffusivity at high temperatures are not suitable for low temperature measurements, in this thesis the oxygen diffusion coefficient in silicon has been deduced between 350°C and 700°C by using a novel technique which will be described in detail in Chapter 2.

3.2 Oxygen precipitation

As mentioned before in Section 2, precipitation of oxygen in silicon wafers has become a technologically important process since it provides the so-called internal gettering by which it is possible to remove the fast diffusing metallic impurities from the active regions of devices.

The first stage of oxygen precipitation in silicon is nucleation, a process leading to the formation of aggregates of a few oxygen atoms, the so-called “nuclei”, within the silicon lattice. Once formed, precipitate nuclei can grow into oxide precipitates or dissolve, depending on various crystal parameters and thermal treatments performed. The fundamental parameter for nucleation (and, therefore, precipitation) is the ratio between the concentration of interstitial oxygen present in the silicon crystal and the oxygen solubility limit (which is a function of temperature, as shown in Fig. 1-2). Another important

parameter for nucleation is the critical radius r_c , distinguishing the nuclei which grow further ($r > r_c$) from those which are going to dissolve ($r < r_c$) upon thermal treatment. The critical radius r_c for oxygen in silicon depends on self-interstitial and vacancy concentration, impurity type and content, elastic properties and temperature. In the case of oxygen, the typical size of a precipitate nucleus is less than 5 nm²⁸.

If the conditions are favourable for nuclei growth, oxygen precipitation takes place during further annealing. As a consequence, small oxide particles (SiO_x , with $1 \leq x \leq 2$) form within the silicon crystal, normally with uniform spatial distribution. It is largely accepted that precipitation is driven by diffusion kinetics over a wide temperature range. Ham²⁹ in 1958 published a general theory to explain the kinetics of precipitation in a supersaturated solution by considering the phenomenon as diffusion limited. The validity of the model has been verified by different authors and experimentally confirmed for silicon in the range from 650 to 1050°C³⁰. Starting with some basic hypotheses (defect-free crystal, regular distribution of precipitates, etc.) and solving the following Fick's equation (with appropriate boundary conditions),

$$\frac{\partial C_{ox}(r,t)}{\partial t} = D \nabla^2 C_{ox}(r,t) \quad (1.2)$$

where D is the oxygen diffusion coefficient, Ham's theory allows the calculation of the oxygen concentration profile $C_{ox}(r, t)$ as a function of the time t and distance r from the centre of the precipitate. The small oxide particles generated by using a specific heat treatment can grow during further annealing of silicon crystals at high temperatures. The temporal evolution of the oxide precipitate radius $r(t)$ can also be deduced from Ham's calculation in the case of spherical precipitates and, according to this theory, at the early stage of precipitation r increases as $t^{1/2}$. Similarly, the major semi-axis $a(t)$ can also be predicted in the case of spheroid precipitate growth where the aspect ratio of the precipitates is known.

The morphology of precipitates depends mainly on the annealing temperature and can be justified on the basis of thermodynamics, considering the different contributions to the total free energy ΔG_{tot} associated with the oxygen precipitation process and their dependence on precipitate shape, annealing time, and temperature. The total free energy will contain terms associated with the phase change at the silicon/precipitate interface ΔG_K , the free energy contribution related to the oxygen transport ΔG_S , the interface energy ΔG_γ , the strain energy ΔG_σ and the formation energy for interstitial point defects ΔG_I . Each of these terms can be plotted as a function of the aspect ratio of the precipitate. The dominant energy terms among those listed above will control the actual shape of the precipitates (disk, sphere, needle, etc.) at different temperatures. A detailed discussion about the role of these various contributions to the total free energy can be found in ref. [9]. At low temperatures (about 400-650°C) the strain-energy contribution ΔG_σ and term associated with the creation of an interface energy ΔG_γ dominate and thus precipitates grow as *needles* in this temperature range. At intermediate temperatures (650-950°C), ΔG_σ decreases as the strain-relieving processes (interstitial and dislocation generation) become important, whereas ΔG_γ and ΔG_I increase such that *disk-shaped* precipitates (or *platelet*, Fig. 1-8) are typical. At high temperature (over 950°C) strain is completely released and the precipitates take the preferential shape of the *octahedron* with eight equivalent $\{111\}$ faces (the surface energy of silicon is minimum in these planes) instead of the spherical shape (Fig. 1-8). Truncated octahedral shapes are also possible at high temperatures. This trend has been confirmed by many direct TEM observations from different authors and is in good agreement with the theory of diffusion limited oxygen precipitation in silicon³¹.

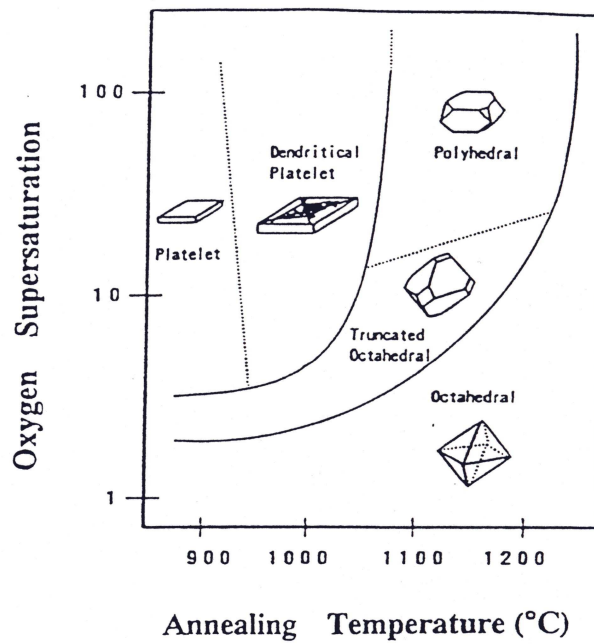


Figure 1-8. Shape of oxide precipitates as a function of annealing temperature and supersaturation level (after Fujimori ³²)

For every two oxygen atoms that are added to a precipitate, the ejection of one interstitial atom (I-atom) is required to accommodate the local increase in volume³³. Therefore, in parallel with oxygen diffusion there is also an I-atom diffusion leading to the clustering of I-atoms. Diffusion and aggregation of the generated I-atoms together with the local build-up of stress lead to the formation of small punched-out dislocation loops adjacent to the SiO₂ precipitates. This kind of defect will be described in Section 6.1.

The precipitation process is reversible to some extent, thus there is partial dissolution of existing SiO₂ particles during a second anneal at a higher temperature. It has been noted that extended anneals lead to continued growth of the larger precipitate particles and a progressive loss of the smaller particles due to their dissolution (Ostwald ripening)³⁴.

Recent experimental and theoretical studies on the density of precipitates in Cz-grown silicon³⁵ have shown a good agreement of predicted values (according to the classical theory of nucleation) with the experimentally measured number of precipitates, at nucleation temperatures above 650°C. Below this temperature, however, serious disagreements

between the calculated and experimental data are evident. The explanation could be found in the previously mentioned enhanced diffusion of oxygen at temperatures below 650°C. In fact, because the nucleation rate is proportional to the atomic mobility, an enhanced diffusion would give a larger nucleation rate and consequently increase precipitate density over that calculated assuming normal oxygen diffusion.

Enhanced oxygen precipitation has recently become a matter of debate. The interest in this topic is due to the fact that future integrated circuit production will require temperatures below 650°C because of the smaller feature sizes. On the other hand, a satisfactory level of oxygen precipitation, even at low temperature, is necessary to trap diffusing metallic contaminants. Recent work proved that carbon atoms can actively participate in oxygen precipitation³⁶. In analogy with carbon (but technologically more interesting), other studies have shown that nitrogen-doped Cz-silicon crystals show enhanced oxygen precipitation at temperatures over 1000°C³⁷. In fact, nitrogen increases the number of oxide precipitate nuclei that are stable at high temperature compared to the number of precipitates in conventional (not N doped) Cz- silicon crystals, as will be explained in the following section.

From a mechanical point of view, oxygen precipitation has a detrimental effect on silicon wafers. It is known empirically that the presence of oxide precipitates in the silicon lattice strongly affects the mechanical stability of the crystal¹² at high temperatures. The misfit stress generated at the precipitate/matrix interface (Fig 1-9) is responsible for the formation of dislocation loops which in turn can lead to wafer warpage under certain stress and temperature conditions. However, the dependence of this process on precipitate parameters (size, density, shape) has not been properly investigated and the mechanism of dislocation generation is not fully understood. This study is important since in VLSI technology the requirement is to find an appropriate configuration for the oxide precipitates in silicon wafers by which precipitates do not release dislocations whilst remaining effective

gettering centres for impurities, as may be the case of very small oxide particles in the silicon matrix.

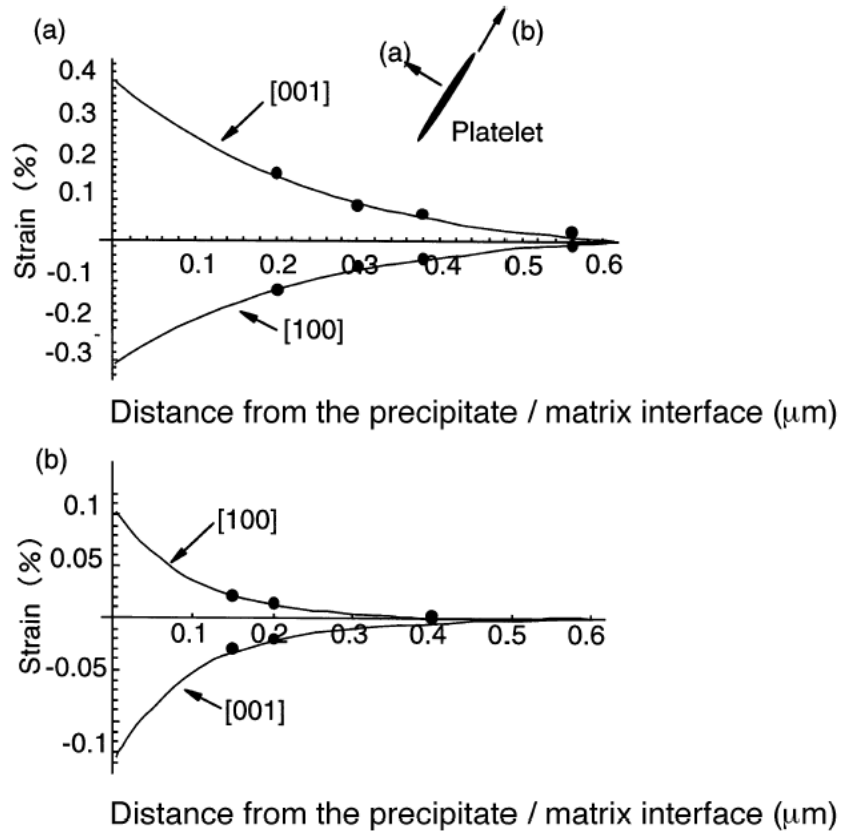


Figure 1-9. Variation of the lattice strain as a function of the distance from the precipitate/matrix interface in the case of the measured direction (a) vertical to the flat plane of the platelet, (b) parallel to the flat plane of the platelet. The strain was measured by using CBED on a precipitate with size 50 nm (after Sueoka³⁸).

4. Nitrogen impurities in silicon

4.1 Overview of nitrogen incorporation in silicon

Doping silicon with nitrogen impurities has recently become attractive because nitrogen can suppress the generation of oxygen-related donors³⁹ and enhance oxygen precipitation for intrinsic gettering⁴⁰. Void defects in Cz-grown silicon are known to reduce the yield and reliability of VLSI devices⁴¹. Recently, nitrogen was found to suppress the generation of such void defects and to improve the gate oxide integrity (GOI) of devices⁴². In addition, nitrogen allows a significant increase in the mechanical stability of wafers^{43,44,45,46} and reduces wafer warpage, especially when oxygen is not present in high concentrations⁴⁷ (below 10^{17} cm^{-3}). Therefore, nitrogen-doped Cz-silicon is expected to be a key material in the VLSI device industry in the future.

It is known that interstitial nitrogen is electrically inactive in silicon⁴⁸ (although it becomes active when it forms complexes) and has a strong capability for immobilizing dislocations even at very low concentrations. Thus, nitrogen could be used as a dopant in FZ-silicon to reduce wafer warpage during device processing. Moreover, nitrogen-doped FZ-silicon represents a relatively simple system to investigate, whereas complicated nitrogen-oxygen interactions are usually present in Cz-silicon.

Quantitative data of the chemical and physical properties of nitrogen in silicon are rare, although nitrogen in silicon was detected over 40 years ago⁴⁹. This is partly because nitrogen has a low solubility in silicon and measurements become difficult at very low concentrations. The solubility of nitrogen in molten silicon⁵⁰ was determined to be about $6 \times 10^{18} \text{ cm}^{-3}$, whereas the concentration in solid silicon at the melting point is dependent on the growth velocity of the crystal. This is due to weak nitrogen incorporation caused by a very small segregation coefficient, approximately 7×10^{-4} , which is defined as the equilibrium concentration ratio between solid and liquid⁶¹. The solid solubility at the melting

point was deduced to be $(4.5 \pm 1.0) \times 10^{15} \text{ cm}^{-3}$ by extrapolation to zero growth velocity. This value is much smaller than solid solubility values of carbon and oxygen or other group V elements.

In high-purity FZ-silicon crystals, nitrogen can be incorporated as strongly bound nitrogen pairs, single interstitial atoms, substitutional atoms and as complexes with interstitials or vacancies. Early theoretical studies⁴⁸ suggested that nitrogen molecules are the more stable species: nitrogen molecules can be accommodated in a tetrahedral interstice since their molecular length is $2.2 \text{ \AA}$, whereas the diameter of tetrahedral interstice in silicon is $2.34 \text{ \AA}$. More recently, *ab initio* calculations have shown that in oxygen-free silicon crystals the dominant species is the nitrogen pair (or *dimer*, N_2) consisting of two neighbouring $\langle 100 \rangle$ oriented nitrogen-silicon split interstitials⁵¹ (or *monomers*, N_1) arranged in an antiparallel configuration as shown in Fig. 1-10 where the four N-Si bonds form a square lying on $\{011\}$.

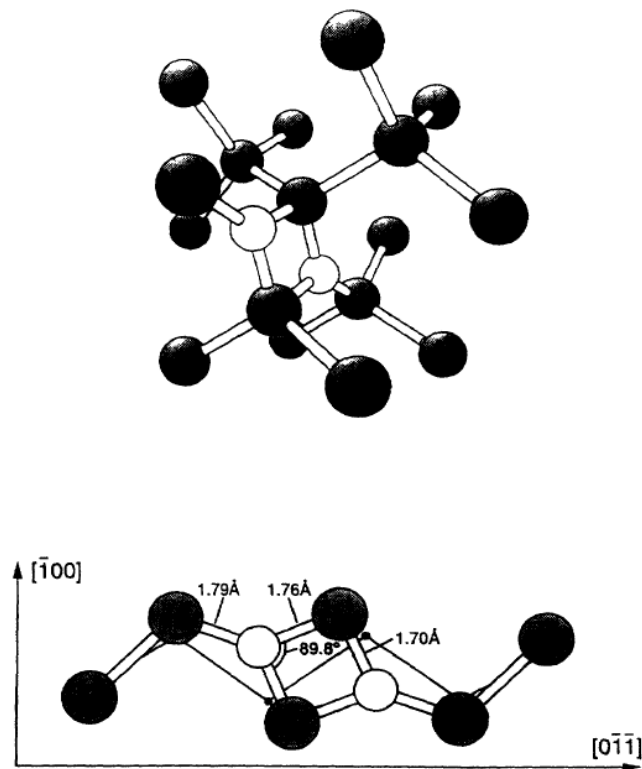


Figure 1-10: The antiparallel model for N-pair defect in silicon (after Jones⁵¹).

Although substitutional nitrogen, N_s , is a rare defect, it has been detected by electron-paramagnetic-resonance (EPR)⁵² and localized vibrational mode (LVM) spectroscopy⁵³. However, both experimental and theoretical data agree that the nitrogen pair configuration is significantly more stable than single interstitial or substitutional nitrogen at low temperatures^{54,55}. In addition, the presence of nitrogen as pairs could explain the electrical inactivity of nitrogen in silicon. Nitrogen dimers N_2 will partially dissociate into nitrogen monomers N_1 upon increasing temperature. The dissociation reaction for nitrogen dimers can be written as:



and the dissociation constant is given by:

$$k_d = \frac{[N_1][N_1]}{[N_2]} = \exp\left(\frac{\Delta G}{kT}\right) \quad (1.4)$$

where ΔG is the free energy change associated with forming the dimer from single interstitial atoms.

The central question concerning the nitrogen species in silicon is which state (N_2 or N_1) prevails in certain relevant temperature ranges, such as at the melting point, when nitrogen affects the incorporation of vacancies and self-interstitials⁵⁶. In turn, transport properties of nitrogen strongly depend on the dominant nitrogen species in the particular temperature range of interest. The first-principle calculations for the binding energy of nitrogen dimers, as reported in the literature, are strongly scattered: from 4.3 eV⁵⁷ down to 1.7 eV⁵⁸. The former energy would imply that the dimer state is stable up to the melting point. The latter energy would imply a strong dissociation of nitrogen pairs above a certain temperature. However, the more recent studies favour the nitrogen pair being the dominant species even near the melting temperature⁵⁷.

Isolated nitrogen monomers have been observed in nitrogen-implanted silicon, although they lie below the detection limit in doped as-grown material⁵¹. Moreover, monomers are mobile and diffuse very quickly during annealing of silicon crystals at high temperatures, thus rapid cooling is necessary for the incorporation of nitrogen in the form of the monomer rather than forming other defect complexes⁵⁹. Recent theoretical investigations have suggested the formation of nitrogen complexes with vacancies (N_2V and N_2V_2) instead of simple nitrogen pairs. In fact, it is known that in nitrogen-doped FZ-grown (NFZ) silicon wafers, nitrogen can suppress interstitials and vacancy related micro-defects even at very low concentrations⁶⁰, with a significant improvement of the wafer defect-free area and device yield. The dominant reaction for the suppression of vacancies in FZ-grown silicon is suggested to be⁶¹:

$$N_2 + V \leftrightarrow N_2V \quad (1.5)$$

whereas the reaction for the interstitial aggregation is:



It was demonstrated by first principle calculations that the nitrogen pair can indeed form stable N_2V and N_2V_2 complexes, the latter being more stable due to a larger formation enthalpy⁶² (Fig. 1-11).

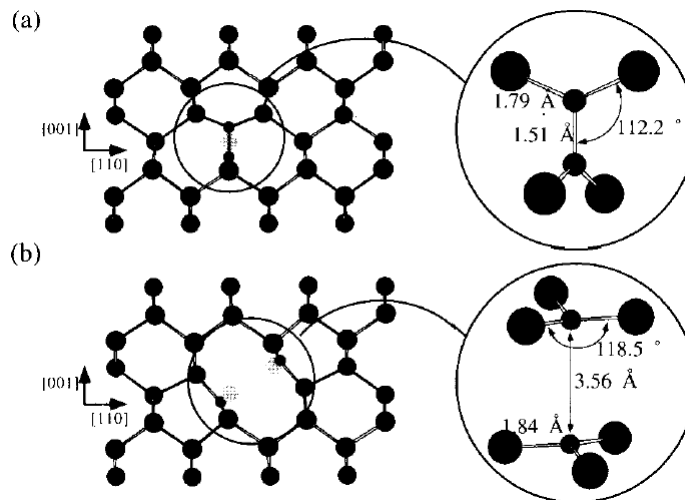


Figure 1-11. Atomic configurations for (a) the defect complex formed by one silicon vacancy and two N atoms and (b) that constructed with two Si vacancies and two N atoms (after Kageshima⁶²).

While nitrogen in FZ wafers inhibits the generation of vacancy-related defects, in nitrogen-doped Cz-grown silicon crystals, the oxygen content favours the formation of N-O complexes at high temperatures:



Thus, no N_2 is available for the reaction with vacancies and the desirable defect suppression effect is reduced. However, at lower temperatures, the equilibrium of the reaction (1.7) shifts to the left-hand side and N_2V complexes can form again, suppressing the vacancy-vacancy aggregation⁶¹. Depending on the temperature at which an appreciable N_2 concentration builds up, the aggregation temperature of vacancies and hence the density/size distribution of voids varies. In fact, it was demonstrated⁶¹ that nitrogen has a notable effect on the density/size distribution of vacancy aggregates: the higher the nitrogen concentration the higher the defect density, but the lower the defect size. The increase of free vacancy concentration and then the increase of stable precipitate nuclei at high temperature gives rise to an enhanced oxygen precipitation in nitrogen-doped Cz-grown silicon^{63,64}. This behaviour could be important in order to improve the gettering efficiency of metallic contaminants in low thermal budget processes. The small size of nitrogen atoms suggests that the Si-Si bonds along [011] are dilated, and are therefore sites where oxygen atoms would preferentially precipitate. Studies using IR-absorption suggested the existence of NNO complexes^{65,66}, which is shown in Fig. 1-12.

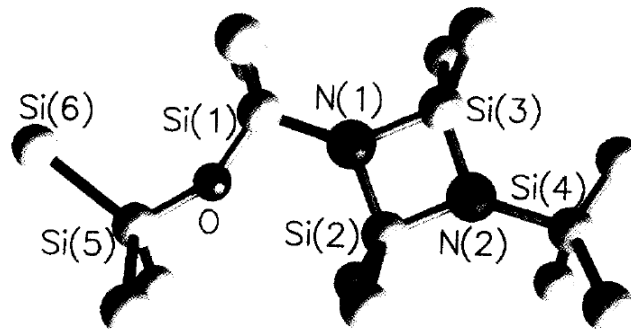


Figure 1-12. Structure of the nitrogen-pair oxygen defect shown in the (110) mirror plane of the defect (after Rasmussen⁶⁶).

4.2 Nitrogen diffusivity in silicon

Diffusion of impurities in silicon is usually determined by measuring the depth profile of the free carrier concentration or of radio-isotopes. Measurement of nitrogen diffusion in silicon is difficult because of its limited electrical activity and absence of suitable radioactive isotopes. The diffusion coefficient of substitutional nitrogen atoms was first determined by Clark *et al.*⁶⁷. They implanted nitrogen atoms in 100 $\Omega\cdot\text{cm}$ p-type silicon and annealed at different temperatures up to 1200°C. The diffusivity was obtained from the dependence of the p-n junction depth on the annealing time, which was caused by diffusion of the electrically active nitrogen species. The expression of diffusivity given by Clark is:

$$D_N^{(\text{Clark})} = 0.87 \exp\left(-\frac{3.29}{kT} \text{eV}\right) \text{ cm}^2\text{s}^{-1} \quad (1.8)$$

However, this expression is considered not very accurate and probably refers to those nitrogen complexes which are electrically active. A method to measure the diffusivity of nitrogen pairs based on the irradiative activation of nitrogen was suggested by Denisova *et al.*⁶⁸. The following expression for the diffusivity of nitrogen pairs was deduced from conductivity measurements in conjunction with etching techniques:

$$D_N^{(\text{Denisova})} = 3 \times 10^{-2} \exp\left(-\frac{2.63}{kT} \text{eV}\right) \text{ cm}^2\text{s}^{-1} \quad (1.9)$$

More recently, Itoh and Abe⁶⁹ determined the diffusion coefficient from the measurement of out-diffusion profiles in FZ-crystals doped with nitrogen during crystal growth. The annealing temperature range was 800-1200°C and the nitrogen concentration was determined by using secondary ion mass spectrometry (SIMS). The diffusivity expression in this case was found to be

$$D_N^{(\text{Itoh})} = 2.7 \times 10^3 \exp\left(-\frac{2.8}{kT} \text{eV}\right) \text{ cm}^2\text{s}^{-1} \quad (1.10)$$

The expression (1.10) is widely considered the most reliable^{71,72} for nitrogen diffusivity and the values are about five orders of magnitude higher than previous results (Fig. 1-13). These values were partly confirmed by Hara⁷⁰ (a single data point) during his experiments with electrically active nitrogen-oxygen complexes in Cz-grown silicon.

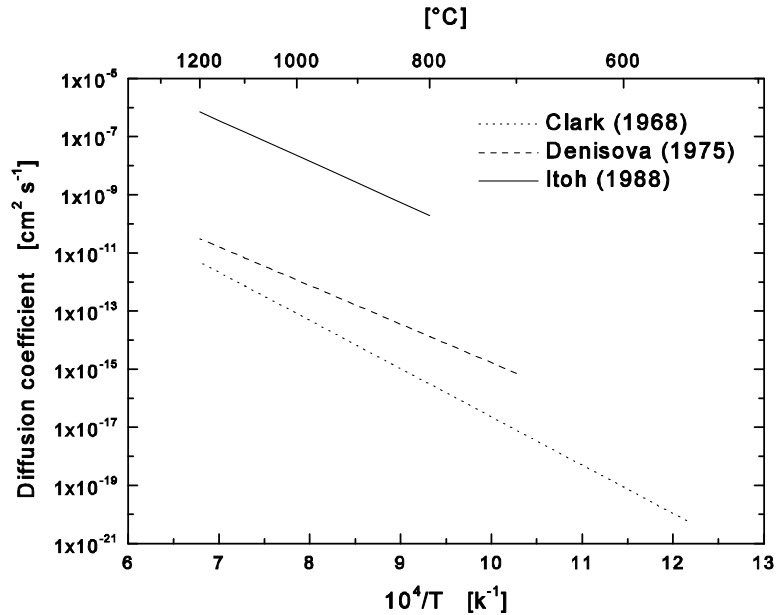


Figure 1-13. Diffusion coefficient of nitrogen measured by Clark (1968), Denisova (1975) and Itoh (1988) represented within the respective temperature range of investigation.

It is interesting noting that the nitrogen diffusion coefficient is three orders of magnitude larger than the value of oxygen at 1100°C (see Fig. 1-6). The authors⁶⁹ justified these results considering nitrogen dimers as the very fast diffusing species, although there was no direct evidence. However, it is not trivial to associate a well defined nitrogen species responsible for transport (monomer, dimer) to the expression for diffusivity (1.10) deduced by Itoh in the temperature range 800-1200°C. Hockett *et al.*⁷¹ observed anomalous diffusion in nitrogen ion implanted samples and suggested that the results cannot be explained by considering the nitrogen dimers as the only species responsible for nitrogen transport. The anomalous behaviour of nitrogen during diffusion experiments was also confirmed by

Mannino *et al.*⁷², but in this case it was suggested that nitrogen monomers have high diffusivity, whereas nitrogen dimers are practically immobile. This conclusion is obviously in contrast with that proposed by Itoh. Hockett and Mannino found diffusion profiles which show two peaks (Fig. 1-14): the stationary peak is associated with dimers which are the dominant species (this peak is always at the same depth for all the temperatures investigated) and the other is due to fast diffusing monomers or nitrogen-oxygen complexes (spreading peak).

In this work, new data regarding nitrogen transport have been produced and the results will be presented and discussed in Chapter 5.

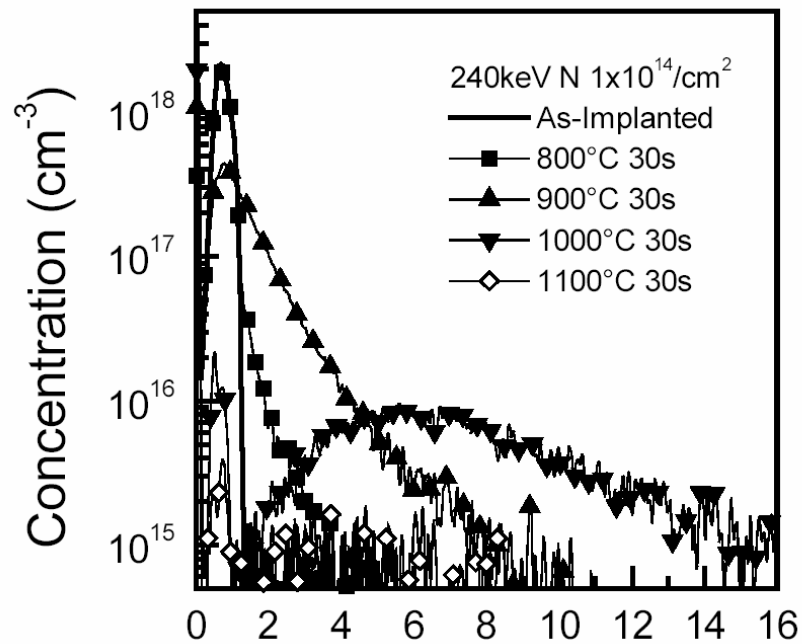


Figure 1-14. SIMS depth profiles of nitrogen implanted in Cz-grown silicon before and after RTA (30s). Some of the curves show two peaks due to diffusion of different nitrogen species (after Mannino⁷²). Similar data obtained using nitrogen implanted FZ-grown silicon can be found in ref. [71].

5. Mechanical stresses during wafer processing

Warping of silicon wafers is caused, broadly speaking, either by thermal or gravitational stresses undergone during device fabrication at high temperatures. Thermal stresses are produced by a non-uniform temperature distribution during the heating or cooling of wafers⁷³. In order to calculate the stress due to thermal variations in silicon wafers, consider a thin circular wafer of radius R and thickness $h \ll R$, where the temperature difference between the wafer edge T_e and the wafer centre T_0 is $\Delta T = T_e - T_0$. It is assumed that the temperature is uniform throughout the thickness of wafer. If the temperature distribution on the wafer surface $T(r)$ follows the relationship $T(r) = T_0 + \Delta T(r^2/R^2)$ and the stress component normal to the wafer surface is neglected, then the radial stress σ_r and the tangential stress σ_θ can be written as⁷⁴

$$\sigma_r(r) = \frac{1}{4} \alpha E \Delta T \left(1 - \frac{r^2}{R^2} \right) \quad (1.11a)$$

and

$$\sigma_\theta(r) = \frac{1}{4} \alpha E \Delta T \left(1 - \frac{3r^2}{R^2} \right) \quad (1.11b)$$

where α is the linear thermal expansion coefficient and E is the Young's modulus for silicon. Dislocations are usually generated in the peripheral regions of silicon wafers during the insertion or withdrawal of wafers from the furnace. For these regions ($r \cong R$) the equation (1.11b) becomes

$$\sigma_\theta(r) = -\frac{1}{2} \alpha E \Delta T \quad (1.12)$$

where ΔT can be up to 180°C considering an insertion rate of 15 cm/min when using 6-inch wafers for a normal furnace⁷⁴. According to equation (1.12), this (high) value of insertion rate can produce a tangential stress near the edge of approximately 70 MPa, which would

have a catastrophic effect on the mechanical stability of wafers at high temperatures. The sign of stresses (tensile or compressive) according to equations (1.11) are represented in Fig. 1-15 which shows the radial and tangential stress distribution as a function of the radius r in the case of insertion with $\Delta T = 10^\circ\text{C}$. During wafer withdrawal, the wafers are subjected to a compressive stress in the central region and a tensile stress in the outer region due to temperature gradients generated during cooling. The stress can be relieved by creation of dislocations in preferred glide-systems provided the resolved shear stress overcomes the critical stress (CRSS) for dislocation generation and motion. The temperature gradient across the wafer and hence the thermal stress distribution can be modified by changing the furnace design and/or by changing the placement of the wafers.

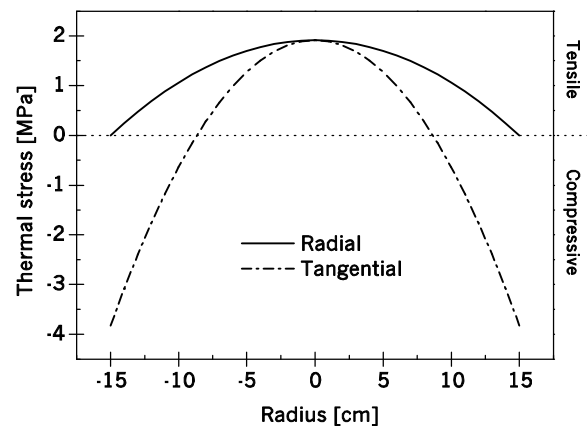


Figure 1-15. Calculated radial and tangential thermal stress distribution for a 300 mm wafer when $\Delta T = 10^\circ\text{C}$ (during insertion).

With increasing wafer diameter, gravitational stresses become important⁵. In a vertical-type furnace, for example, the circular wafers are set horizontally on a supporting jig with either three-point, four-point or ring-like contacts. At high temperatures, the wafers can bow elastically because of the gravitational stress due to their weight. This stress potentially activates nucleation sites for dislocation loops and promotes the collective motion of dislocations. It is worth noting that the area of a 300 mm wafer is 2.25 times larger than a

200 mm wafer, but its thickness ($\sim 700\mu\text{m}$) is only 7% greater. This produces a significant increase of the gravitational bending stress generated during processing. The calculated gravitational resolved shear stress for 200 mm and 300 mm wafers are shown in Table 1 where different geometries of support are considered⁷⁵.

The design and production of harder and mechanically stable silicon single-crystals is of crucial importance in the transition from 200 to 300 mm wafers since the risk of wafer warpage increases significantly when the stresses arising from temperature gradients become larger due to increasing wafer size. However, from Fig. 1-15 and from Table 1 it can be seen that both thermal and gravitational stresses are usually not very large (of the order of a few MPa or less) and their magnitude is comparable to that of stresses opposing the dislocation motion arising from the interaction between dislocations and impurity atoms⁴⁷. Hence, an appropriate use of the interaction between different defects could lead to a reduction of slip and thus to improved mechanical strength of wafers at high temperatures.

Wafer diameter	Support design	Gravitational stress [MPa]
200 (mm)	Ring at the edge	-0.07
	Ring at 0.7 R	-0.03
	Symmetrical 3-point edge	-1.01
	Symmetrical inner (0.7 R) 3-point	-0.49
	Symmetrical 4-point edge	-0.70
	Symmetrical inner (0.7 R) 4-point	-0.34
300 mm	Ring at the edge	-0.14
	Ring at 0.7 R	-0.07
	Symmetrical 3-point edge	-2.12
	Symmetrical inner (0.7 R) 3-point	-1.04
	Symmetrical 4-point edge	-1.46
	Symmetrical inner (0.7 R) 4-point	-0.72

Table 1. Gravitational resolved shear stress calculated for different geometries of wafer support (after Fischer⁷⁵).

6. Dislocations in silicon

6.1 Overview

The role of dislocations in semiconductor technology and in particular their effect on wafers processing is briefly discussed in this section. For a general review of dislocations in crystals see the work of Hirth⁷⁶ or Nabarro⁷⁷. Recently, Sumino⁷⁸ has also published a work specific to the behaviour of dislocations in semiconductors. In the last century, the study of dislocations in metals and related plastic deformation led to the fabrication of harder alloys and innovative materials for industry. More recently, with the development of semiconductor technology and integrated circuits, it was found that dislocations give rise to important effects in electronic devices. Some of these effects are beneficial and others are detrimental for integrated circuits. The concept of gettering⁷⁹ (the removal of impurities and defects from junction regions of the crystal) is very important in order to control leakage current for very shallow junctions in very-large-scale integration (VLSI) application. Many devices, for example dynamic random access memories (DRAM), require low junction leakage currents, but in many cases it is not easy to fulfil such a requirement because metallic impurities in silicon can precipitate in the form of electrically conductive silicides that act like shorts (pipes) along the junction.

Oxygen precipitates and associated defects, such as stacking faults and dislocations, play an important role in gettering impurities from the active region of devices because dislocated areas represent favourable trapping sites for fast diffusing transition metal species. In fact, the strained region close to a dislocation has higher energy than the perfect lattice. Therefore, diffusing impurity atoms prefer to reside in such a region because this allows the reduction of the lattice strain and minimises the total energy of the crystal. The impurities trapped at the dislocation line are electrically harmless for the circuits provided the dislocations are sufficiently far from the active area of devices. Hence, the presence of

dislocations in the bulk and their capacity to trap impurities represent a beneficial effect for integrated circuits. On the other hand, if a dislocation decorated with metal atoms crosses the junction, then the dislocation becomes electrically active, degrading the junction characteristics and the device quality. This constitutes the dominant failure mechanism for devices and various models have been proposed in the past to explain emitter-collector shorts⁸⁰, as shown in Fig. 1-16.

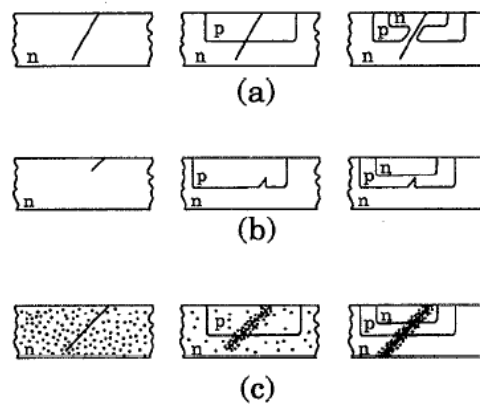


Figure 1-16. Three different schematic sequences proposed to explain emitter-collector shorts: (a) enhanced diffusion of emitter dopant along the dislocation; (b) locally retarded base-dopant diffusion; (c) precipitation of fast diffusing impurities (after Lawrence⁸⁰).

Another important effect of the presence of dislocations in crystals is the reduction of mechanical strength of the material. This problem is very important in silicon wafer manufacturing where more stringent technical specifications such as wafer flatness and very low defect concentration are required. As mentioned before, the high temperature treatments of silicon wafer processing produce considerable mechanical and thermal stresses which can induce the formation of dislocations^{4,12}. In the presence of a sufficient shear stress, the dislocations can propagate within the silicon crystal forming long microscopic steps, called *slip lines* or *slip bands*, when they reach the silicon surface. Optical studies of slip bands in silicon wafers⁸¹ have shown that the failure of built-in MOS devices is clearly correlated

with the presence of slip lines on the surface of the wafer (Fig. 1-17). The relationship between dislocation density and transistor leakage current⁸² is also shown in Fig. 1-18. Moreover, slip dislocations and related warpage of silicon wafers are particularly harmful for lithographic processes and wafer bonding⁸³. Therefore, it is clear that the study and the control of mobile dislocations in silicon crystals is crucial in order to produce higher quality materials for new technologies.

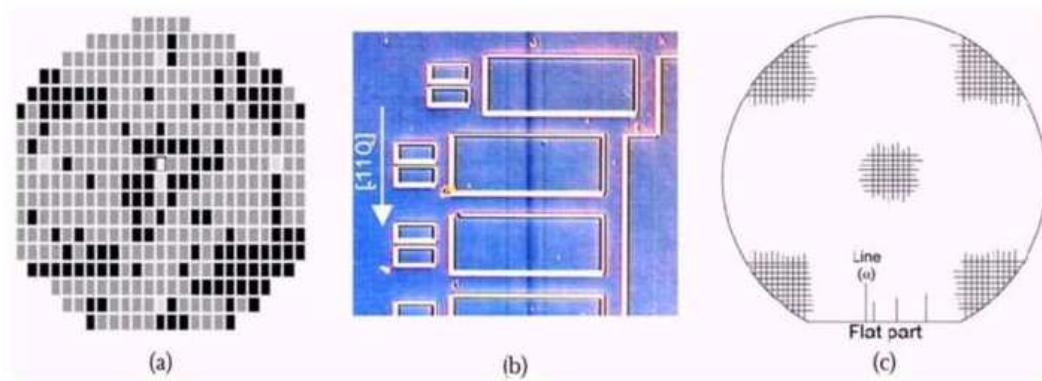


Figure 1-17. Slip lines in Si wafers and failure test of devices: (a) map obtained from electrical probing where the bad dice are in black, the good dice in grey and the test dice in white; (b) optical microscopy observation of slip traces along [110]; (c) location of the slip traces on a (001) wafer surface (schematics). Note the correlation between slip line location and the defective dice (after Rivière-Jerôme⁸¹).

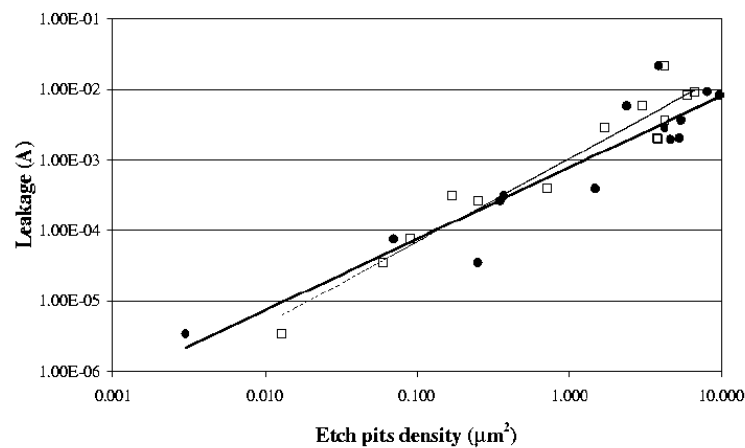


Figure 1-18. The density of dislocations can be estimated by counting the etch pits on the surface after chemical treatment. The graph above shows the transistor leakage current as a function of the etch pit density (after Mica⁸²).

Dislocations in silicon can move in the $\{111\}$ planes and generally are present in form of hexagonal loops⁸⁴ (Fig. 1-19). The Burgers vector for a perfect dislocation in silicon was determined to be $\mathbf{b} = a/2 \langle 110 \rangle$, where a is the lattice constant, by X-ray topographic study⁸⁵. Depending on the Burgers vector, the character of a dislocation in silicon is usually screw, 60° or edge. A schematic of the configuration of a dislocation loop in silicon is shown in Fig. 1-19.

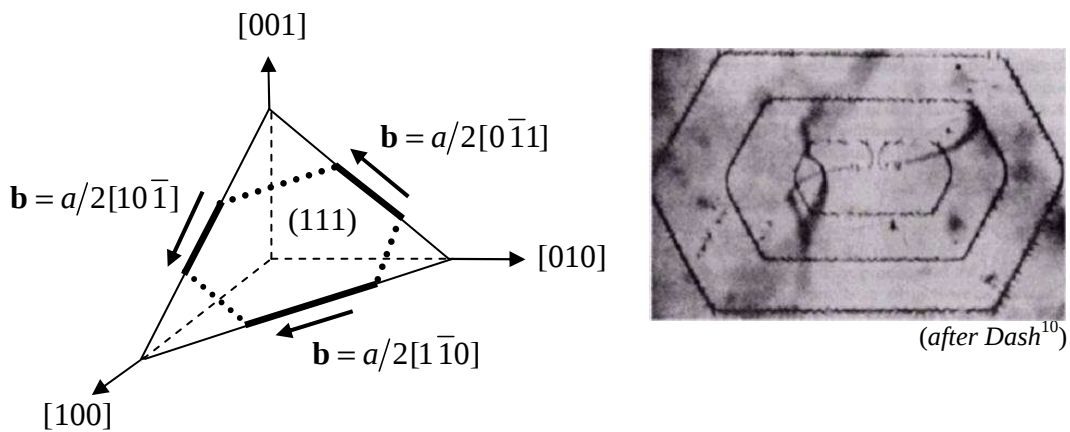


Figure 1-19. Schematic of three possible Burgers vectors for a dislocation loop (hexagonal loop) lying in the (111) plane, although only one of them is allowed within a real loop. Each of the three Burgers vectors associated with the (111) plane define a different glide system in silicon. The famous micrograph on the right shows copper decorated dislocation loops in a real silicon crystal.

In silicon, however, a dislocation (in the glide set⁸⁶) can dissociate into two partial dislocations having Burgers vector of $(1/6)a\langle 112 \rangle$ which bound a strip ($\sim 4\text{-}8$ nm) of stacking fault⁸⁷. In fact, by dissociating into partials, the dislocation can reduce the elastic strain energy. Such a dislocation in the dissociated state is called an *extended dislocation* and the two partial dislocations are called *Shockley partials* (Fig. 1-20).

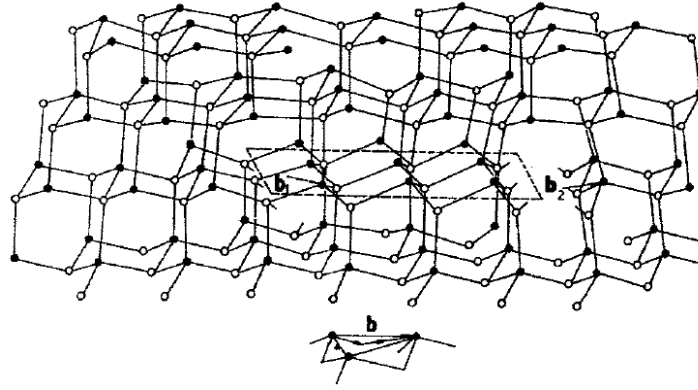


Figure 1-20: Three-dimensional view of a dissociated 60° glide dislocation. On the left side is the 30° partial, on the right side is the 90° partial (after Weber⁸⁸).

It is well known that dislocations can multiply by the Frank-Read mechanism⁸⁹, which is based on the expansion of a dislocation segment with fixed extremities. Another similar mechanism for dislocation multiplication is based on the cross-slip of the screw part of a dislocation loop. The results obtained by Sumino and Harada⁸⁵ using *in situ* techniques provided considerable evidence that the cross-slip mechanism is the principal multiplication mechanism in silicon crystals.

Dislocations can expand and multiply only when subjected to an applied shear stress. Schmid introduced the concept of *critical resolved shear stress* (CRSS) to quantify the strength of materials⁹⁰. It is known from experimental studies that a certain value of resolved shear stress is required for the initiation of crystallographic glide. This stress, necessary for initial glide, is the CRSS. Measurements of the critical resolved shear stress are important in order to establish the limit of elasticity and hence the mechanical behaviour of a particular material under a stress condition. When a shear stress τ greater than the CRSS is applied to a crystal, the dislocations can move with an average velocity given by^{91,92,47}:

$$v = v_0 \tau^m \exp\left(-\frac{U}{kT}\right) \quad (1.13)$$

where v_0 is a phenomenological mobility coefficient, k is Boltzmann's constant, U is the activation energy for dislocation glide, τ is the applied stress resolved on the glide plane

along the glide direction and T is the absolute temperature. The values of m and U depend on the type of dislocations (edge, screw and mixed), but in silicon the difference between values is only approximately 10%. In the case of 60° dislocations in silicon, the values are⁷⁸ $\nu_0 = 1 \times 10^{-2} \text{ m} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$, $m = 1$, $U = 2.2 \text{ eV}$.

In this work, a dislocation loop (or half-loop intersecting the surface) that is free to expand in a plane containing both the dislocation line and its Burgers vector and that can eventually multiply when subjected to a certain resolved shear stress is generically called a *glide dislocation*. In comparison, a prismatic dislocation loop produced by the local stress field associated with a precipitate is called a *punched-out prismatic dislocation (PPD) loop*. A prismatic dislocation loop is a closed dislocation line (quadrilateral in the case of silicon) which can glide conservatively along a prism, but without shrinking or expanding, since its Burgers vector is out of plane of the loop. The typical geometry for punched-out prismatic dislocations in silicon is shown in Fig. 1-21. It is worth noting that in silicon each segment of a PPD loop is edge in character.

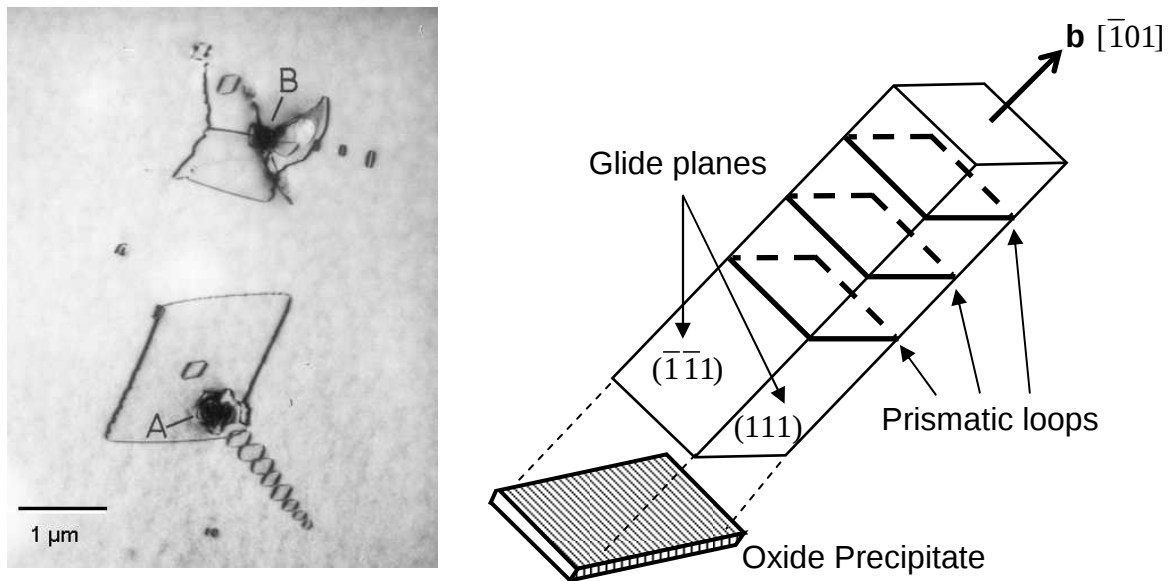


Figure 1-21. TEM image of a silicon specimen containing large precipitates (A and B in the picture) with punched-out prismatic dislocation loops. Some larger dislocations resulting from the interactions of prismatic loops are also shown (source: www.tf.uni-kiel.de). A schematic example of the glide prism with prismatic loops is represented on the right.

6.2 Dislocation sources in silicon wafers

The density of mobile dislocations determines the mechanical strength of a crystal. Therefore, immobilisation or retardation of dislocation motion can suppress multiplication processes and significantly improve the mechanical properties of silicon wafers. During device processing, possible sources of glide dislocations are:

1. Unintentional damage at wafer surface
2. Devices themselves
3. Oxide precipitates and the associated punched-out dislocations.

Each of the abovementioned cases is discussed as follows:

1. In silicon specimens prepared in a normal laboratory environment, dislocations can be easily generated from damaged areas and surface flaws during annealing at high temperatures. However, this is not the case for commercial mirror-polished wafers in which the surface is very smooth and defect free. Nevertheless, surface damage can be produced at some point during wafer handling and device processing. As will be shown in Chapter 6, if we calculate the maximum shear stress due to a light load distributed uniformly over a small contact area on the silicon surface, then it turns out that such stress can be several GPa, which is close to the theoretical shear strength of a perfect silicon crystal (~ 14 GPa). This huge stress can also induce a phase transformation beneath the loaded surface from crystalline to amorphous silicon⁹³. Since amorphous silicon starts to recrystallise at 500°C ⁹⁴, the stress-induced amorphous regions re-transform to a crystalline structure during heat treatments. The recrystallised area will contain tangled dislocations which may propagate and multiply under applied stress at elevated temperatures.

2. In microelectronic devices, a large lattice strain may build up in the silicon substrate as a result of device isolation processes. This localized large strain can result in the formation of crystal defects such as dislocations and can degrade the device performance.

Recently, shallow trench isolation (STI) has begun to be used as an isolation technique in scaled devices. It was found that, at the trench bottom corner, the large resolved shear stress on slip systems $[011](1\bar{1}1)$ and $[10\bar{1}](1\bar{1}1)$ may be due to the corner shape (acting as stress concentrator) or the intrinsic stress induced during oxidation⁹⁵. Therefore, to control dislocation around STI, the oxidation-induced stress at the trench bottom corner must be reduced during processing and the shape of the bottom corner must be controlled.

Dislocations are also generated during processes involving ion implantation. The dislocation density in this case varies widely depending on the dopant and annealing conditions⁹⁶.

3. The formation of glide dislocations in Cz-silicon wafers is often a consequence of oxygen precipitation within the wafer. The generation of dislocations from oxide precipitates (usually with a diameter up to a few hundreds of nanometers) is basically due to the misfit strain at the precipitate/matrix interface which can be relaxed locally by the strain relieving mechanism of dislocation punch-out (Fig. 1-21). According to TEM investigations, mobile dislocations generated from precipitates are originally in form of prismatic loops^{97,98}. Under particular conditions, such loops can interact, each with the other, resulting in more complicated dislocation geometries (tangles of dislocations).

7. Interaction of impurities with dislocations in silicon

There is strong experimental evidence that the introduction of dopants in silicon crystals affects dislocation motion. The effects of electrically active doping on the mechanical properties of semiconductors have been studied by Hirsch⁹⁹ and Roberts¹⁰⁰ using a simple technique based on micro-indentation. Sumino *et al.*¹⁰¹ have published different reviews about the effects of electrically active impurities on dislocation dynamics in silicon crystals.

However, such slow diffusing dopant impurities are not the subject of this thesis and are not considered further.

7.1 General aspects of dislocation locking by impurities

In single-crystal silicon, impurities can interact with linear defects, in particular with stationary or slowly moving dislocations. The resulting effect of this interaction is principally an immobilization of the dislocations due to accumulation of impurities in the core regions during annealing at high temperatures. This effect is called *dislocation locking*¹⁰². After dislocation decoration by impurity atoms, an extra stress is needed to move a dislocation immobilized by impurities. The stress necessary to start a locked dislocation into motion is called the *unlocking stress*. The magnitude of the unlocking stress generally depends on the concentration of impurities in the crystal and its thermal history.

The theory describing the effect of a solute atom atmosphere on dislocations was mainly developed in the early 50s by Cottrell¹⁰³ and Eshelby¹⁰⁴. The most important contribution to the interaction energy between an impurity atom and a dislocation is usually that due to the strain field produced by the impurity in the surrounding crystal. The distortion may interact with the strain field of the dislocation to increase or decrease the elastic strain energy of the crystal. This change in energy contributes to the *interaction energy* E_i of the impurity atom with the dislocation. If an impurity atom occupies a site along the dislocation where E_i is large and negative, then a certain work $|E_i|$ will be required to separate the dislocation from the impurity and the dislocation cores will tend to be occupied by a higher concentration of impurities than that present in the bulk. This is also the basic mechanism of the so-called internal gettering effect used in microelectronics to trap metallic impurities in non-electrically active regions.

Together with the elastic interaction, other dislocation-impurity interactions of a different nature, such as electrical or chemical, can contribute to change the total interaction energy E_i . Hence, any measured value of E_i will include the effect of several interactions of different types. Especially in covalent crystals, such as silicon, the relative importance of other possible interactions is less clearly understood. Moreover, an electrostatic interaction can take place if conduction electrons are captured by the dangling bonds which may exist in some particular dislocation core configuration, as shown in Fig. 1-20 for partial dislocations in silicon. Heggie¹⁰⁵ and Jones¹⁰⁶ investigated the chemical interaction of impurities with dislocation cores in silicon using a cluster method with local density-functional pseudopotential theory. Impurities can participate in lattice reconstruction and passivation of dangling bonds along the dislocation core. According to Jones, the energy difference between states also contributes to the segregation of impurities to a dislocation and their locking effect. However, in most theoretical calculations, the interaction between an impurity atom and a dislocation is often considered as a pure elastic effect (long-range interaction)^{107,108,109}

If C_0 is the average bulk concentration of a certain impurity in the crystal (measured at distance far from the dislocation, where no impurity-dislocation interactions are present), then the equilibrium concentration $C(\mathbf{r})$ of the impurity at a position $\mathbf{r}$ close to the dislocation can be written, according to Boltzmann's statistics, as:

$$C(\mathbf{r}) = C_0 e^{\frac{E_i(\mathbf{r})}{kT}} \quad (1.15)$$

where it is assumed that there is always a large number of non-occupied sites at the dislocation core and that the impurities do not interact each with the other. E_i can be expressed in terms of the variation in Gibbs free energy ΔG (binding energy) as follows:

$$-E_i = \Delta G = \Delta H - T\Delta S \quad (1.16)$$

where ΔH is the enthalpy change and ΔS is the entropy change due to the interaction between impurity atoms and the dislocation. Therefore, Equation (1.15) can be rewritten in cylindrical coordinates as:

$$C(r, \theta) = C_0 e^{\frac{\Delta G(r, \theta)}{kT}} \quad (1.17)$$

In general, the value of the interaction energy (binding energy) of a single impurity atom with a dislocation is calculated typically to be less than 1 eV⁴². Impurities tend to congregate in core regions, where ΔG is larger, and form dense atmospheres of solute atoms even when a very low initial impurity concentration C_0 is present in the crystal. The accumulation of impurities at the dislocation core can occur at sufficiently high temperatures for impurity migration. However, the temperature should not be so high that the thermal energy causes the aggregation of impurities to evaporate into the crystal matrix.

Under certain conditions, the dislocation can behave as a site for heterogeneous nucleation of precipitates. For example, in the case of oxygen interstitial impurities contained in Cz-grown silicon, small oxide precipitates form along the dislocations after sufficiently long annealing, as demonstrated by Sumino et al. (Fig. 1-22)¹¹⁰. The morphology of impurity precipitates formed along a dislocation plays an important role in determining the strength of dislocation pinning. Small precipitates along the dislocation can act like pinning points with much higher interaction energy (several eV) than a single impurity atom.

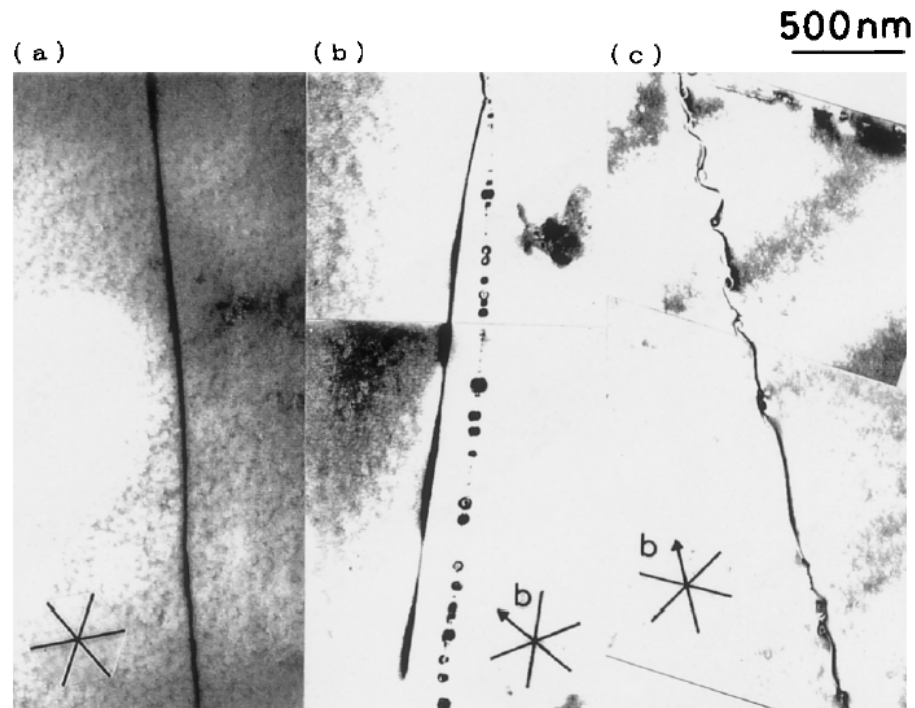


Figure 1-22. TEM micrographs of silicon oxide particles precipitated on dislocations in silicon at 900°C. a) A dislocation line before precipitation occurs, b) particles originally precipitated on a 60° dislocation, and c) those precipitated on a screw dislocation (after Sumino¹¹⁰).

7.2 Dislocation locking by oxygen

Although the strength of dislocation locking due to impurities has been evaluated theoretically since the 1950s¹¹¹, quantitative measurements of dislocation pinning by oxygen in silicon crystals were difficult to explain. This is because the locking depended on several parameters such as temperature and time of annealing, initial oxygen concentration and amount of precipitated oxygen. In fact, an incorrect interpretation of early experimental results (in 1975) led authors to give explanations that were contradictory to the theory, showing no appreciable locking effect either by dissolved oxygen, nor by SiO₂ precipitates¹¹². Only two years later, in 1977, a definitive proof of the existence of a dislocation pinning effect by oxygen atoms in silicon was achieved¹¹. Ambiguities caused by

uncertain material variables in different crystals or different parts of a crystal were avoided in this new investigation by forcing oxygen out-diffusion from a wafer, creating a continuous variation of oxygen concentration in a $<60\text{ }\mu\text{m}$ -deep surface layer. Also, a confirmation of the dislocation locking effect in doped silicon was given by Sumino⁴⁷ in 1982 with the development of the *in situ* X-ray topographic technique. Oxygen, nitrogen and phosphorus atoms were found to be effective in locking dislocations while carbon atoms were not. Sumino observed that the magnitude of the locking force, at a particular temperature, is determined uniquely by the number of impurity atoms decorating a unit length of dislocation.

More recent studies carried out by Yonenaga¹¹³ *et al.* about the role of oxide precipitates in the locking effect have demonstrated that in silicon, although the unlocking stress generally increases during the precipitation of small oxide particles along the dislocations, further growth of these precipitates after additional annealing at high temperatures produces a large misfit strain at the precipitate/matrix interface. If the temperature is sufficiently high, then a stress-relieving mechanism can take place locally by means of punching out prismatic dislocation loops from the precipitates. In other words, the small precipitates that at the initial stage of annealing acted like pinning points for dislocations, in a second stage can become themselves sources of new loops. The punching of prismatic dislocations and the subsequent motion and multiplication of glide loops can significantly reduce the mechanical stability of wafers, as the density of free or weakly locked dislocations in the crystal becomes higher. In this thesis, the dislocation locking by interstitial oxygen atoms has been investigated both experimentally and theoretically, together with the generation of glide dislocations from pre-existing oxide precipitates.

7.3 Dislocation locking by nitrogen

The beneficial effects of nitrogen on the mechanical strength of silicon crystals has been demonstrated experimentally. Like oxygen atoms in Cz-grown silicon, nitrogen atoms congregate on slowly moving dislocations or stationary dislocations during annealing at elevated temperatures. It was found that nitrogen atoms have a high energy of interaction with dislocations¹¹⁴ and are capable of strongly immobilising the dislocations even when the concentration of nitrogen is very low ($\sim 10^{15} \text{ cm}^{-3}$). Sumino¹¹⁴ gave the first evidence of improved yield strength in nitrogen-doped FZ-grown silicon crystals. Compared with standard FZ-grown crystals, nitrogen-doped FZ-grown silicon crystals are less susceptible to the occurrence of dislocation slip (Fig. 1-23).

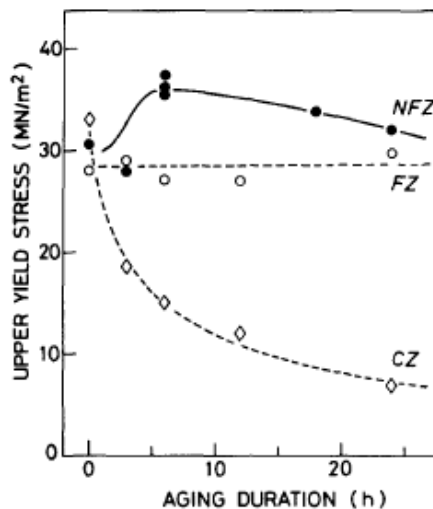


Figure 1-23. Variation of the upper yield stress¹⁰⁸ as a function of duration of annealing at 1050°C for nitrogen-doped FZ-grown (NFZ) silicon crystals, usual FZ-grown crystals and Cz-grown crystals. The upper yield stresses refer to tensile deformation at 900°C under a strain rate of $1.1 \times 10^{-4} \text{ s}^{-1}$. (after Sumino¹¹⁴)

It was found that the dislocation locking in a silicon crystal with a nitrogen concentration as low as $5.4 \times 10^{15} \text{ cm}^{-3}$ is stronger than that in a crystal with an oxygen concentration of $1.5 \times 10^{17} \text{ cm}^{-3}$ (available data exists only at 647°C⁴⁷). This result led the authors to claim that nitrogen atoms have an extraordinarily strong locking effect on dislocations compared

with that of oxygen. However, data were collected at only one temperature and the measured parameter (the upper yield stress at a strain rate of 10^{-4} s) was difficult to interpret directly in terms of the interaction of nitrogen with dislocations. Moreover, the dependence of the upper yield stress on annealing duration was not properly investigated.

Recent experiments have proved that nitrogen doping of FZ-silicon can considerably increase the fracture strength of wafers at room temperature^{115,116}. In the past, a direct application of these mechanical effects of nitrogen has been the use of nitrogen-doped FZ-silicon wafers in the production of charge coupled devices (CCD); the use of these wafers led to a significant reduction of the amount of process induced defects and hence to an improvement in the device yield¹¹⁷. The nature of the strong interaction of nitrogen atoms with dislocations is matter of debate. In fact, electron concentration measurements on N-doped FZ-silicon, for different nitrogen concentrations, demonstrated that the nitrogen atoms accumulated on dislocations are electrically inactive¹¹⁸. This fact suggests that electrostatic forces do not govern the interaction between nitrogen atoms and dislocations and other explanations for the strong binding energy to the dislocations have to be found.

In conclusion, there is a lack of quantitative information about the diffusion and aggregation of nitrogen atoms at the dislocation core in silicon crystals. More data are required to understand the mechanisms by which nitrogen improves significantly the mechanical properties of silicon crystals. In this thesis, important information about the interaction between nitrogen and dislocations for a wide range of temperature and duration of thermal treatments will be given in Chapter 5.

8. Overview of dislocation unlocking experiments

Most of the conventional techniques for the determination of oxygen diffusivity in silicon are not suitable at low temperatures since transport is then so slow that accurate measurements are impossible. Consequently, there is a lack of information regarding the oxygen diffusion coefficient between 400° and 700°C. However, this problem was in part overcome by Senkader *et al.*^{119, 120} who developed a novel experimental technique based on dislocation locking by oxygen atoms. This technique has been used in the present work to measure oxygen and nitrogen diffusivity under different experimental conditions and hence will be fully reviewed in Chapter 2 (experimental details) and Chapter 3 (model). Originally, the method introduced by Senkader *et al.* was used to study oxygen in Cz-silicon and consisted of the following. Firstly, uniformly distributed dislocations were decorated with oxygen atoms by annealing for different times at different temperatures. After this thermal treatment, the unlocking stress τ_u for dislocations was measured at 550°C and plotted as a function of the annealing time t . Fig. 1-24 shows, as an example, two sets of data collected at 700° and 800°C using specimens with two different initial oxygen concentrations. For more details, see the work of Senkader *et al.* in ref. 119 and 120. Experiments showed that initially the unlocking stress increases almost linearly with increasing annealing time. The rate of increase in the unlocking stress is higher when the temperature is more elevated and/or the oxygen concentration is larger, indicating that more oxygen atoms have diffused to the dislocations and have accumulated at the core.

The general behaviour of the unlocking stress is shown schematically in Fig. 1-25. It can be observed that the transport of oxygen to the dislocation and its segregation to the core shows five well-defined regimes. However, the present work is concerned only with regime 1 and 2 (increase and saturation), since it is believed that the other regimes 3, 4 and 5

(second increase, saturation and decrease) are due to oxygen precipitation at the dislocation core^{110,119}, although this is still under investigation.

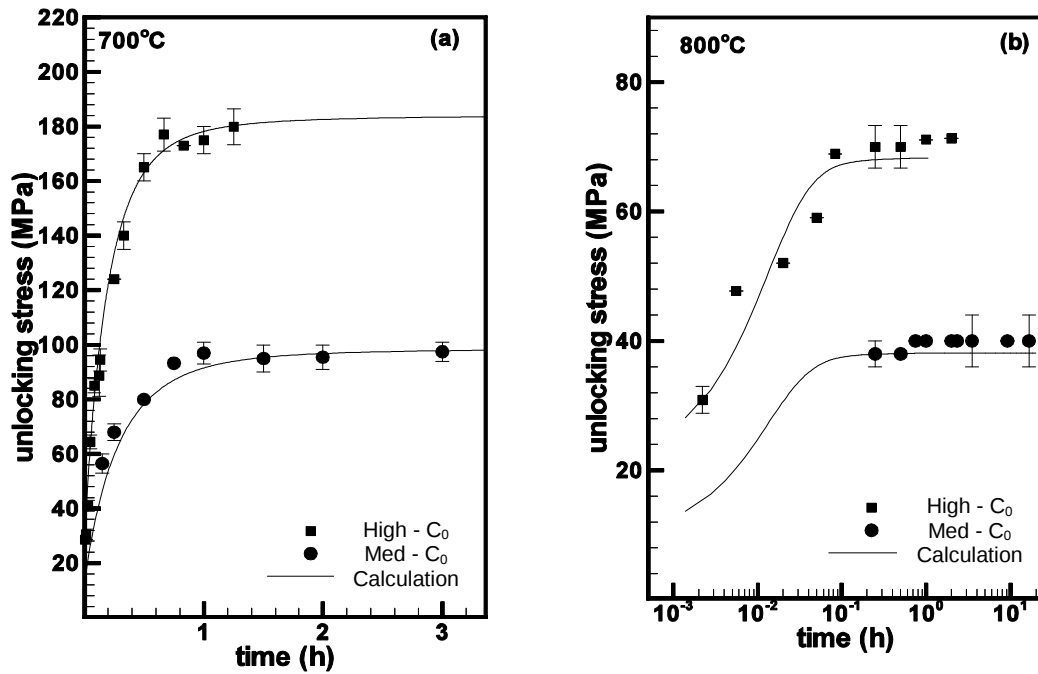


Figure 1-24. Experimental results (symbols) for the unlocking stress as a function of annealing time at the temperatures (a) 700°C and (b) 800°C, for high ($10.4 \times 10^{17} \text{ cm}^{-3}$) and medium ($6.3 \times 10^{17} \text{ cm}^{-3}$) initial oxygen concentration C_0 in the wafer. Lines represent the calculated values according to the model described in the text.

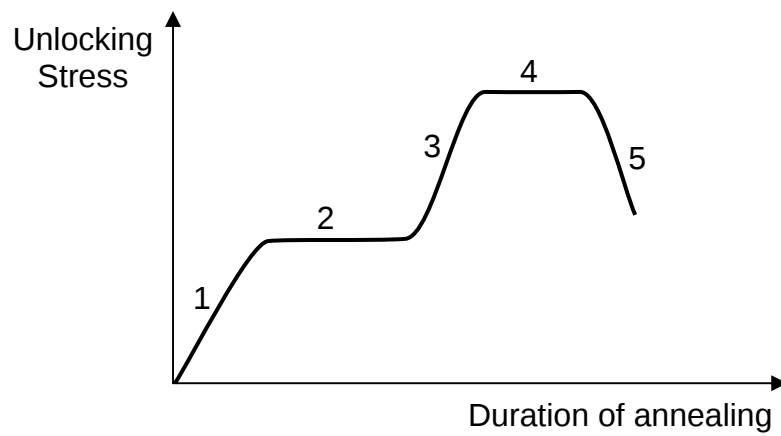


Figure 1-25: General behaviour of the unlocking stress as a function of annealing time in Cz-silicon.

In the early stages of annealing, the concentration of oxygen at the core is small and far from equilibrium. Therefore, the oxygen concentration at the dislocation core and hence the unlocking stress increases rapidly (regime 1). At higher temperatures and larger oxygen concentrations, the transport to the core is quicker. Thus, as expected, the rate of increase in unlocking stress is higher for higher temperatures and oxygen concentrations.

Following the initial rise of the unlocking stress, a steady-state is achieved when the local-equilibrium with the background oxygen concentration is established (regime 2). This steady state manifests itself as a saturation of the unlocking stress. At this stage, the oxygen concentration at the dislocation does not depend anymore on annealing time as the absorption of oxygen atoms by the core is balanced by the emission of oxygen atoms from the core due to thermodynamic effects. From unlocking stress data collected during regime 1 and 2, important information about oxygen diffusivity and the binding energy of oxygen to dislocations was deduced. In general, the dislocation unlocking stress in the first two regimes is governed by:

(Regime 1) - the transport of oxygen atoms to the dislocation core;

(Regime 2) - the thermodynamics that control the oxygen concentration at the core.

Therefore, in conjunction with the experiments, a model was developed to calculate the number of oxygen atoms at the dislocation core by simulating the oxygen transport to an isolated perfect dislocation during regime 1. In this model, the oxygen diffusivity is used as a fit parameter to obtain agreement between the calculated results and experiments (Fig. 1-24). Similarly, the thermodynamics that control the oxygen concentration at the core during regime 2 were also simulated. The theoretical results were used to deduce the binding energy of an oxygen atom to the dislocation core. These results achieved by Senkader *et al.* are described in this section, but the details of the model will be explained in Chapter 3.

In Fig. 1-26, values of the unlocking stress normalised by the oxygen concentration are shown for temperatures between 650°C and 850°C. The value of the oxygen-dislocation

interaction enthalpy, estimated by the method of least squares from experimental data in Fig. 1-26, is $\Delta H = 0.74 \pm 0.04$ eV.

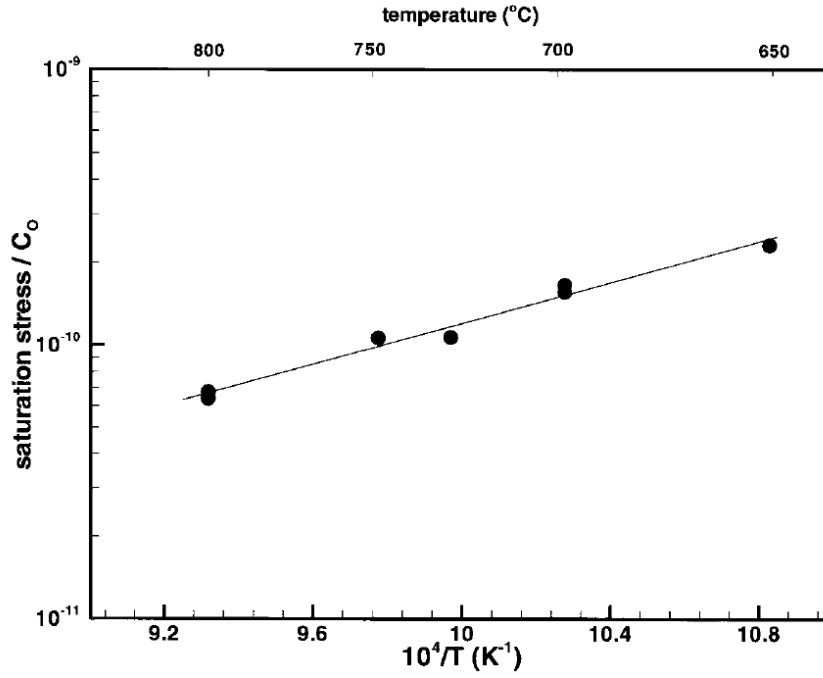


Figure 1-26. Dislocation unlocking saturation stress divided by oxygen concentration as a function of reciprocal temperature. The value of ΔH deduced from the plot is 0.74 ± 0.04 eV. (after Senkader¹¹⁹)

Two different values, depending on the initial concentration of oxygen, were deduced for oxygen diffusivity using the numerical model to fit the data. In samples with medium oxygen content ($6.3 \times 10^{17} \text{ cm}^{-3}$) the diffusion coefficient was:

$$D_O^{M-C_o} = 7.33 \times 10^{-7} \exp\left(-\frac{1.52 \text{ eV}}{kT}\right) \quad [\text{cm}^2 \text{ s}^{-1}] \quad (1.18)$$

and in samples with high oxygen content ($10.4 \times 10^{17} \text{ cm}^{-3}$) was:

$$D_O^{H-C_o} = 2.16 \times 10^{-6} \exp\left(-\frac{1.55 \text{ eV}}{kT}\right) \quad [\text{cm}^2 \text{ s}^{-1}] \quad (1.19)$$

The results achieved by Senkader and co-workers represent the most complete set of data concerning oxygen transport in the temperature range of interest. These results are in

agreement with the aforementioned impression given in the literature¹⁸. At temperatures greater than 700°C there is an excellent overlap between Senkader's data and those from other authors¹⁸, both represented in Fig. 1-27. At lower temperatures, transport of oxygen seems to be controlled by a new mechanism different than single oxygen jump. In particular, at 350°C where diffusivity data for single oxygen jump is available in the literature, new results obtained with dislocation unlocking experiments indicate a three orders of magnitude “enhancement” in oxygen transport. The diffusivity enhancement mechanism is not yet fully understood, but is of crucial importance since it controls the rate of oxygen aggregation at low temperatures (less than 700°C) and hence the formation of thermal donor defects. Oxygen dimers are the major candidate for the fast diffusing species and the existence of stable oxygen dimers in silicon has been indeed demonstrated experimentally¹²¹.

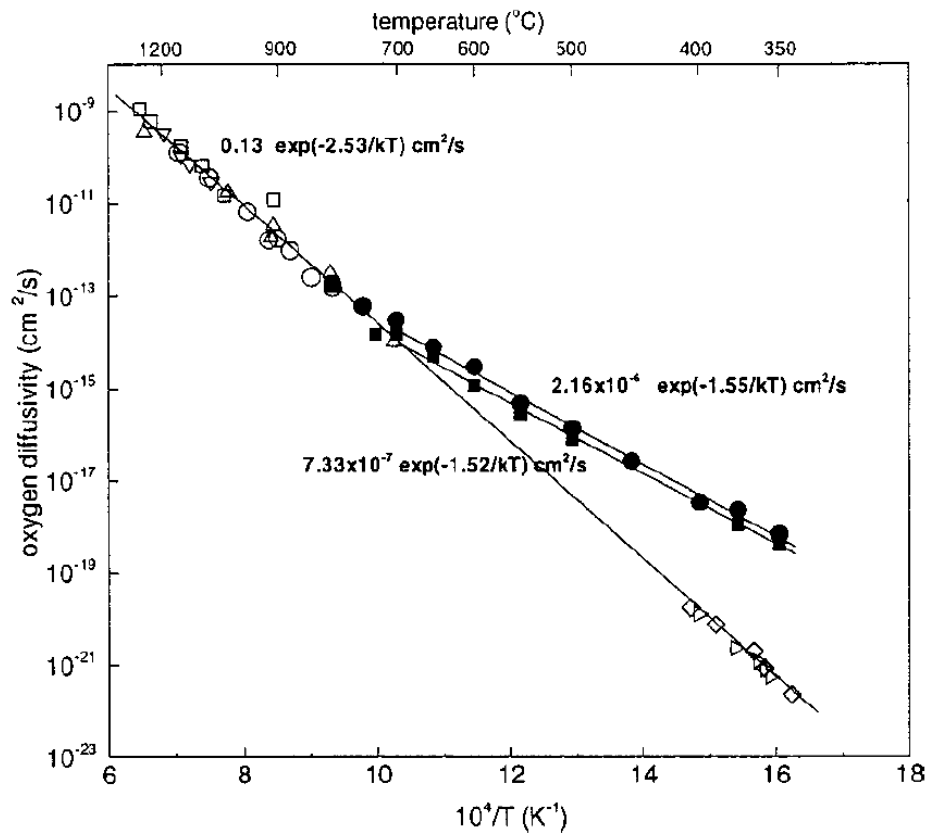


Figure 1-27: Non-filled dots represent “normal” diffusivity data from Fig. 1-15 (SIMS,CPAA,dichroism, and kinetic data). The filled dots represent data from Senkader *et al.*¹²⁰ showing an enhanced diffusivity in the range 350-650°C.

9. Generation of dislocations from oxide precipitates

Several investigations have shown that the mechanical strength of silicon crystals depends on the size and morphology of oxide precipitates^{122,123}. In the literature there are two different approaches to interpret these experimental results. One hypothesis is that during device processing, an applied stress (thermal or gravitational) can nucleate glide dislocations at oxygen precipitates. The precipitates act as stress concentrators¹²⁴ and dislocation nucleation occurs independently of the presence/absence of punched-out prismatic loops in the crystal. This hypothesis would predict that the density of dislocation sources is practically equal to that of precipitates. Other authors¹²⁵ believe that not all the precipitates can be sources of glide dislocation loops that can expand and multiply. This is because the stress concentration coefficient for an oxide precipitate is rather low (~ 2). Hence, the second hypothesis is that the growing precipitates in the wafer produce punched-out dislocations. At the early stages of precipitation, the oxygen concentration is sufficiently high that these dislocations are effectively locked when the wafer is cooled. However, during the later stages of precipitation the residual oxygen concentration is so low that efficient locking does not occur and it is the subsequent movement and multiplication of these dislocations that produces wafer warpage¹²⁶.

In order to study the effect of oxide precipitates on the mechanical stability of wafers, experiments with samples containing precipitates in different concentrations and with different sizes were carried out by Jurkschat *et al.*¹²⁶. Bending techniques were used to measure the critical shear stress necessary to detect slip lines on the surface of silicon wafers after application of an external force at high temperatures. This critical shear stress was called the *slip stress* τ_{slip} . The main experimental results can be summarized as follows¹²⁶:

- τ_{slip} decreases with increasing precipitate size for any given precipitate density and initial oxygen concentration. Samples with the smallest precipitate diameter (about

100 nm) show a τ_{slip} value of 200–250 MPa while samples with the largest precipitate diameter (about 400 nm) show τ_{slip} to be about 50 MPa.

- τ_{slip} decreases slightly with increasing precipitate density for small precipitates, whereas it remains virtually unchanged for precipitate diameters larger than 100 nm.

The above experimental results were explained in terms of the shear stress needed to activate a Frank-Read source with initial length equal to the precipitate size. Although theoretical stress calculations for the stress to activate a Frank-Read source agree with the experimental results (within a reasonable error range), other recent observations cannot be easily explained just considering the simple Frank-Read mechanism. In fact, further experiments carried out during this thesis work have shown that, for a given temperature, the slip stress τ_{slip} is strongly dependent on the duration of stress application. In this thesis, the investigation initiated by Jurkschat, Currie and Senkader^{119,120} at the University of Oxford is extended to the dependence of the slip stress on other technologically important parameters and a fuller description of the effect of oxygen precipitation as a function of precipitate size, duration of stress application and annealing treatments will be given in Chapter 6.

10. Aims of this thesis

Silicon crystal growth is the most expensive and technologically advanced process in the sequence of 300 mm wafer production. The successful growing of dislocation-free crystals and the fabrication of defect-free silicon substrates is of crucial importance for semiconductor industry. Impurities and other defects affect enormously the mechanical properties of silicon wafers at high temperatures. Several studies have been carried out in the past to investigate the effect of impurities on dislocations, but the interaction between these defects is complex and the mechanism that leads to plastic deformation depends often on

many parameters. Published data on this topic are rare and often insufficient for a full understanding of the exact processes by which silicon crystals deform.

Therefore, the aims of this thesis are:

1. The measurement of oxygen diffusivity in silicon samples with low oxygen content by using dislocation unlocking experiments at low temperatures. This should clarify the oxygen monomer/dimer behaviour and probably will provide the evidence for the dominant species in oxygen transport. This information is very important for the understanding of thermal donor formation and oxygen precipitation for internal gettering at low temperatures. (Chapter 4).
2. The development of a tool to predict the critical conditions leading to wafer warpage at any time during a certain thermal process. This requires a full understanding of oxygen behaviour in silicon and dislocation locking by oxygen in a wide range of temperatures. If this is achieved, then it may be possible to develop a numerical model to predict the unlocking stress during the course (time evolution) of different heat treatments typical of VLSI processing. Thus, it should be possible to design wafer defect distributions and/or device processing to minimise wafer warpage. (Chapter 4).
3. The investigation of nitrogen-dislocation interaction in high-purity silicon crystals (FZ-silicon) by using dislocation unlocking experiments. In analogy with the work on silicon, this study will provide new important information about the diffusivity of nitrogen in silicon and its binding energy to a dislocation. (Chapter 5).
4. The collection and completion of a set of data regarding the shear stress required to generate glide dislocations in standard Cz-silicon wafers as a function of applied stress, temperature, initial oxygen concentration and annealing duration. This is needed to understand the deformation mechanism applicable to wafers which predominates at different conditions. (Chapter 6).

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Chapter 2: Experimental techniques

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1. Introduction

In this thesis, two kinds of experiments were carried out: those to investigate dislocation locking by impurities and those to study dislocation generation at oxide precipitates. In each case, the experiments were performed by subjecting a silicon specimen to load at elevated temperatures. The load was either applied by using standard bending techniques, such as three-point and four-point bending, or less well-known annular bending geometries. The bending experiments required the development of particular mechanical test rigs that were used in conjunction with an Instron testing machine, a furnace and a system for providing an argon gas ambient.

2. Overview of dislocation unlocking experiments

The dislocation locking effect induced by impurity atoms was investigated in precipitate-free silicon samples containing interstitial impurities (oxygen or nitrogen) in known concentration. The unlocking stress was measured as a function of annealing duration at different temperatures. Initially, controlled dislocation half-loops were introduced in rectangular silicon specimens by means of indentation followed by a constant stress application (four-point bending) at 550°C. Such a high temperature was needed because dislocations are inconveniently slow at lower temperatures. In a second stage, the dislocations were decorated with impurities during annealing of certain durations (0-10⁴ hours) at elevated temperatures (350-850°C). This treatment produced an immobilisation of the dislocations previously introduced in the material. After dislocation decoration, the unlocking stress was measured using three-point bending at high temperatures; during this treatment, only the dislocations that were subjected to a stress higher than the unlocking

stress could move and expand on their glide planes, whereas those subjected to a lower stress remained immobile at the same position. At room temperature, all the dislocations intersecting the surface were then revealed using selective etching techniques and optical microscopy. The position of the unlocked dislocations at the sample surface and the subsequent calculation of the applied shear stress at that position during three-point bending allowed the determination of the unlocking stress.

The procedure described above was needed to produce a single data point in a graph showing the unlocking stress as a function of annealing time and temperature. It is clear that because of the complexity of the experiment and the care needed in both sample preparation and processing, the collection of data was very time-consuming. Moreover, the probability of sample failure due to breakage under the application of high stresses was large.

Plastic deformation of silicon single-crystals subjected to high temperature treatments is a consequence of the microscopic movement of linear defects. For this reason, the approach adopted in the present study is quite different from those used in the past by other research groups which have collected data using “traditional” stress-strain tests¹, producing a macroscopic deformation of samples. Stress-strain measurements involve nucleation and/or multiplication of a large number of dislocations and therefore the fundamental mechanism by which the plastic flow first begins may not be evident if more macroscopic deformation occurs. In fact, conventional stress-strain measurements are limited by the sensitivity of the apparatus, often to strains $\geq 1\%$, which is equivalent to the formation and movement of many thousands of dislocations. It is important to note that in the context of semiconductor device processing, even a single dislocation reaching the wafer surface can kill a device at that point, therefore stress-strain investigations are not ideal to study the effect of dislocations in semiconductors.

In this chapter, the presentation of the experiments will begin with the description of the experimental techniques, following the order in which they were used. All specimens

prepared for the unlocking experiments were cleaved from either (001) or (111) silicon wafers in the form of rectangular bars. The direction of cleavage was nominally $\langle 110 \rangle$. The possible misalignment of the specimen sides in respect to the [110] direction, especially after mechanical polishing, was estimated to be less than $\pm 2^\circ$. Such a small misalignment did not have a significant influence on the results if compared with larger errors due to other parameters, for example the temperature control. The dimensions of each specimen were accurately measured with a micrometer. These are important in order to calculate the stress distribution to which a specimen is subjected during bending. The error in the determination of sample thickness was given by the sensitivity of the micrometer ($10 \mu\text{m}$), whereas the variation in width was usually bigger (up to $100 \mu\text{m}$) due to not perfect alignment of the specimen sides along [110] directions, but was again measured to an accuracy of $10 \mu\text{m}$. The sample length was not as important as thickness and width because this parameter was not necessary for the calculation of the applied stress distribution along the bar.

3. Indentation techniques

In order to carry out accurate and reliable dislocation unlocking experiments there was a need to introduce in the silicon crystals a uniform distribution of dislocations with regular shape. In fact, the unlocking stress measurements are reproducible and comparable only if the dislocation distribution in the crystal is controlled and well known in each specimen. In addition, the fabrication of a system consisting of regularly spaced dislocations in silicon crystals is very important to develop models and carry out numerical simulations of the experiments. To achieve this, dislocations were initially introduced in the samples by using Vickers micro-indentation at room temperature. The Vickers indenter is a highly polished, pointed square-based pyramidal diamond with face angles of 136° (Fig. 2-1). With the

Vickers indenter, the depth of indentation is approximately one seventh of the diagonal length²

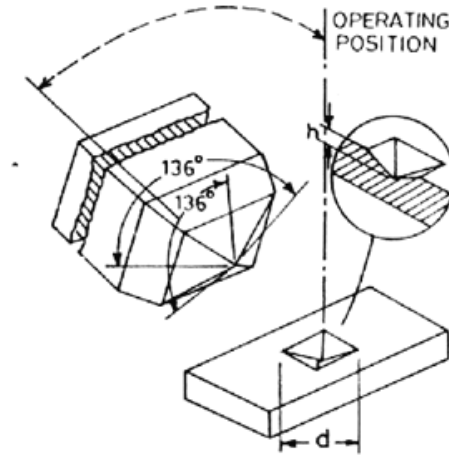


Figure 2-1. Vickers indenter (after Bushan²)

In dislocation unlocking experiments, 10^{-2} N load was applied during Vickers indentation at room temperature for a dwell time of 5 seconds. This produced an indent with diagonal of approximately $5\ \mu\text{m}$ and depth of roughly $1\ \mu\text{m}$. After indentation and upon heating, the residual stress associated with the indent is frozen in the crystal structure until a sufficiently high temperature is reached. At a certain transition temperature, a stress-relieving mechanism takes place and the crystal relaxes its structure by punching prismatic dislocation half-loops from the indent. The prismatic loops punched-out from the indent are very similar in character to that described in Chapter 1 for the case of dislocation punching from oxide precipitates. The geometry of dislocation punching from an indent in the case of (001) wafers is schematically shown in Fig. 2-2a. Tangles of dislocations can also form underneath the indent and these can act like sources of mobile dislocations under applied stress. Application of an external stress along the [110] direction was used to grow the

dislocations (introduced by indentation) in a regular array of controlled dislocation half-loops subsequently used for the unlocking experiments.

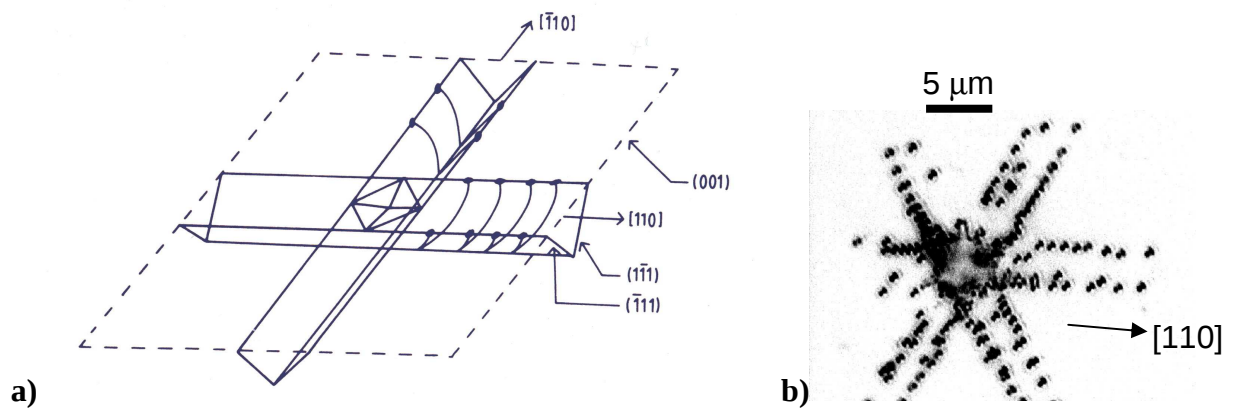


Figure 2-2. a) Geometry of indentation rosette on a (001) silicon surface (*after Roberts*³). **b)** Optical microscope image of etch pits revealing dislocations at the (111) silicon surface after indentation with 10^{-2} N applied load. This particular sample was subjected to a 15 min anneal at 600°C after indentation.

4. Mechanical test rig

Bending of silicon samples at high temperatures was performed using an apparatus specially designed and fabricated for this purpose. The test rig used in the experiments consisted of different parts, all contained in a silica tube as shown in Fig. 2-3a, where the position relative to each single part is represented schematically. The molybdenum rig was essentially the only part of the equipment that needed to be changed depending on the specific bending technique used, that is three-point, four-point or annular bending. The rig used for three-point and four-point bending is shown in Fig. 2-3b and Fig. 2-3c: one or two removable knife-edges consisting of 12 mm molybdenum wires (diameter = 1 mm) were utilised for three-point and four-point bending respectively. The other molybdenum rig used for annular-bending will be described in detail in Section 9. Molybdenum was chosen as the material for those parts in contact with the sample because of its stability and low solubility

in silicon at high temperatures. Alumina was chosen as the material for spherical contacts because the alumina balls are capable of retaining the spherical shape at elevated temperatures ($<700^{\circ}\text{C}$) with an insignificant deformation.

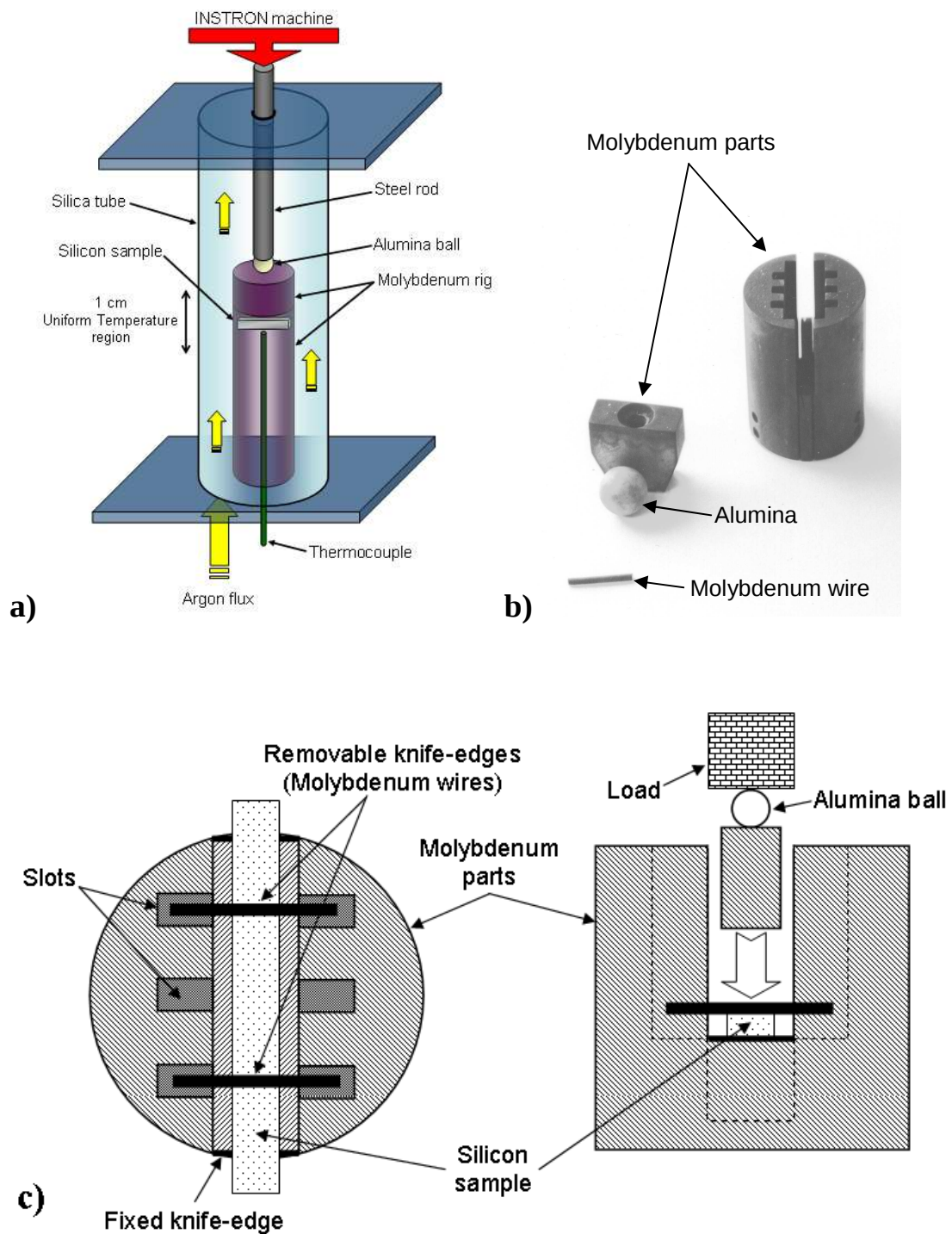


Figure 2-3. **a)** Schematic representation showing the experimental set-up. The silica tube was encapsulated in a cylindrical furnace (not shown) which provided the heating for the whole system. **b)** The molybdenum rig used for three and four-point bending. **c)** Top view (left) and side view (right) of the molybdenum rig in the configuration used for four-point bending.

The non-split cylindrical furnace (from Severn Furnaces Ltd) used for heating the whole system allowed working temperatures up to 1000°C and provided a region of uniform temperature at the furnace core, about 1 cm long. Typical heating time for the system was 10 minutes or less, starting from room temperature up to 600°C. Since the duration for cooling was much longer, all the samples were taken out of the rig and cooled in air to room temperature within 20 seconds. Silica tubes were used to contain the molybdenum rig inside the furnace because of the high melting point of silica (more than 1700°C) and its transparency. In addition, to prevent the oxidation of the molybdenum parts (and the silicon sample itself) during annealing in the temperature range 550-750°C, pure argon gas was allowed to flow through the silica tube for the whole duration of the experiments.

The temperature of the molybdenum rig in the furnace, within the area of uniform temperature, was controlled by using a thermocouple with the probe set very close to the silicon sample. Temperature calibration within the rig was carried out using four thermocouples with the probes placed in different positions, in vicinity of the sample. From the analysis and comparison of data collected from all the thermocouples at different temperatures, it was observed that the value of temperature given by the probe placed underneath the sample (Fig. 2-3a) could be considered as the real temperature (°C) of the specimen within a percentage error of ± 0.5 %.

The external bending force was supplied by an Instron 1195 universal testing machine, on the cross-head of which the specially designed rig was mounted. The load (up to ~100 N) was transferred from the Instron machine to the molybdenum rig by using a steel rod in contact with an alumina ball at one end; this kind of contact allowed the rod to self-align centrally along the cylinder axis and perpendicular to the sample.

5. Standard bending techniques

5.1 Overview

Many hard-to-grip materials are commonly tested with either three-point or four-point bending because a plain rectangular bar shaped sample can be used and no grips are required. These two bending geometries have been used in this work mainly to study the interaction between dislocations and impurity atoms in silicon crystals. Most of the experiments were carried out such that the dislocations studied were under tensile stress conditions at high temperature.

Although the geometry used with three and four-point bending is very simple, careful polishing of the sample is needed in order to prevent the formation of unwanted dislocations from surface flaws introduced in the sample during its preparation. In the present work, this did not present too much of a problem where the dislocations studied had been purposely introduced at specific locations by microhardness indentation since these could be distinguished from those generated from surface flaws. However, to study the generation of mobile dislocations from a random spatial distribution of pre-existing oxygen precipitates it was necessary to undertake experiments for which the effect of surface flaws was minimised.

The surface of as-received wafers was of very high quality and very nearly defect-free. Flaws are introduced when the wafers are cut up to produce the test specimens. Thus, by arranging a test geometry where the cut edges of the specimen experience little or no stress, it was possible to use as-cut samples without polishing their sides. With this approach it was possible to reduce considerably the effect of flaws generated during specimen preparation. The test geometry used was that of the annular bending in which the applied stress is mostly contained within a circular knife-edge and then no dislocations are produced

from the edges of the sample, as these are subjected to very low stresses. Three-point bending and four-point bending are described in the following sections, whereas annular bending is illustrated in Section 9.

5.2 Three-point bending

Elasticity theory can predict the stress distribution in a beam subjected to certain bending conditions. The material investigated in this thesis experienced some plastic deformation due to dislocation movement in the crystal, but this was very small and did not change appreciably the shape of the specimens. Therefore, since the deformation was not macroscopically large, the elasticity theory was used as a good approximation to calculate the stress distribution along the beam. In general, for a rectangular bar subjected to three point bending (Fig. 2-4), the maximum tensile stress at surface, $\sigma_{\max}$, is located in the middle of the bar and it is given by the following equation^{4,5}:

$$\sigma_{\max} = \frac{3Pl}{wh^2} \quad (2.1)$$

where $\sigma_{\max}$ = bending stress (MPa), P = load (N), l = loading span (mm), w = beam width (mm) and h = beam thickness (mm).

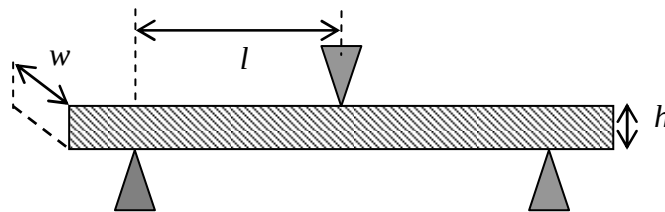


Figure 2-4. Three-point bending geometry.

According to the theory of errors, the percentage error in $\sigma_{\max}$ deduced from equation (2.1) was calculated to be a maximum of $\pm 6\%$ using values for typical experimental conditions (see Table 2.1). In addition, $\sigma_{\max}$ decreases linearly with depth z and becomes zero when $z=h/2$ (the neutral axis). The resolved shear stress τ in the glide plane of a dislocation has to be non-zero for slip to occur. Expression (2.1) gives the tensile stress $\sigma_{\max}$ on the surface plane, but it is necessary to multiply $\sigma_{\max}$ by the Schmid factor calculated for the specific slip system in order to deduce the resolved shear stress τ on the glide plane of interest. In the particular geometry used for the experiments, shown in Fig. 2-5, the Schmid factor calculated for the $a/2[10\bar{1}](111)$ slip system is $\cos(\varphi)\cos(\theta) = \frac{1}{\sqrt{6}}$ and then the maximum resolved shear stress $\tau_{\max}$ responsible for the dislocation motion in this geometry is

$$\tau_{\max} = \frac{\sigma_{\max}}{\sqrt{6}} \quad (2.2)$$

The stress distribution along the beam during three-point bending is shown schematically in Fig. 2-6. The resolved shear stress τ decreases linearly to zero moving from the middle of the bar (maximum value) to the external knife-edges. Because of this linear dependence, once $\tau_{\max}$ is known, it is possible to deduce the value of τ at any other position on the bar just considering the distance from the knife-edge. Table 2.1 reports the typical values used in this work for the calculation of the resolved shear stress from Equation (2.1) and (2.2).

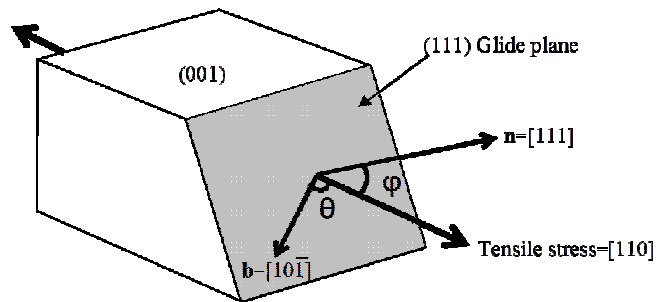


Figure 2-5. (111) activated glide plane during bending in the three-point geometry.

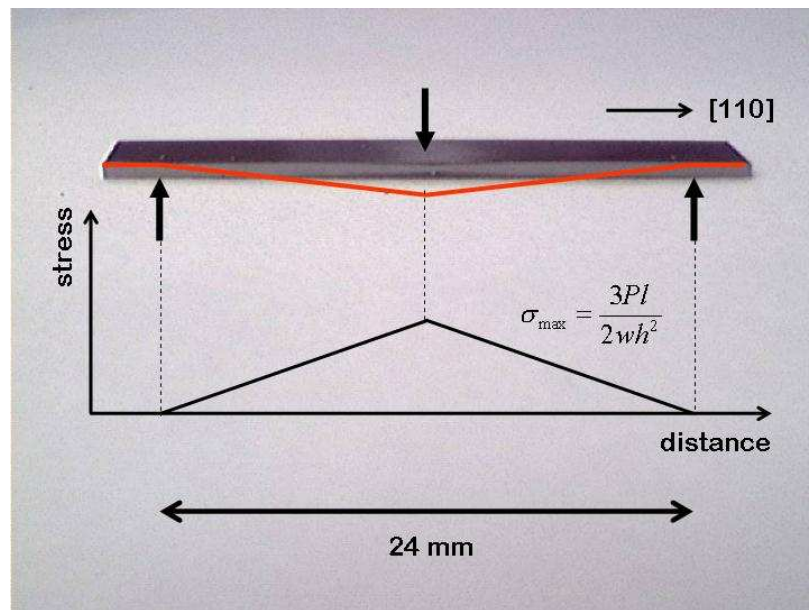


Figure 2-6. Schematic distribution of the stress during three-point bending of a silicon bar.

Description	Symbol	Value
Sample thickness	h	$1.3 \text{ mm} \leq h \leq 0.550 \text{ mm}$
Loading span	l	$(12 \pm 0.4) \text{ mm}$
Sample width	w	$4 \text{ mm} \leq w \leq 2 \text{ mm}$

Table 2.1. Typical values used in Equation (2.1).

5.3 Four-point bending

The geometry used for four-point bending is similar to that of three-point bending and is shown in Fig. 2-7. However, there is an important difference in four-point bending since the

region in between the inner knife-edges is subjected to a uniform tensile stress. Its value at the surface, σ_{const} , is given by

$$\sigma_{\text{const}} = \frac{3Pa}{wh^2} \quad (2.3)$$

where a is the distance between an outer knife-edge and the nearest inner knife-edge.

The stress distribution during four-point bending is shown schematically in Fig. 2-8 and the values used in Equation (2.3) are shown in Table 2.2. The separation between the inner knife-edges was fixed to (12 ± 0.4) mm during the experiments.

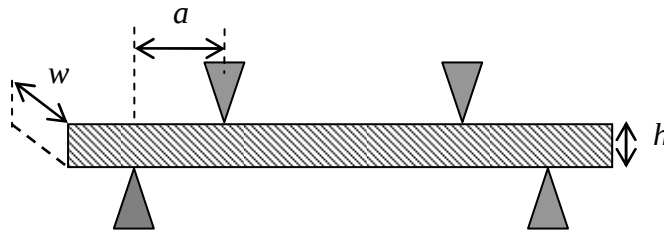


Figure 2-7. Geometry of four-point bending.

Description	Symbol	Value
Sample thickness	h	$1.3 \text{ mm} \leq h \leq 0.550 \text{ mm}$
Loading span	a	$(6 \pm 0.4) \text{ mm}$
Sample width	w	$4 \text{ mm} \leq w \leq 2 \text{ mm}$

Table 2.2. Typical values used in equation (2.3).

It is known that during three-point and four-point bending, the dislocations are generated in well characterised slip planes⁶. The activated glide systems in the case of (001) or (111) silicon wafers are shown in Fig. 2-9. In the present work, the four-point bending technique was mainly used to generate controlled dislocation half-loops from indents in the region where the stress was constant and uniform. Due to the uniformity of the shear stress to

which the dislocations were subjected, the distance travelled by the very first dislocations generated from different indents (within the inner knife-edges) was constant. This is shown schematically in Fig. 2-9, although the case of dislocations generated from a surface scratch, rather than from indents, is illustrated.

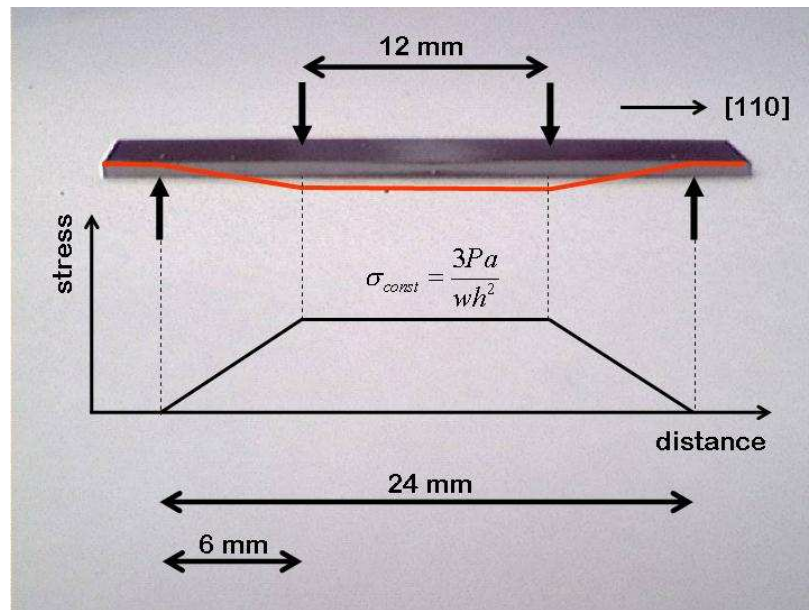


Figure 2-8. Schematic distribution of the stress during four-point bending

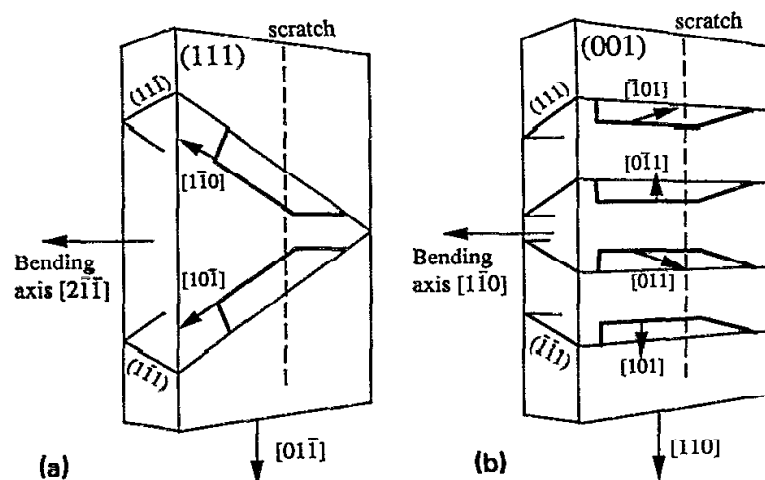


Figure 2-9. Slip system geometries for a) (111) silicon samples and b) (001) silicon samples (after Mariani⁵). In this representation, the dislocations are generated from a surface scratch.

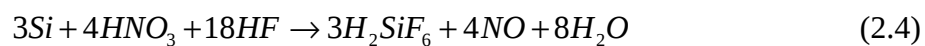
6. Chemical etching of silicon

6.1 Use of etching during the experiments

Wet chemical etching of silicon has been widely used in this experimental work mainly to remove surface damage whilst leaving a smooth surface without stress concentrators. During sample processing, chemical etching was chosen as the method to remove 30-50 μm of material from surface and was also used to reveal dislocations as etch pits. It is known that several flaws and microscopic scratches can be produced at a surface during cleavage and preparation of silicon samples. This happens even when the specimens are cut from high-quality and mirror-polished wafers. For this reason, all surface damage produced during sample preparation needed to be removed before the mechanical tests. In order to achieve this by a simple method, chemical solutions with an etching rate not strongly dependent on crystallographic orientations (isotropic etching solution) were used. The etching mechanism involved oxidation-reduction processes, followed by dissolution of the oxidation product.

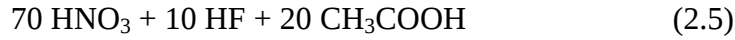
6.2 Planar etching

The most common solutions for isotropic wet etching of silicon use the nitric/hydrofluoric/acetic acid system^{7,8,9}, where nitric acid (HNO_3) is the oxidising agent and hydrofluoric acid (HF) dissolves the oxidised products according to the following reaction:



Acetic acid (CH_3COOH) dilutes the system so that the etching process can be better controlled¹⁰. A HNO_3 -rich solution is usually isotropic and the etching rate is limited by the dissolution process. This kind of solution is also known as the “planar” etch. After several tests, it was found that the best proportions for an isotropic solution in relation to our

purpose of removing damage (in particular the indents) whilst leaving a smooth surface are the following:



The etching rate at room temperature was deduced by measuring the height of some silicon “mesas” produced on the sample surface by using tiny wax drops (<1mm) spilled on the specimen (before etching) as a mask against oxidation and acid attack (Fig.2-10). After several minutes of wet etching, the mesas were examined under the Nomarsky microscope and their height was measured by using the z-axis calibrated control of the microscope (sensitive to approximately 1 μm height variation). The above procedure was repeated with three different samples for etching durations of 10 minutes, 20 minutes and 30 minutes, after which the measured height of the mesas was respectively 12 μm , 22 μm and 30 μm . Thus, the etching rate of the solution was deduced to be roughly 1 $\mu\text{m}/\text{minute}$ at room temperature without using any agitation of the mixture. In order to remove a <2 μm deep indent from the top surface, the sample was left in the etching solution for at least 10 minutes to assure the removal of approximately 10 μm of material. However, it was found that the etching rate of the solution was only constant for the first 30 minutes of the work time after which the dissolution process slows down significantly, as the active constituents are consumed. Hence, to remove more than 30 μm of material from the surface, two different baths in fresh planar etch solution was used.

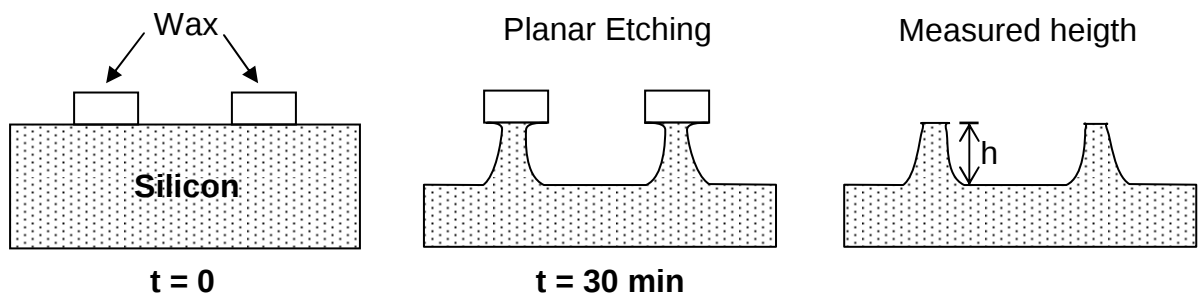


Figure 2-10. Determination of the solution etch rate. Wax drops were spilled on the silicon surface; after 30 minutes of immersion in the etching solution, the wax was removed in acetone and the height of the remaining mesas measured.

6.3 Preferential etching

Chemical etching of silicon was used to reveal the presence of defects such as dislocations and oxide precipitates near the surface. Since the silicon etching consists of oxidation followed by dissolution, if the chemical reaction is such that the dissolution is difficult and slow, then the etching process may become easier at defect sites where the atomic bonds are weakened. Thus, the higher etching rate for weakly bonded atoms induces a sort of selection in the etching process, which will be enhanced at surface defects. For this reason, these types of chemical mixtures are called preferential etching solutions. After preferential etching, well defined etch pits (usually looking like pointed etch cones) can be observed at the intersection points of dislocations and the surface. Precipitates will appear as shallow pits with varying diameter, depending on the precipitate size. Preferential etching solutions are prepared by replacing the HNO_3 of the planar etch with a weaker oxidant, although this should be sufficiently strong to produce a thin oxide layer at surface. A well known preferential etching solution for silicon is the so called “Sirtl” etch¹¹ which is a mixture of CrO_3 , HF and H_2O . This kind of etching is generally sensitive to crystallographic orientations and the delineation of the etch pits at defect sites is controlled by the ratio between CrO_3 (the oxidation agent) and HF . In this work, the composition of the etching solution for defect delineation was the following:



respectively in a ratio of 5:4. This mixture was used to reveal glide dislocation half-loops, in the form of sharp etch pits intersecting either $\{001\}$ or $\{111\}$ surfaces, depending on the orientation of the silicon wafers used for the experiments. Fig. 2-11 shows a secondary electron microscope (SEM) image of etch pits revealing a dense group of dislocations in (111) silicon generated from surface damage during bending at high temperatures.

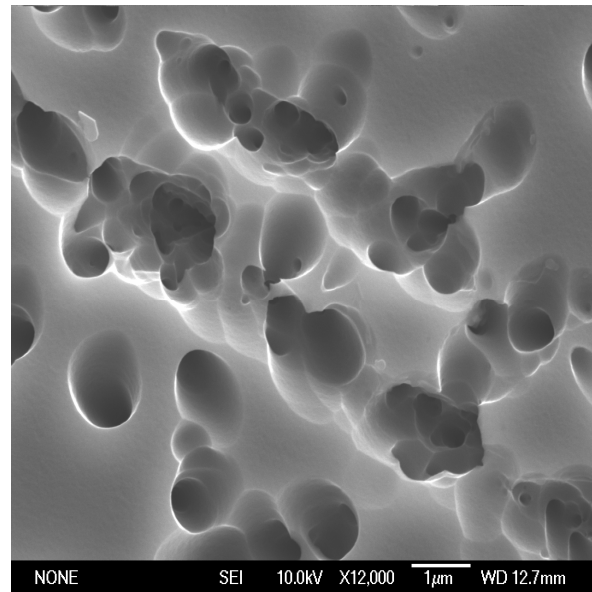


Figure 2-11. SEM image of etch pits revealing the presence of glide dislocations on the polished surface of (111) silicon samples.

The diameter of the surface etch pits depends on the etching duration: after 5 minutes of immersion in the above solution, the diameter of the pits at sample surface was approximately $1\ \mu\text{m}$. Fig. 2-12 shows an optical image of etch pits revealing oxide precipitates and associated punched-out prismatic loops in a (001) silicon sample containing precipitates.

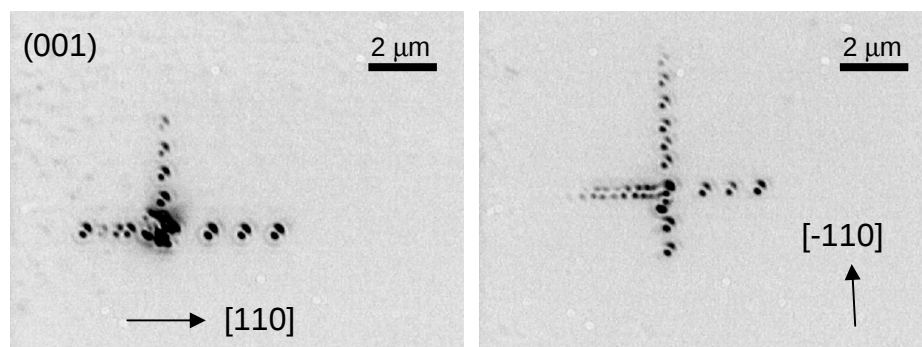


Figure 2-12. Optical images showing real etch pits in a (001) silicon sample containing large oxide precipitates. In this case, the extended defects revealed after preferential etching are prismatic loops punched-out from the precipitates (the larger etch pit at the centre) along the $\langle 110 \rangle$ directions.

7. Differential Interference Contrast (DIC) microscopy

Reflected light microscopy is one of the most common techniques used in the examination of specimens that do not absorb or transmit a significant amount of the incident light. Irregularities on the surface of the specimen create optical path differences, which are transformed by reflected light *Differential Interference Contrast* (DIC) microscopy into intensity variations that reveal the topographical profile of the sample. The image created with the reflected light DIC technique can be interpreted as a real three-dimensional representation of the surface, since a clear distinction can usually be made between raised and lowered regions in a specimen. The Nomarski birefringent prism¹² is the essential part of a DIC microscope, as shown in Fig. 2-13.

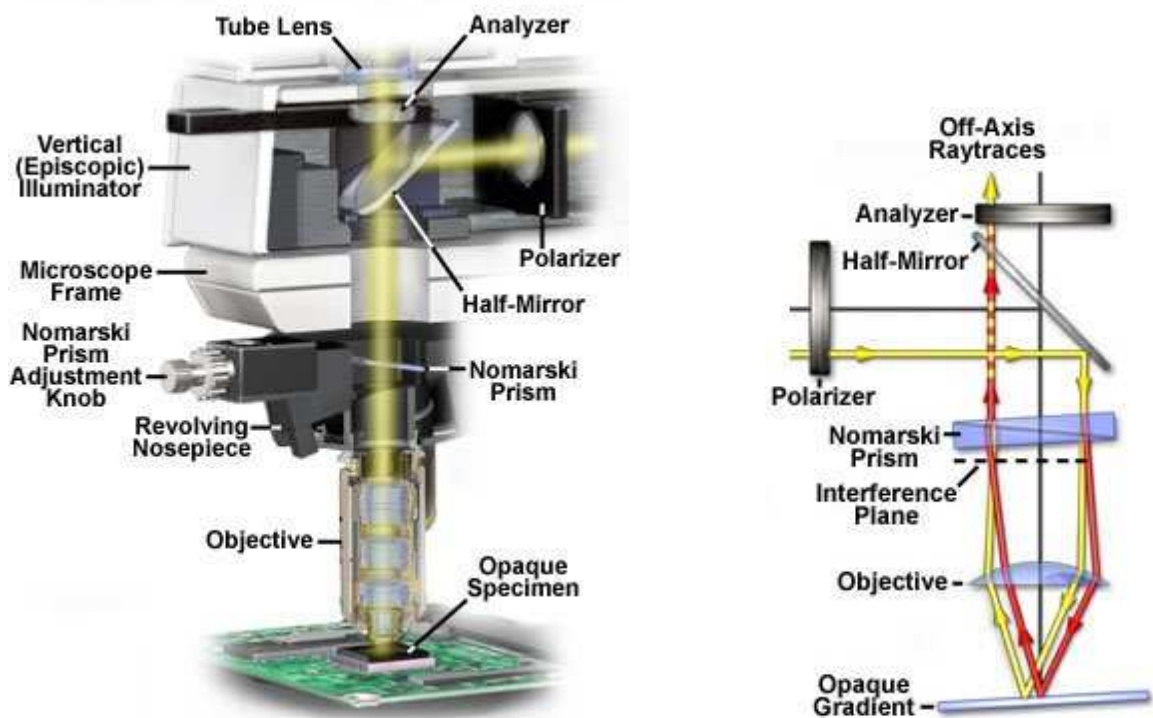


Figure 2-13. (Left) Reflected light DIC microscope optical path. (Right) The optical pathway for a single off-axis light ray (after Nikon).

The prism can be laterally translated along the optical axis of the microscope to enable adjustment of the relative phase shift between wave fronts. In this manner, fine-tuning of the

relative intensity in the image can be manipulated to produce the distinctive contrast associated with DIC microscopy. Images appear as if they were illuminated from a highly oblique light source originating from a single point (see for example Fig. 2-12).

A good optical microscope working in DIC mode can allow the detection of features as small as 5 nm height. Assuming that every dislocation half-loop that intersects the surface produces slip equal to that component of the Burgers vector perpendicular to the surface, the DIC microscopy should allow the detection of surface slip lines produced by approximately 15 or more dislocations. The sensitivity of the technique can be extended to the detection of a single (isolated) dislocation at surface if DIC microscopy is used in conjunction with chemical etching techniques, as will be shown in the following section.

8. Determination of the unlocking stress

8.1 Dislocation locking by oxygen in CZ-silicon

Rectangular samples with dimensions of approximately 0.67 mm × 3.5 mm × 30 mm (each sample was precisely measured as described in Section 2) were cleaved along $\langle 110 \rangle$ directions from precipitate-free and dislocation-free (001) Cz-Si wafers (p-type, 10 Ω cm, mirror polished on one side). The wafers had an initial oxygen concentration $C_0 = 2.6 \times 10^{17} \text{ cm}^{-3}$ (Low- C_O) measured by FT-IR, according to specifications DIN 50 438-I.

Some samples consisting of high-purity FZ-grown silicon and some other samples from Cz-grown wafers with high vacancy content¹³ (up to 10^{15} cm^{-3} , whereas normal Cz-silicon contains $< 10^{12} \text{ cm}^{-3}$) were also prepared for control purposes. These samples followed exactly the same experimental procedure used for the specimens with low-oxygen content described above and were tested to see whether a locking effect was observable in absence

of oxygen or to investigate the possible variation in dislocation locking due to the influence of intrinsic point defects. Prior to sample preparation, a specific thermal treatment (*tabula rasa*)¹⁴, consisting of 15 minutes annealing at 1000°C followed by a rapid cool, produced a uniform concentration of oxygen in the Cz-grown wafers and dissolved any oxide precipitates present in the bulk. After sample cleavage, the edges of the rectangular specimens were polished mechanically (using 1 μm diamond paste) and then by immersion in the planar etch solution for 2 minutes to obtain a smoother surface. This treatment was needed to suppress the generation of undesired dislocations from the irregular edges of the sample during its processing at high temperatures. The following procedure was then used to introduce a controlled array of dislocations in the rectangular silicon specimen.

1. In order to produce dislocation sources, several Vickers indents, all aligned in a row along the length of the sample, were introduced on the polished side by using a microhardness tester at room temperature. The load used for indentation was 10 g and the dwell time was about 5 seconds per indent. The distance between indentations along the sample was 250 μm (Fig. 2-14).

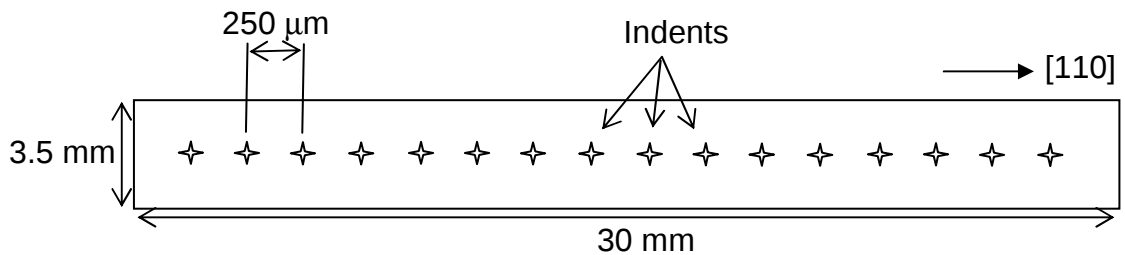


Figure 2-14. Typical geometry used during sample indentation.

2. The sample was then annealed under four-point bending conditions at temperatures between 550 and 600°C. With this operation, a constant stress (~ 100 MPa) was applied to that region of the sample between the two inner knife-edges of the rig. Under these stress conditions, dislocation loops were allowed to grow from indented

areas for 20-30 minutes. After sample cooling to room temperature (in less than 20 seconds), the resulting dislocation half loops were up to 200 μm in diameter.

3. The top 5 μm of the surface region was etched away to remove completely any surface damage left by the indentation.

Four glide systems were activated using the above bending conditions (Fig. 2-9b):

$$(a/2)[0\bar{1}1](111), (a/2)[\bar{1}01](111), (a/2)[011](\bar{1}\bar{1}\bar{1}), (a/2)[101](\bar{1}\bar{1}\bar{1}).$$

The dislocations created with this procedure were elongated half-loops with three segments parallel to the three $\langle 110 \rangle$ directions in the glide plane⁶: a long straight segment parallel to the surface and two shorter emerging segments. The character of these segments was either screw or 60° .

Following the introduction of dislocations, an annealing step without any applied load allowed the segregation of oxygen to the dislocations, which in turn produced the locking effect. During annealing, the specimens were placed in a silica tube and were in contact only with high-purity quartz parts to avoid the incorporation of contaminants at elevated temperatures. In addition, a flow of pure argon was used during annealing to prevent the oxidation of the samples in presence of air. In order to minimize the influence of temperature transients, samples were loaded into a pre-heated furnace and the specimen temperature required was quickly reached within a few minutes. Similarly, after annealing the samples were taken out of the furnace and cooled to room temperature within 30 seconds. Different lengths of time (10^{-1} - 10^4 hours) and different temperatures (400-850°C) were used to accumulate different amounts of oxygen at the dislocations. Subsequently, a surface layer 30-50 μm thick was removed to eliminate any effect of out-diffusion of oxygen that may have occurred during the annealing. This removal was by isotropic chemical etching using the planar etch described in Section 6.2.

A third high-temperature treatment was then performed under three-point bending conditions at 550°C. Since the stress distribution during three-point bending is such that the stress increases linearly from the external knife-edge to the internal one, as shown in Fig. 2-6 and Fig. 2-15, only those dislocations which were subjected to a stress larger than the unlocking stress could move, whereas all the other half-loops remained pinned at the original position. The correct Schmid factor was taken into account in the calculation of the resolved shear stress in the (111) glide plane (see Section 5.2). The loading conditions were chosen such that the unlocking stress was located well away from the inner and outer knife edges to avoid the irregularities in the stress field close to the knife edges. The loops which were exposed to a stress larger than the unlocking stress expanded and travelled a certain distance according to the stress that they experienced. Fig. 2-15 shows the correlation between dislocation lengths and unlocking stress. A preferential etching solution was used to determine the position of dislocation loops, which were revealed by etch pits, as shown in Fig. 2-16.

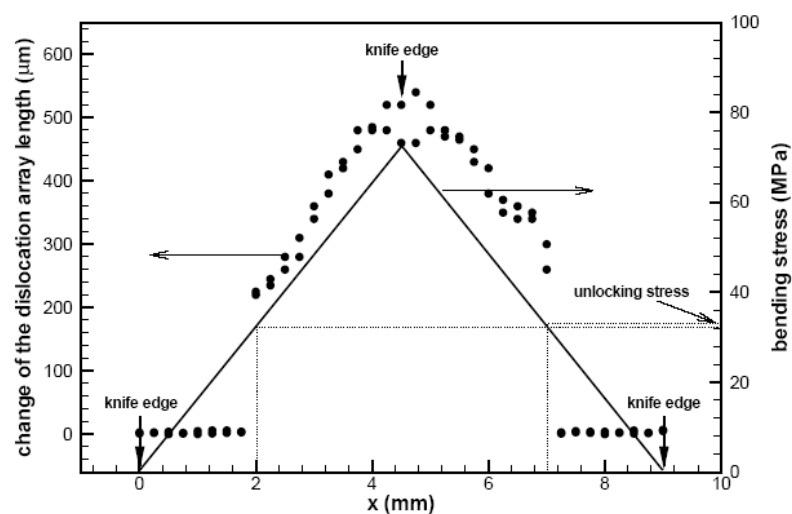


Figure 2-15. A typical example showing how to determine the unlocking stress. The graph shows the stress distribution and the change of dislocation array length during a three-point bend test as a function of position on the specimen (after Senkader).

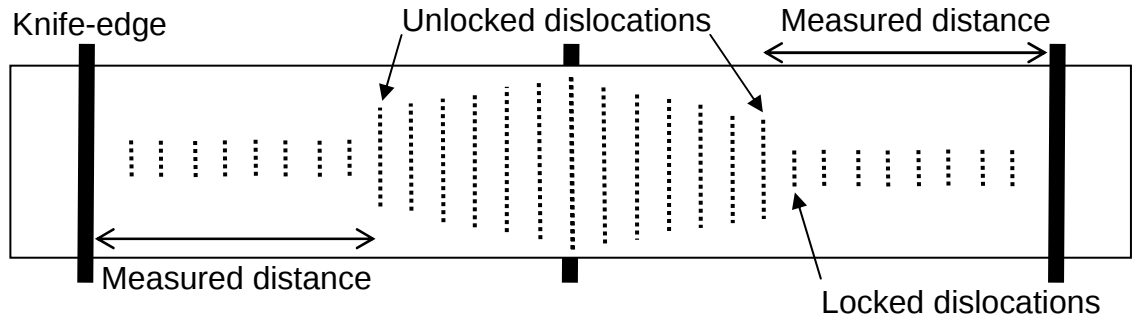


Figure 2-16. Distribution of etch pits (revealing dislocations) after three-point bending. The unlocking stress is deduced by measuring the distance shown in the figure.

By measuring the position of the unlocked dislocations along the silicon bar and knowing the applied stress distribution (see Section 5.2), the unlocking stress was determined within an experimental error of approximately $\pm 5\%$. It is noted that the three-point bending experiment gives two measurements of the unlocking stress τ_u for each sample, one per single arm of the silicon bar. The mean of these two measurements of τ_u was taken as the value for the unlocking stress and the error bar for each data point was given by the difference between the two.

8.2 Dislocation locking by nitrogen in FZ-silicon

The experimental procedure adopted for the study of nitrogen in FZ-silicon is similar to that described in the previous paragraph. However, since differences exist between the two procedures, following is a description of the experimental technique used to deduce the dislocation unlocking stress by nitrogen in FZ-silicon wafers.

Two nitrogen-doped FZ-silicon (NFZ) wafers were cut from the tail-end of a silicon ingot grown in a mixture of nitrogen ($<1\%$) and argon gas. The ingot was phosphorus-doped to a resistivity of $220 \, \Omega\text{cm}$. The orientation of these wafers was (111), although this was not

a predetermined choice, but rather a condition imposed by the availability of material. Due to the very low segregation coefficient of nitrogen, the final concentration of nitrogen in the as-grown crystal increases along the ingot length, thus the nitrogen content is higher in regions close to the ingot tail. The nitrogen concentration within the wafers (of thickness ~ 1.5 mm) was measured by the wafer supplier (Topsil S.A. - Denmark) using Fourier-Transform Infra-Red spectroscopy (FT-IR) and was found to be $\sim 2 \times 10^{15} \text{ cm}^{-3}$ (detection limit for nitrogen was $1 \times 10^{15} \text{ cm}^{-3}$), whereas the content of oxygen and carbon was below their detection limit ($\sim 5 \times 10^{15} \text{ cm}^{-3}$). All silicon samples were initially cut from the above NFZ wafers into long rectangular bars (up to 100 mm long) having width of approximately 3 mm and thickness of 1.5 mm using a circular diamond saw. The long bars were successively cleaved into shorter specimens about 30 mm long. Mechanical polishing and subsequent isotropic chemical etching were used in order to mirror polish at least three sides of the bars. After this procedure, the final dimensions of the silicon bars were approximately $2 \text{ mm} \times 1 \text{ mm} \times 30 \text{ mm}$, although each sample was accurately measured before bending, as described in Section 2.

Control samples of high purity FZ-silicon without any intentional nitrogen doping were also used as a reference; in these samples, the content of nitrogen, oxygen and carbon was below the detection limit and the phosphorus concentration was such that the resistivity was approximately $10 \text{ k}\Omega\cdot\text{cm}$.

The bars were then indented at room temperature on the (111) side by using a micro-hardness tester equipped with a Vickers diamond tip (Fig. 2-17a), with the same conditions described in the previous section for Cz-silicon samples. After this stage, the bars were annealed under stress by using standard four-point bending (typically 40 N load was applied for 30 minutes) at 550°C in pure argon atmosphere: this treatment allowed the generation and propagation from the indent of controlled dislocation half-loops (with diameter of

approximately 200 μm) along the two $[011]$ and $[\bar{1}01]$ preferential directions (Fig. 2-17b)⁶. The samples were then re-annealed (without applying any stress) at different temperatures (550-830°C) for a certain time (0.5-1500 hours) in order to allow the segregation and accumulation of nitrogen to the previously generated dislocations, which consequently become locked.

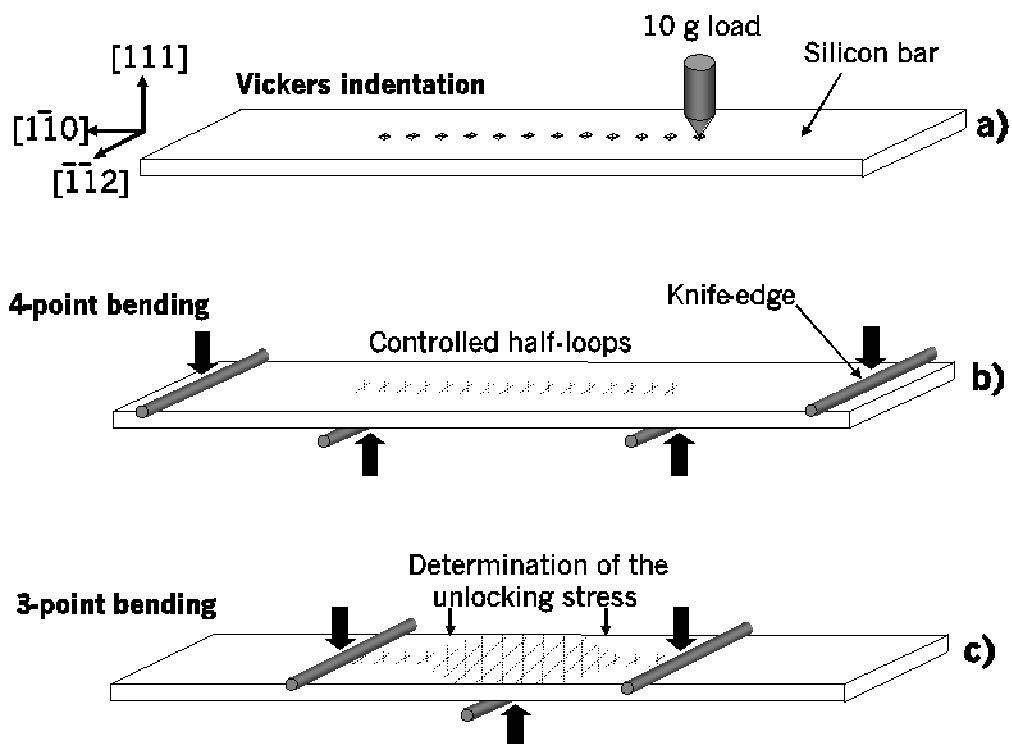


Figure 2-17. Schematic representation of the dislocation locking experiment for the determination of a single data point. Between steps B and C, a thermal treatment at constant temperature was introduced to allow the diffusion of nitrogen impurities to the dislocation core.

After the removal by chemical etching of about 30 μm of silicon from the top surface (this avoided the generation of new dislocations from the indents and removed the effect due to out-diffusion of nitrogen from the surface), the silicon bars were finally annealed under

three-point bending conditions (Fig. 2-17c). The stress was applied at 550°C for a few hours (2-6 hours, according to the magnitude of the stress applied). The loads, usually in the range 5-8 kg, were chosen in order to produce a wide range of resolved shear stresses (0-150 MPa) on the glide planes of dislocations according to their position along the bar. Dislocation segments intersecting the surface were detected by selective etching. As in the case of oxygen, it was possible to estimate the unlocking stress for dislocations in samples subjected to a certain heat treatment by calculating the resolved shear stress at the point from which the dislocations started moving during bending (Fig. 2-18). The more the nitrogen impurities accumulated at the dislocation core, the stronger the pinning effect that was measured.

In this work, the dislocation unlocking stress due to accumulation of nitrogen has been measured at the temperature of 550°C, although it is known that the unlocking stress has an intrinsic temperature dependence¹⁵.

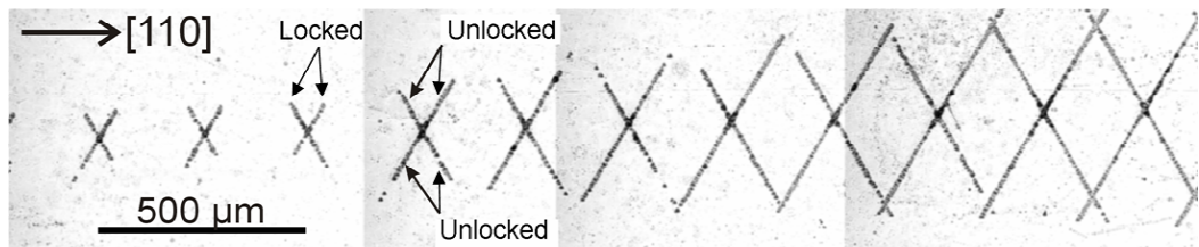


Figure 2-18. Dislocation etch-pits forming typical patterns on (111) silicon surface after selective etching. Some dislocations which have been unlocked during three-point bending are indicated by arrows. The unlocking stress τ_u was measured at these positions. Locked dislocations which have been subjected to a stress lower than τ_u and thus have not moved are also visible on the left.

9. Annular bending

For three and four-point bending experiments described above, sample preparation was time consuming because of the difficulty and care required when polishing the specimen sides to remove surface flaws. Thus, there was a need to develop a different bending technique that allowed to use as-cleaved silicon samples from wafers with high quality surface and does not need a careful polishing of the sample edge. A brief description of a less common bending test which involves a circular symmetry¹⁶ is given in the following. The exact geometry and dimensions of the molybdenum rig used for the “annular” bending are shown in details in Appendix A. During annular bending, a square sample (2 cm × 2 cm) taken from a silicon wafer is rested on an annular knife-edge and the load is applied through a small sphere made of alumina placed at the centre of the sample (Fig. 2-19). In such a mechanical test, the applied stress is mostly contained within the circumference of the knife-edge. The specimens are subjected to a stress which is larger at the centre of the sample and decreases monotonically with increasing distance from the centre. With this bending geometry, the problem of uncontrolled dislocations generated along the cleaved edges of the sample is avoided because there is insufficient shear stress at the sample edge to produce mobile dislocation loops.

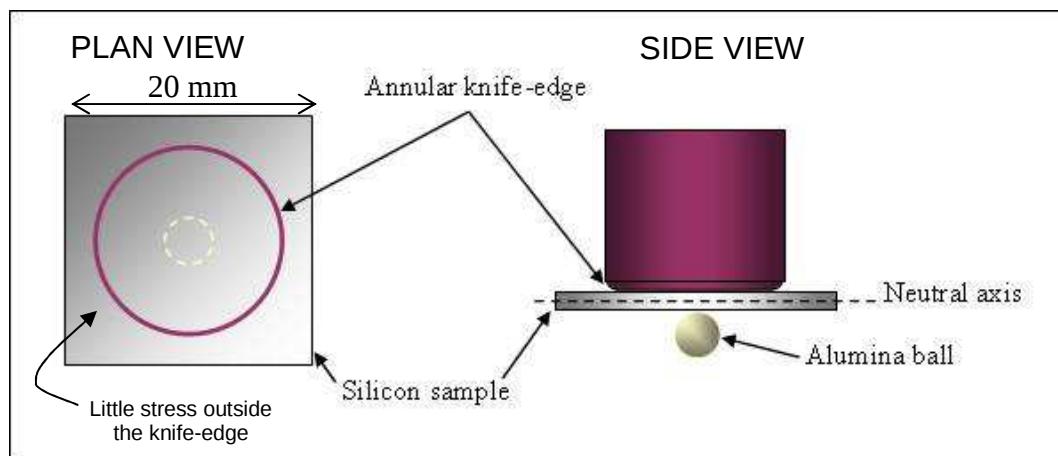


Figure 2-19. Plan view (left) and side view (right) of the annular-bending set-up.

While this technique removes the problems related to the generation of unwanted dislocations from the sample edges, it has the advantage of activating several glide systems in the crystals, thus it is possible to extend the results to a more general case.

The calculation of the stress distribution during a bending test with circular geometry was carried out using the bending theory of circular plates developed by Timoshenko¹⁷; the expressions for the radial stress (σ_r) and the tangential stress (σ_θ) during annular bending are deduced in Appendix B. Because of the biaxial stress distribution generated during annular bending, in the case of silicon crystals there are twelve activated glide systems for dislocations (consisting of four $\{111\}$ planes, each with three possible burgers vectors). However, only five out of these twelve systems are independent¹⁸, with five different values of resolved shear stress τ . For (001) silicon samples, the calculated shear stresses τ resolved in the five (independent) activated glide systems are the following:

Glide system	Resolved shear stress (τ)
$[\bar{1}0\bar{1}](\bar{1}11)$	$\frac{\sqrt{6}}{12}[(\sigma_\theta - \sigma_r)(\sin 2\theta - \cos 2\theta) + \sigma_\theta + \sigma_r]$
$[01\bar{1}](\bar{1}11)$	$\frac{\sqrt{6}}{12}[(\sigma_\theta - \sigma_r)(\sin 2\theta + \cos 2\theta) + \sigma_\theta + \sigma_r]$
$[110](\bar{1}11)$	$\frac{\sqrt{6}}{12}(\sigma_\theta - \sigma_r)\cos 2\theta$
$[0\bar{1}\bar{1}](11\bar{1})$	$\frac{\sqrt{6}}{12}[(\sigma_r - \sigma_\theta)(\sin 2\theta - \cos 2\theta) + \sigma_\theta + \sigma_r]$
$[\bar{1}0\bar{1}](11\bar{1})$	$\frac{\sqrt{6}}{12}[(\sigma_r - \sigma_\theta)(\sin 2\theta + \cos 2\theta) + \sigma_\theta + \sigma_r]$

(2.7)

The values of resolved shear stress for the other seven possible glide systems are either the same values given above or with opposite sign.

Table 2-3 reports all the constant parameters considered for the above stress calculation and used for the experiments.

Description	Symbol	Silicon	Alumina	Molybdenum
Young's modulus	E	(160 ± 30) GPa [19]	(343 ± 43) GPa [20, 11]	-
Poisson's ratio	ν	(0.25 ± 0.03) [9]	$0.22 (-0.01)$ [21]	-
Sample thickness	h	(0.67 ± 0.01) mm	-	-
Knife-edge radius	X	-	-	(7.75 ± 0.05) mm
Ball radius	R	-	(3 ± 0.05) mm	-

Table 2-3. Values used to calculate the resolved shear stress using the equations in Appendix B and also Equations (2.7).

As an example, Fig. 2-20 shows the calculated angular distribution of τ in six different glide systems for a given load (100 N) and a certain radius ($r = 5$ mm) during annular bending. It can be seen that the resolved shear stress τ reaches the maximum value at the angle $\frac{\pi}{8}(1+2n)$, where $n = 0, 1, 2, 3, \dots$. This stress distribution generates a typical rosette pattern which is also visible when we observe the distribution of real slip lines on the silicon sample after annular-bending at high temperatures (Fig. 2-21). The experimental evidence in Fig. 2-21 is the best proof of the reliability of the calculation described above, even if it was carried out in the elastic limit. Better resolution can also be obtained by etching the silicon samples and looking at the etch-pit distribution. Measuring the distance r to the origin of the outermost slip lines from the centre of the specimen (the ball contact) and using Equations (2.7) it was possible to deduce the critical resolved shear stress τ necessary to detect dislocations at the silicon surface as slip lines (the *slip stress*). All measurements, if not otherwise specified, were done in tensile stress conditions, that is with the mirror polished surface of samples facing the annular knife-edge.

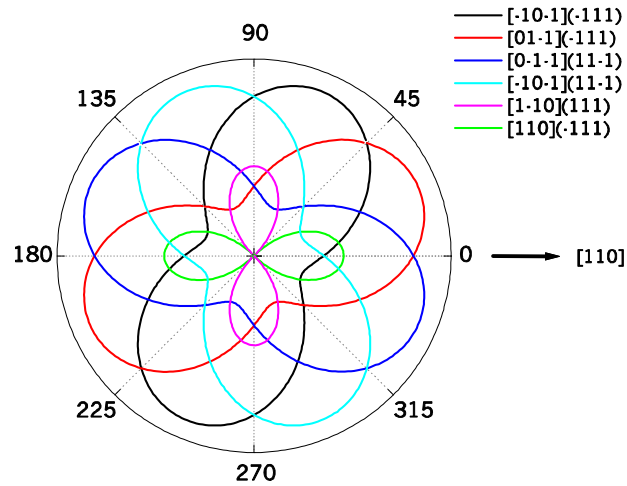


Figure 2-20. Angular distribution of the resolved shear stress for different glide systems in silicon subjected to annular bending. The calculated curves refer to a load of 100 N applied on the (001) surface and a distance from the ball contact of 5 mm.

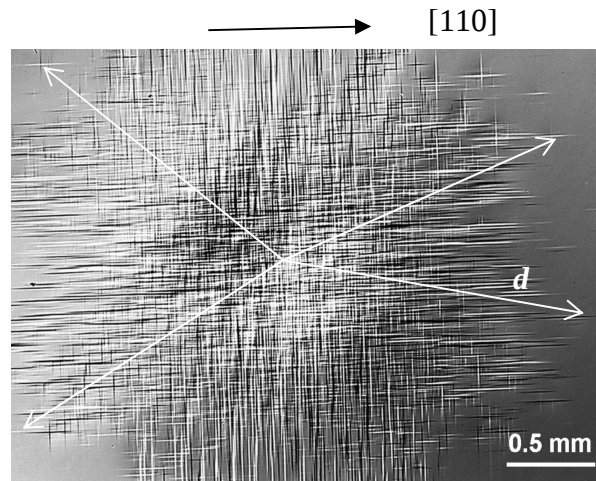


Figure 2-21. Real distribution of slip lines on the (001) silicon surface after annular-bending. The picture was taken using a differential interference contrast (DIC) microscope. The distance d was taken as the average to the origin of the outermost slip lines along the eight directions for which the resolved shear stress is a maximum, $d = 1/8 \sum_{i=1}^8 d_i$.

In addition, test measurements performed with annular bending, three-point and four-point bending gave similar results in each case for the critical resolved shear stress to produce slip lines at surface, as reported in Fig. 2-22. It can be deduced from Fig. 2-22 that the percentage error in the determination of the slip stress considering all the bending techniques

is approximately 5%. The effect of different applied loads on the stress distribution during annular bending was also investigated, but no appreciable difference in the slip stress was found after changing the load.

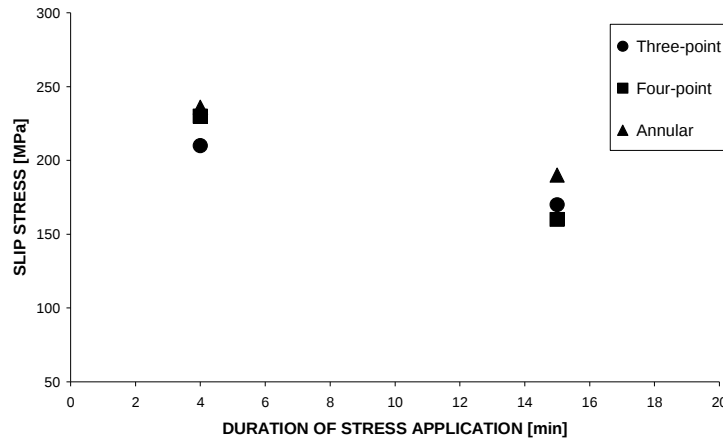


Figure 2-22. Measurements of the slip stress as a function of time using different bending techniques and silicon samples containing small oxide precipitates, in concentration of 10^8 cm^{-3} . It was found that the slip stress measured by using all the bending techniques at 585°C has roughly the same value within a percentage error of approximately 5%.

The use of elasticity theory for this kind of stress calculation is usually accepted in most cases. In fact, the presence of microscopic deformation due to dislocation movement across the surface does not appreciably affect the calculation of the stress distribution, provided such deformation is controlled and does not alter macroscopically the shape of the specimen. Certainly this assumption is valid for short duration of stress application, with a low load applied on the sample, as in this case the dislocations have not much time to grow and multiply, thus the plastic deformation is limited.

The radial distribution of the resolved shear stress during annular-bending is shown in Fig.2-23 where the maximum value of the stress over the five different glide systems has been considered in the plot as a function of the radius r . Note that the calculation is not exact when the distance from the ball contact is shorter than approximately $300 \mu\text{m}$. This is due to

the nature of the contact between the ball and the silicon sample. For this reason, the measurement of the stress in regions close to the ball contact was always avoided during the mechanical tests on the silicon samples. If X is the knife-edge radius, typically the load was chosen such that the surface region of interest was distant at least $X/3 \sim 2.5$ mm from the ball contact, where the shear stress on the slip systems is surely well defined by Equations (2.7).

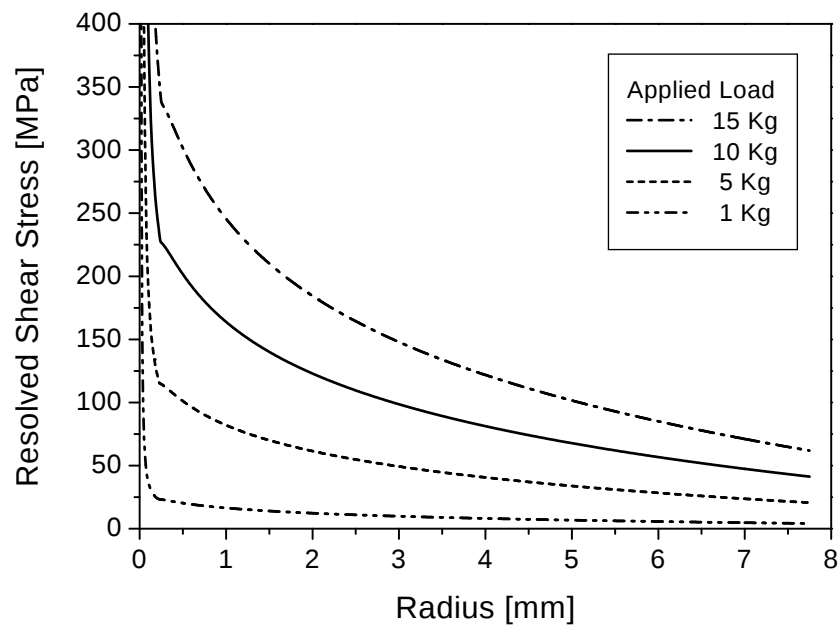


Figure 2-23. Radial distribution of the resolved shear stress for different values of applied load.

10. Dislocation generation from oxide precipitates

Different experiments were carried out to investigate the mechanism by which Cz-silicon wafers are weakened by oxygen precipitation within the material during heat treatments at high temperatures. All wafers used in these experiments were produced by M.E.M.C. Electronic Materials S.p.A. (Italy) using commercial fabrication facilities. The technique used to grow silicon ingots allowed an accurate control of impurities diffused to the as-

grown crystals. Thermal treatments of wafers to nucleate and grow oxide precipitates in different concentration and size were performed in clean rooms at M.E.M.C. All TEM investigations shown in this chapter were carried-out by the group of Dr V. Reznik at the ‘Giredmet’ Institute of Rare Metals in Moscow.

10.1 Thermal treatment of wafers

The material used in the experiments was taken from Czochralski-grown (001) silicon wafers (p-type, 10–20 Ωcm) with thickness of 670 μm and mirror-polished on one side. The initial oxygen concentration in the crystals was measured to be approximately 12 ppma, or equivalently, $6 \times 10^{17} \text{ cm}^{-3}$ (DIN 50438/I) by using Fourier-Transform Infra-Red (FTIR) spectroscopy.

The as-cut wafers were subjected to an annealing sequence consisting of four major thermal treatments in order to obtain oxygen precipitates of different sizes within the bulk. An initial homogenization anneal carried out at 1000°C for 15 min (*tabula rasa*)¹⁴ allowed the dissolution of grown-in precipitates since, if not eliminated, the grown-in precipitates may cause large variations in the following precipitation treatment.

A nucleation anneal carried out at 650°C for 6, 8, 16 and 32 hours provided the formation of oxide precipitate nuclei with density ranging from 10^8 cm^{-3} to 10^{11} cm^{-3} according to the duration of treatments. The concentration of nuclei achieved with this operation affects the concentration of bigger oxide particles grown in the next treatments.

A final two-step annealing process was used to grow oxide precipitates in different sizes from the oxide nuclei that were developed during the nucleation treatment. This consisted of a “drift” anneal at 800 °C for 4 h which was followed by annealing at 1000°C for 0.5, 1, 2, 4, and 8 hours, during which the precipitate size increases with increasing

duration of these thermal treatments at 1000°C, as demonstrated by TEM analysis (see for example Fig. 2-24 and Table 2.4).

10.2 Density and size of precipitates in the wafers

In all samples, the average precipitate size was calculated using Ham's theory of diffusion-limited growth²². According to Ham, the actual shape of a precipitate can be approximated by an oblate spheroid with semiaxes a and c ($a > c$); the growth rate of the precipitate is then given by the following differential equation:

$$\frac{da}{dt} = \frac{D_o \Omega_p e}{c \sin^{-1} e} (C_o^\infty - C_o^{eq}) \quad (2.8)$$

where D_o is the diffusivity of oxygen, Ω_p is the volume of a SiO₂ molecule ($4.5 \times 10^{23} \text{ cm}^3$), C_o^∞ is the oxygen concentration at the far field of diffusion and C_o^{eq} is the equilibrium concentration of oxygen in silicon. The eccentricity e is given by

$$e = \sqrt{1 - \frac{c^2}{a^2}} \quad (2.9)$$

A numerical calculation was carried out by means of a Fortran code (see Appendix C) which was written specifically to solve the ordinary differential Equation (2.8) in the case of oblate precipitates, using the well known Runge-Kutta method. The real size of the oxide precipitates has also been detected by TEM investigation of different annealed samples and the observed oxide particles were found to have a size ranging from 50 nm to 500 nm (Table 2.4), in good agreement with the theoretical values predicted by Equation (2.15). Fig. 2-24 shows that not only the precipitate size, but also the defect morphology changes with annealing time. The excessive growth of oxide precipitates can lead to the release of punched-out prismatic dislocation (PPD) loop²³ and subsequently, after longer annealing, to the formation of larger dislocation tangles.

The density of oxide precipitates and/or related complex defects has been determined by optical microscopy, etching techniques and, in some cases, by TEM analysis. Results are shown in Table 2.5, where the shaded boxes indicate samples for which TEM examination was carried-out successfully. After the thermal treatments described above, the wafers were cut in either 20 mm × 20 mm square samples to be used for the mechanical tests with annular bending, or 4 mm × 30 mm bars for the three/four-point bending tests.

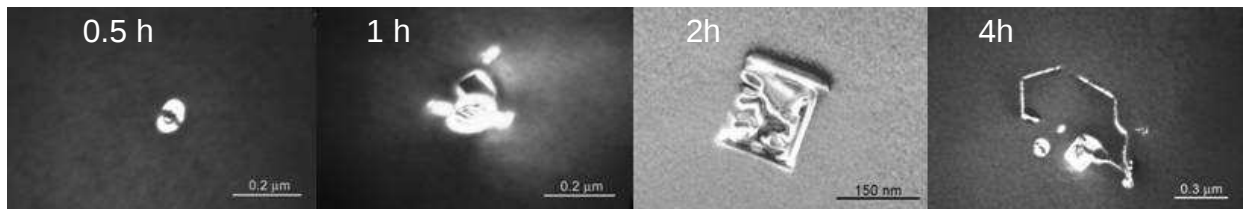


Figure 2-24. TEM pictures of oxide precipitates in samples subjected to (from left to right) 0.5 h, 1 h, 2 h, 4 h of annealing at 1000°C (after Reznik, private communication).

Growth ann. Time ⇒ Nucleation anneal. Time ↓	1 h	2 h	4 h	8 h	16 h
6 h	-	-	-	-	-
8 h	-	-	-	50nm platelet	50nm platelet
16 h	-	-	100nm platelet	180nm platelet	250(500)nm platelet
32 h	30nm spherical	120nm platelet	180nm platelet	220nm platelet	300nm platelet

Table 2.4. Variation of the precipitate size (and morphology) with annealing time as observed by TEM. Empty boxes correspond to samples in which it was not possible to detect the presence of any oxide precipitate using TEM (after Reznik, private communication).

Growth anneal. time $\Rightarrow$ Nucleation annealing time	0.5 h	1 h	2 h	4 h	8 h	16 h
6 h	[Oi]=11.998 ppma OM Cl. $2.0 \times 10^7 \text{ cm}^{-3}$	[Oi]=12.103 ppma OM Cl. $6.2 \times 10^7 \text{ cm}^{-3}$	[Oi]=11.981 ppma OM Cl. $2.5 \times 10^8 \text{ cm}^{-3}$ TEM no	[Oi]=12.052 ppma OM Cl. $2.1 \times 10^8 \text{ cm}^{-3}$ TEM no	[Oi]=12.067 ppma OM Cl. $2.1 \times 10^8 \text{ cm}^{-3}$ Pl. $1.9 \times 10^8 \text{ cm}^{-3}$ TEM no	[Oi]=12.024 ppma OM Cl. $4.2 \times 10^8 \text{ cm}^{-3}$ Pl. $4.2 \times 10^8 \text{ cm}^{-3}$ TEM $3.9 \times 10^8 \text{ cm}^{-3}$
8 h	[Oi]=12.037 ppma OM Cl. $7.9 \times 10^7 \text{ cm}^{-3}$	[Oi]=12.074 ppma OM Cl. $3.3 \times 10^7 \text{ cm}^{-3}$	[Oi]=11.937 ppma OM Cl. $1.3 \times 10^8 \text{ cm}^{-3}$ TEM no	[Oi]=11.848 ppma OM Cl. $5.6 \times 10^8 \text{ cm}^{-3}$ TEM no	[Oi]=12.237 ppma OM Cl. $7.4 \times 10^8 \text{ cm}^{-3}$ TEM $7.0 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.161 ppma OM Cl. $9.5 \times 10^8 \text{ cm}^{-3}$ Pl. $4.7 \times 10^8 \text{ cm}^{-3}$ TEM $7.6 \times 10^8 \text{ cm}^{-3}$
16 h	[Oi]=12.104 ppma OM Cl. $1.1 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.028 ppma OM Cl. $4.9 \times 10^7 \text{ cm}^{-3}$	[Oi]=12.100 ppma OM Cl. $6.6 \times 10^7 \text{ cm}^{-3}$ TEM no	[Oi]=12.084 ppma OM Cl. $1.6 \times 10^8 \text{ cm}^{-3}$ TEM $2.3 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.085 ppma OM Cl. 9.0×10^8 TEM $7.1 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.060 ppma OM Cl. $8.6 \times 10^8 \text{ cm}^{-3}$ Pl. $5.7 \times 10^8 \text{ cm}^{-3}$ TEM $9.3 \times 10^8 \text{ cm}^{-3}$
32 h	[Oi]=12.008 ppma OM Cl. $1.0 \times 10^8 \text{ cm}^{-3}$ Pl. $7.0 \times 10^7 \text{ cm}^{-3}$	[Oi]=11.926 ppma OM Cl. $1.8 \times 10^8 \text{ cm}^{-3}$ Pl. $2.0 \times 10^8 \text{ cm}^{-3}$ TEM $2.1 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.100 ppma OM Cl. $2.4 \times 10^8 \text{ cm}^{-3}$ Pl. $5.5 \times 10^8 \text{ cm}^{-3}$ TEM $6.7 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.202 ppma OM Cl. $2.0 \times 10^8 \text{ cm}^{-3}$ Pl. $3.0 \times 10^8 \text{ cm}^{-3}$ TEM $1.4 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.074 ppma OM Cl. $5.4 \times 10^8 \text{ cm}^{-3}$ Pl. $3.0 \times 10^8 \text{ cm}^{-3}$ TEM $8.3 \times 10^8 \text{ cm}^{-3}$	[Oi]=12.087 ppma OM Cl. $2.2 \times 10^{10} \text{ cm}^{-3}$ Pl. $2.0 \times 10^{10} \text{ cm}^{-3}$ TEM $2.5 \times 10^{10} \text{ cm}^{-3}$

Table 2.5. Optical Microscopy (OM) and Transmission Electron Microscopy (TEM) results for precipitate densities as function of annealing duration for nucleation and growth. [Oi] indicates the initial oxygen concentration that was approximately $6 \times 10^{17} \text{ cm}^{-3}$ in all wafers. Shaded boxes indicate samples on which TEM investigation has been carried out (*after Reznik, private communication*).

10.3 Determination of stress to activate intrinsic dislocation sources

Annular bending was initially used to measure the critical shear stress necessary to produce slip lines at the surface of silicon wafers after application of an external load for a certain time at high temperatures. In the following, this critical shear stress will be called the *slip stress* τ_{slip} . The geometry and the distribution of the applied stress during annular bending has already been discussed in Section 9. During bending at high temperatures, glide dislocations can be nucleated in silicon samples at sites where oxide precipitates and their related defects are formed. The use of DIC optical microscopy allowed the detection (without any etching) of slip lines due to formation of nanometer-scale steps after the

emergence at surface of several glide dislocations generated from the precipitates during heat treatments, as shown in Fig. 2-21. Although the formation of slip lines represents a real problem for device processing, the information gained in this work by studying slip lines did not reveal the more fundamental aspects of dislocation generation. This was because slip lines represent the product of several slip events, hence the information concerning the generation of the very first dislocation from a precipitate is not clear. However, single dislocation generation events can be investigated under certain conditions by using etching techniques, as described below.

During dislocation generation experiments, the sensitivity of detection was improved to the level of single dislocations by selective etching techniques. This combination of bending and etching allowed measurement not only of the slip stress to generate a slip line at the surface, but also the stress needed to reveal a single glide dislocation produced from an oxide precipitate and associated punched-out dislocations. Both annular and three-point bending were used for this kind of experiment. While annular bending is advantageous since it does not require a particularly careful polishing of the sample edges, the inaccuracy in the determination of the shear stress with this technique is larger than that with three-point bending. This is because in annular bending the distribution of slip lines at the surface is more complicated and the determination of the distance between the outermost slip line and the centre of the sample (measured in the eight directions along which τ_{slip} is maximum) is more difficult than in the case of three-point bending (see Fig. 2-20 and 2-21).

During **annular bending** tests, the load (up to 10 Kg) was applied on Cz-silicon samples containing precipitates (described above) at 585°C in pure argon atmosphere; the duration of stress application was 3-15 minutes. After cooling to room temperature, the silicon samples were immersed in the selective etching solution to reveal the presence of dislocations at the surface. Dislocations were then detected by observing the etch pits associated with them under a Nomarski optical microscope. During the application of a load

using the annular knife-edge on the top of the sample, the angular distribution of the shear stress resolved on the different activated slip systems $a/2\langle 110 \rangle\{111\}$ was similar to that shown in Fig. 2-25 (as an example) where the stress values are calculated at 5 mm from the ball contact for different angles (0-360°). In the same figure, a picture showing the real distribution of dislocation etch-pits on the surface is also visible in transparency. It is shown that the distribution of pits matches the contour lines representing the calculated stress. The distance of the outermost etch pits from the centre (the ball contact) was measured, thus it was possible to deduce the critical resolved shear stress necessary to produce and subsequently detect the dislocations at surface.

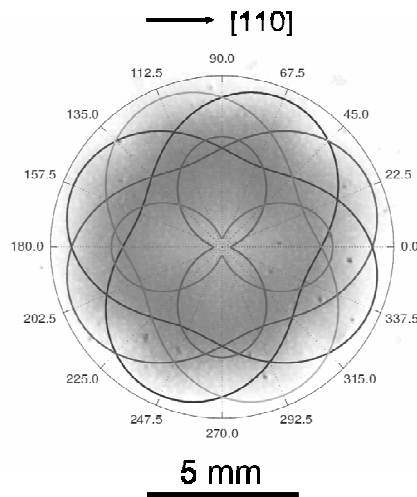


Figure 2-25. Calculated angular distribution of resolved shear stress for different activated slip systems. The real distribution of dislocation etch pits, at low magnification, is also shown.

For **three-point bending** tests, rectangular Cz-silicon bars with initial dimensions 0.65 mm × 3 mm × 30 mm were cleaved along the [110] direction. Careful polishing of the sample surface and sides was then needed to remove any tiny scratches or little flaws that may generate undesired dislocations when a stress is applied at high temperature. The final polishing step was isotropic chemical etching which removed, uniformly, about 20 μm of

material from the surface. The samples were then annealed at 585°C under three-point bending conditions (bending axis was $[\bar{1}\bar{1}0]$) for different times (1-20 min). The resolved shear stress on the activated glide systems for dislocations was calculated at each point on the surface. Dislocation hexagonal loops created through three-point bending, in the above geometry, glide in the (111) and $(\bar{1}\bar{1}1)$ planes. The loop segments are either screw or 60° in character, distributed in equal proportions⁶. A preferential chemical etch was used to reveal the emergent parts of the loops as surface etch pits, visible under differential interference contrast (DIC), as shown in Fig. 2-26.

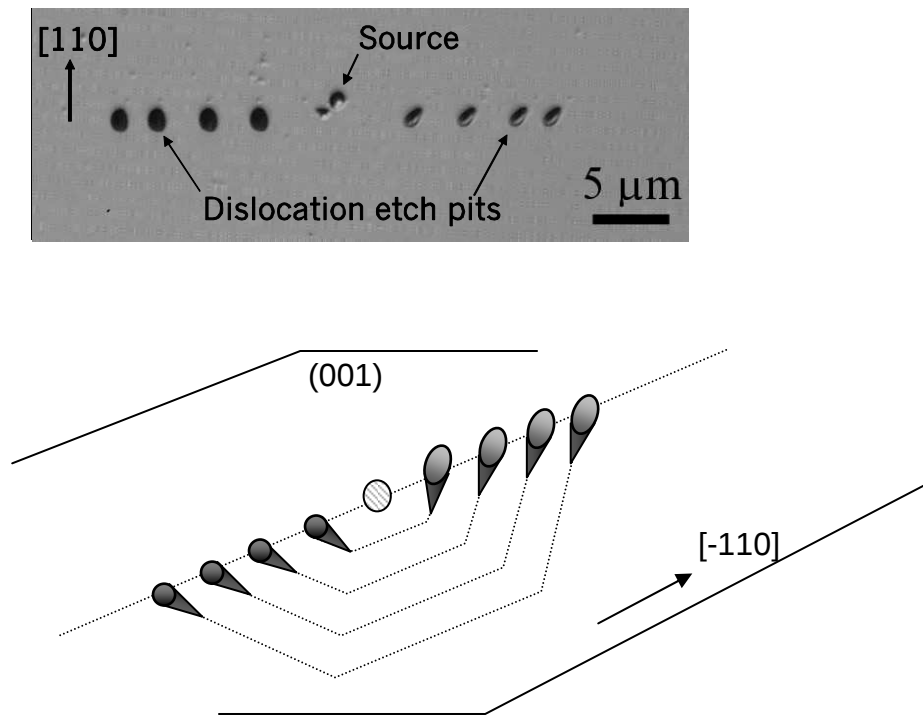


Figure 2-26. Etch pits revealing four dislocation glide loops on the silicon surface. The position of the dislocation source is visible at the centre. A schematic representation is also shown.

Where the shear stress was higher, several dislocation loops were detected as a row of pits. Every etch pit had a symmetrical counterpart because the source was in the centre of the loops. Examining the etch pits from the middle of the silicon bar (maximum stress) to the

outer knife-edges (very low stress) it was possible to count the number of dislocation glide loops generated by each source. The number of pits associated with a single source decreases in number as the applied stress decreases along the [110] direction. Where the dislocations were subjected to a smaller shear stress, they travelled only a shorter distance. At a certain position at the surface, only one single isolated loop could be detected close to the source and at lower stresses, no other dislocations were visible (Fig.2-27). Therefore, the measured resolved shear stress at that point gave the minimum stress required to generate one single dislocation glide loop. This stress τ_c is defined as *critical resolved shear stress to generate a single dislocation glide loop*.

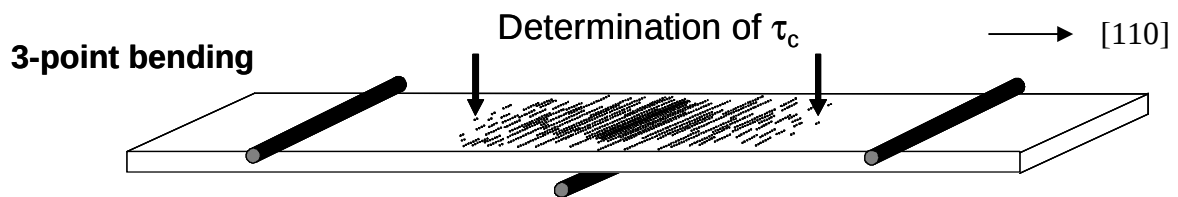


Figure 2-27. Determination of the critical resolved shear stress to generate a single dislocation glide loop by looking at etch pits at surface. Arrows indicate the points where only two pits related to a single dislocation were detected after a certain duration of stress application.

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Chapter 3:

Analysis of dislocation unlocking data in terms of impurity diffusion, binding and other parameters

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1. Binding energy to a dislocation

As described in Chapter 1, Section 8, dislocation locking experiments have shown that the unlocking stress τ_u saturates after a certain annealing time. From the analysis of the saturation value of τ_u as a function of annealing temperature, important information about the binding energy of an impurity atom to a dislocation can be deduced. The diffusion process controls the transport of an impurity to the dislocation, whereas the interaction between an impurity atom and a dislocation is characterised by the binding energy of the impurity atom to the linear defect. If a large number of sites along the dislocation core are available for occupation, then the impurity atoms at the core will establish a Maxwell-Boltzmann concentration distribution at the equilibrium state. Thus, according to Equation (1.17) that can be rewritten in the form

$$C_{core} = C_o \exp\left(\frac{\Delta G}{kT}\right) \quad (3.0)$$

where C_{core} is the impurity concentration at the dislocation core, the first saturation regime (regime 2) is determined by the concentration of impurities at the far field of diffusion C_o and the binding energy between an impurity atom and a dislocation, ΔG . Equation (3.0) shows that the assumption of a large number of sites available for impurities along the dislocation core represents a reasonable hypothesis if the bulk concentration of impurities is sufficiently low and its binding energy to the dislocations is not very high (<1 eV). Taking into account Equation (3.0) and assuming that the unlocking stress is proportional to the number of impurity atoms at the dislocation core, the unlocking stress τ_u can be written as $\tau_u = K C_{core}$ which at equilibrium, during regime 2, becomes

$$\tau_u = K C_o \exp\left(-\frac{\Delta S}{k}\right) \exp\left(\frac{\Delta H}{kT}\right) \quad (3.1)$$

where K is a proportionality factor [Pa cm^3], ΔS and ΔH are respectively the entropy change and the enthalpy change after the impurity-dislocation interaction, k is Boltzmann's

constant, T is the absolute temperature and the thermodynamic relationship $\Delta G = \Delta H - T\Delta S$ is used to write the (maximum) value of the impurity-dislocation binding free energy at the core. An Arrhenius plot of the unlocking stress τ_u observed during the saturation regime can then be used to determine the value of the impurity-dislocation interaction enthalpy, as shown for example in Fig. 3-1 (copy of Fig. 1-26) where ΔH is deduced from the best fit to Equation (3.1).

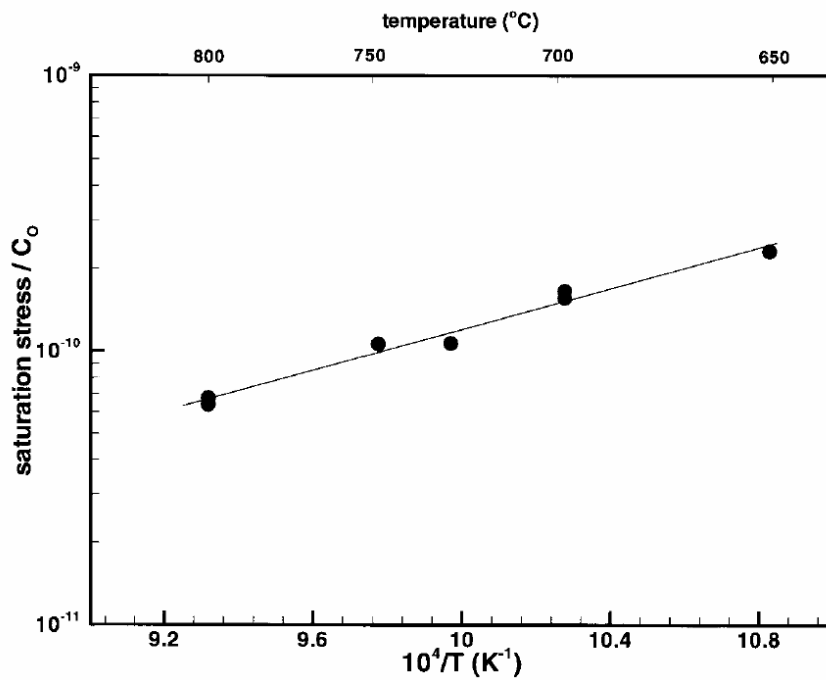


Figure 3-1. Dislocation unlocking saturation stress divided by oxygen concentration as a function of reciprocal temperature (after Senkader *et al*¹).

2. Determination of impurity diffusivity

The core region of a dislocation is considered to have a certain radius r_0 . Within this radius, the energy of interaction is constant. The core radius (a few Ångstroms) can be predicted by using atomistic calculations for the structure of the dislocation core². The impurity diffusion

is described by Fick's equation for stress-assisted diffusion, which is a variation of Equation (1.2):

$$\frac{\partial C}{\partial t} = D \nabla \left[\nabla C + \frac{C}{kT} \nabla (\Delta G) \right] \quad (3.2)$$

where C is impurity concentration, D is its diffusivity, k is Boltzmann's constant, T is the absolute temperature and ΔG is the variation of the Gibbs free energy due to interactions between an impurity atoms and a dislocation (binding energy to the dislocation). This equation is solved numerically using a cylindrical domain where the dislocation core is in the centre. For a dislocation lying along the z -axis of an orthogonal coordinate system, if the impurity concentration is uniform in the z direction, then the diffusion of impurity to the dislocation will occur in the xy plane. With this assumption, the cylindrical coordinates can then be introduced to describe the system and Equation (3.2) becomes one-dimensional (the cylinder radius r is the only independent variable). The two boundary conditions needed to solve Equation (3.2) are considered as follows. The first condition can be written as

$$C(R) = C_0 \quad (3.3)$$

where R is the minimum distance from the dislocation core at which the impurity concentration C does not significantly change for all annealing times and temperatures concerned (and is equal to the initial impurity concentration C_0).

For the other boundary condition, the dislocation core ($r = r_0$) is modelled such that both capture and reemission of atoms to/from the core were considered. In particular, it is assumed that the capture rate is controlled by the impurity concentration next to the core (C_l), the concentration of available sites at the core (C_a), and the concentration of occupied sites in the core (C_c), that is

$$capture \propto C_l \frac{C_a - C_c}{C_a} \quad (3.4)$$

where $\frac{C_a - C_c}{C_a}$ is the fraction of available sites along the core. Emission of impurity atoms from the core is assumed to be a function of the impurity concentration in the core and the escape probability of impurity atoms from the core:

$$emission \propto C_c \exp\left(-\frac{\Delta G}{kT}\right) \quad (3.5)$$

Thus, the net flux J to the dislocation across the boundary at $r=r_0$ can be written as:

$$\mathbf{J} \cdot \mathbf{n} \Big|_{r=r_0} = 2\pi l D \left[C_1 \frac{C_a - C_c}{C_a} - C_c \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right) \right] \quad [\text{s}^{-1}] \quad (3.6)$$

where $\mathbf{n}$ is the unit vector normal to the core and l is the dislocation length (in this calculation $l = 1 \text{ cm}$).

The distribution of impurity atoms throughout the material and the concentration of impurity atoms at the dislocation core is deduced from Equations (3.2) and (3.6) using the finite difference method. The calculation begins by assuming a uniform concentration of impurity throughout the material, initially equal to C_0 , and progresses using small time steps after each of which the entire impurity distribution is recalculated. A copy of the Fortran code used for this purpose is in Appendix C. The simulation outputs the number of impurity atoms N_c per unit length of dislocation core which is considered to be a cylinder of section πr_0^2 (such that $N_c = C_c \pi r^2$). The number of available sites per unit length of dislocation, n_a , is deduced by considering the number of impurity atoms, along a perfect dislocation, that are accommodated in interstitial sites separated each from the other by a Burgers vector ($3.8 \text{ \AA}$). Thus, $n_a = (3.8 \times 10^{-8} \text{ cm})^{-1} = 2.6 \times 10^7 \text{ cm}^{-1}$. Equivalently, this number can also be estimated assuming a core radius $r_0 \approx 2 \times 10^{-8} \text{ cm}$ and a concentration of available sites C_a at the dislocation core approximately equal to the density of silicon atom positions. In this case, the number of available sites per unit length of dislocation can be written as $n_a = (\text{silicon site density}) \cdot (\pi r_0^2)$, which is $n_a \approx (5 \times 10^{22} \text{ cm}^{-3}) \pi (4 \times 10^{-16} \text{ cm}^2) = 2 \times 10^7 \text{ cm}^{-1}$.

However, if less than 100% of available sites is occupied at regime 2 (capture=emission), then it is noted that values for diffusivity and binding energy are very insensitive to the particular value chosen for n_a . Since the unlocking stress τ_u is proportional to the number of impurity atoms accumulated at the dislocation core, the final output of the calculation gives the product

$$\tau_u = N_c \tau_0 \quad (3.7)$$

where τ_0 [Pa·cm] is the unlocking stress due to a single impurity atom pinning a unit length dislocation core. In the above calculations, the unknown parameters are the change of entropy ΔS , the diffusivity of impurity D and the unlocking stress per single impurity atom per unit length of dislocation core τ_0 . These variables are treated as fitting parameters. By comparing the calculation results with the experimental data (as for example in Fig. 1-24), it is possible to deduce these parameters.

3. Application to oxygen and nitrogen in silicon

Senkader *et al.*³ suggested that if oxygen dimers are the dominant species in the mechanism of impurity transport in silicon, then the effective diffusivity at lower temperatures has to be proportional to oxygen concentration in the crystal. This will be demonstrated in Chapter 4 where the oxygen monomer/dimer issues are discussed in detail. If experimentally observed, the proportionality between diffusivity and oxygen concentration should be a strong evidence for the dominant role of dimers in oxygen transport at low temperatures. Although data presented in Fig. 1-27 show a certain dependence of diffusivity on oxygen concentration, the difference in the two values of concentration used in the experiments was

unfortunately insufficient to reveal a clear relationship between diffusion coefficient and oxygen concentration. The collection of a new set of similar data obtained by using silicon samples with a lower oxygen concentration should give a less ambiguous answer to these questions regarding the oxygen species and their diffusion coefficients.

The method used to determine the impurity diffusivity described in this section can be applied generically to various impurities incorporated in silicon crystals (other than oxygen) and in particular to those elements for which the diffusivity represents a difficult parameter to measure. In this thesis, unlocking experiments and the above method for interpretation of data have been used to deduce the diffusivity of nitrogen in FZ-silicon wafers and the results of that investigation will be shown in Chapter 5. The possibility that either nitrogen dimers or monomers can be considered in the model is discussed together with the implications and physical meaning of the parameters deduced.

4. References

¹ S. Senkader, K. Jurkschat, D. Gambaro, R. J. Falster and P. R. Wilshaw, "On the locking of dislocations by oxygen in silicon", *Phil. Mag. A*, **81** (2001) 759

² S. Nandedkar and J. Narayan, *Philos. Mag. A*, **56** (1987) 625, *Philos. Mag. A*, **61** (1990) 873

³ S. Senkader, P. R. Wilshaw, R. J. Falster, "Oxygen-dislocation interactions in silicon at temperatures below 700°C: Dislocation locking and oxygen diffusion", *J. Appl. Phys.*, **89**, 4803 (2001)

Chapter 4:

Dislocation locking by oxygen impurities

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1. Introduction

This chapter describes a new set of experiments carried out to study the effect of oxygen atoms on dislocation behaviour in silicon single-crystals after annealing at high temperatures. A numerical model is developed to simulate oxygen transport and binding at the dislocation core. This model, together with the experimental data, is then used to simulate real wafer processing conditions during device fabrication to show how they may be modified to increase dislocation locking. It is hoped that these results will have relevance to how wafers are processed in order to minimise or eliminate dislocation multiplication and consequent warpage.

In previous dislocation unlocking experiments¹, the binding energy of an oxygen atom to a dislocation could not be measured at temperatures $<650^{\circ}\text{C}$ because of the high oxygen concentration in the material ($>6\times 10^{17} \text{ cm}^{-3}$) which produced a large dislocation unlocking stress in the saturation regime. Such large stresses ($>200 \text{ MPa}$) could not be physically applied on the silicon bars (to unlock the dislocations) without breaking most of the specimens. This problem is overcome in the present work by using Cz-silicon samples with low oxygen content for which the maximum unlocking stress achievable at saturation (prior to oxygen precipitation) is $\sim 150 \text{ MPa}$ at 400°C . In this case, the magnitude of the unlocking stress can still be measured with the bending techniques described in Chapter 2, thus new information is gained at low temperatures concerning the binding energy of oxygen atoms to a dislocation and the oxygen diffusion coefficient. Moreover, the possibility of oxygen transport due to oxygen dimers and monomers is discussed in this chapter. In particular, only one of the two oxygen species present in Cz-silicon is proposed to be dominant for transport at low temperatures, the oxygen dimer.

2. Experimental results

2.1 General considerations

The procedure used in the following experiments was described in detail in Chapter 2, Section 8.1. All the specimens were cleaved from precipitate-free and dislocation-free (001) Cz-Si wafers (p-type, 10 Ωcm , mirror polished on one side) with an initial oxygen concentration $C_0=2.6\times 10^{17}\text{cm}^{-3}$ (*Low- C_O*). The unlocking stress for dislocations was measured in these samples using three-point bending at 550°C after annealing for different durations (0-10⁴ hours), at different temperatures (400-850°C). Similar silicon samples, but with higher initial oxygen concentration $C_0=6.3\times 10^{17}\text{cm}^{-3}$ (*Medium- C_O*), were also used to investigate the unlocking stress as a function of the temperature at which the external stress is applied to the sample to cause the dislocation to move. The temperature at which this process is carried out will be called the unlocking temperature.

The determination of the dislocation unlocking stress was achieved by a long process, already described in Chapter 2. Here it is noted that particular care was needed during sample cleavage and surface preparation in order not to introduce dislocation sources in the specimens other than at the indents. Sample indentation was performed under manual control and this operation required ~30 minutes to produce a single row of indents. Often the annealing conditions were such that the samples needed to rest in the furnace for many months (at low temperatures) to allow the oxygen atoms to segregate to the dislocations to produce the locking effect. After such long annealing, the possibility for the sample to break during the mechanical test was unfortunately not negligible. Therefore, the number of data points in the following graphs showing the unlocking stress as a function of annealing time may appear not particularly large, but on the other hand it should be considered that each data

point has been produced individually and only achieved after many hours. Work, in some cases, spread over several months duration.

2.2 Dependence of the unlocking stress on time and temperature of annealing

In Fig. 4-1 the unlocking stress τ_u as a function of annealing time is shown for different temperatures. Due to the very long time needed to process each silicon sample, the collection of the data in Fig. 4-1 was possible only with the cooperation of Dr. S. Senkader and his valuable help during these experiments is acknowledged. Data in the graphs are related to the samples with low oxygen concentration and show two distinct regimes: regime 1 where τ_u increases as the annealing progresses and regime 2 in which τ_u reaches the saturation. In the early stages of annealing, the concentration of oxygen at the core is small and far from equilibrium. Thus, the oxygen concentration at the core and, in turn, the unlocking stress increases relatively rapidly. Moreover, the rate of increase in the unlocking stress is higher when the annealing temperature is more elevated, indicating that more oxygen atoms have diffused to the dislocations and have accumulated at the core. Following the initial rise of τ_u , a steady state is achieved when the local-equilibrium with the background oxygen concentration is established. This steady state manifests itself as a saturation of the unlocking stress. At this stage, the oxygen concentration at the dislocation does not depend anymore on annealing time, as the absorption of oxygen atoms by the core is balanced by the emission of oxygen atoms from the core due to thermodynamic effects.

In control samples prepared from FZ silicon, no locking was observable. In these FZ samples all dislocations were mobile irrespective of the annealing temperature and applied stress values investigated. In addition, the unlocking stress measured in samples cleaved from wafers with high vacancy content ($\sim 10^{15} \text{ cm}^{-3}$) was equal to that measured in samples with usual vacancy concentration ($< 10^{12} \text{ cm}^{-3}$), suggesting that for the temperature range

investigated, vacancy point defects have negligible influence on oxygen transport and dislocation locking.

All experiments and data points were reproducible within a percentage error of approximately $\pm 5\%$, depending on the annealing conditions and the applied stress. The accuracy was deduced by measuring the unlocking stress in three different samples subjected to same conditions and then comparing the results. Measurements on each sample produced two values of the unlocking stress that were averaged to give a mean value for τ_u .

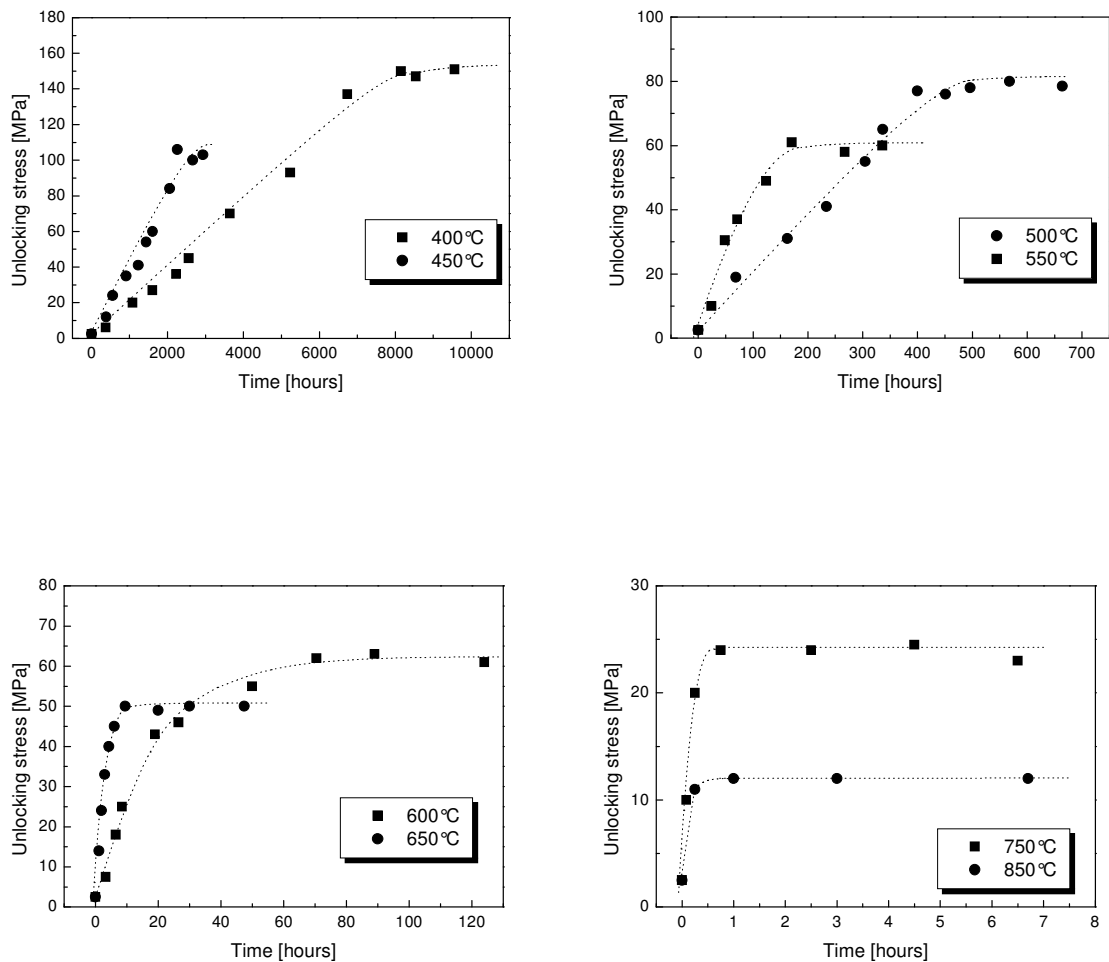


Figure 4-1. The unlocking stress τ_u for dislocations as a function of annealing time and temperature in samples with oxygen concentration equal to $2.6 \times 10^{17} \text{ cm}^{-3}$. Annealing temperatures were in the range 400-850°C. The two regimes of τ_u , corresponding to an increase followed by saturation, are visible for nearly all the temperatures investigated.

In general, samples subjected to shorter duration of annealing at higher temperatures gave larger percentage errors. This was probably due to the segregation of a significant number of oxygen atoms to the dislocations during the heating of the samples to reach the high temperatures. However, most of the data were taken at relatively low temperatures such that the above effect was negligible.

The unlocked dislocations in CZ silicon samples were observed to be mobile without any dragging effect by oxygen for stresses >20 MPa, in agreement with the work of Imai and Sumino². The dislocation velocity was deduced by measuring the distance travelled by the dislocations during the unlocking experiments. It was found that in the stress range studied, the dislocation velocity v agrees well with the empirical relationship deduced by Sumino for 60° dislocations in silicon:

$$v = 10^{-2} \tau \exp\left(-\frac{2.2}{kT} eV\right) \quad [\text{ms}^{-1}] \quad (4.1)$$

where τ is the resolved shear stress [Pa], k is Boltzmann's constant and T is the absolute temperature (Fig. 4-2).

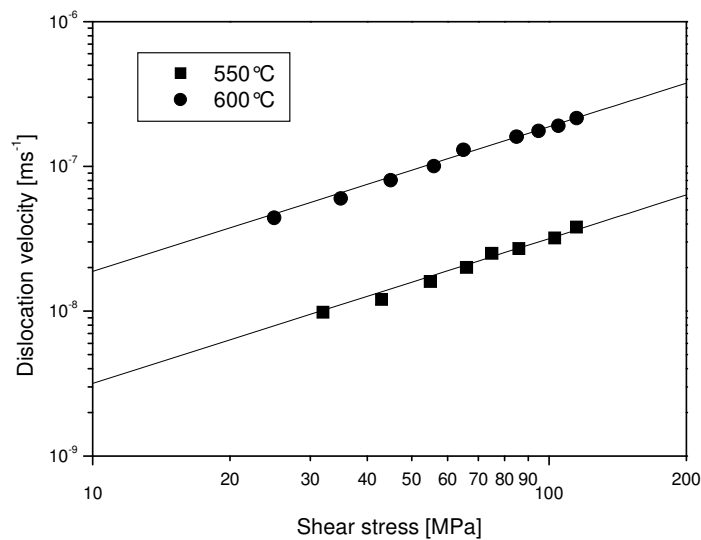


Figure 4-2 Dislocation velocity as a function of resolved shear stress for temperatures of 550°C (squares) and 600°C (circles). Straight lines represent the values calculated using Equation (4.1).

2.3 Dependence of the unlocking stress on unlocking temperature

The results in previous sections were obtained by keeping the temperature of the unlocking process constant at 550°C in order to be able to compare the locking effect created by oxygen diffusion at different temperatures. However, the unlocking process itself is also temperature dependent and plays an important role in the plastic deformation of silicon. Therefore, to gain a full understanding of oxygen-dislocation interactions it is useful to study the role of temperature on unlocking stress.

Measurements were made on two sets of samples (medium oxygen content, $6.3 \times 10^{17} \text{ cm}^{-3}$), each annealed at 730°C, the first for 15 minutes and the second for 1.5 hours. Samples in set 1 corresponded to regime 1 of oxygen locking, that is the anneal was stopped before the steady state oxygen concentration was reached. Samples in set 2 corresponded to regime 2, the situation when steady state has been achieved. These particular samples were chosen to check whether any differences exist in the unlocking stress when the locking is introduced in the two different regimes. Unlocking experiments were then performed on each set of specimens by varying the temperature of the three-point-bend deformation which yielded measurements of the stress required to release dislocations from the oxygen atoms segregated to the core during the previous annealing steps. Temperatures between 450 and 700°C were used. Lower temperatures were not practical since the dislocation velocity was too low. Higher temperatures were also avoided since the amount of oxygen collected at the core during the heating which precedes bending at high temperatures (~10 minutes) was then comparable to that accumulated during the previous annealing step, so that the observation of locked dislocations would not have been reliable.

It was found that the unlocking stress decreases with the increasing unlocking temperature in an approximately linear manner between 450 and 600°C, whereas above 600°C the unlocking stress varies slowly with temperature (Fig. 4-3). In addition, differences

in the unlocking stress between samples in set 1 and those in set 2 were more evident above 500°C.

It is assumed that the unlocking stress τ_u is proportional to the number of oxygen atoms per unit length of dislocation core N_c , thus:

$$\tau_u(T) = \tau_0(T) \cdot N_c \quad (4.2)$$

where τ_0 is the unlocking stress due to a single oxygen atom pinning a dislocation of unit length. If N_c is expressed in cm^{-1} , then τ_0 will have dimensions $[\text{Pa}\cdot\text{cm}]$ from Equation (4.2).

According to our experimental data, the value of τ_0 varies approximately linearly with the temperature in the range 450-650°C, such that an approximate empirical expression for $\tau_0(T)$ can be written as

$$\tau_0 = -0.07 T + 64.61 \quad [\text{Pa}\cdot\text{cm}] \quad (4.3)$$

where T is the absolute temperature (723-923 K). This expression of $\tau_0(T)$ will be used in Section 4 to simulate the effect of real thermal processing on dislocations in Cz-silicon wafers.

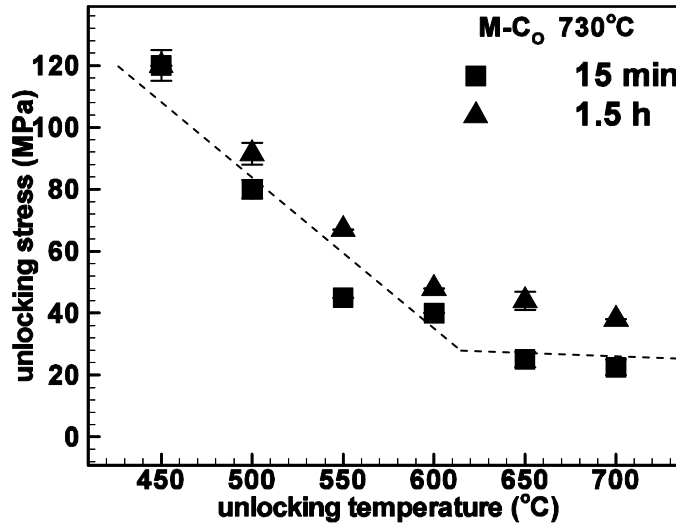


Figure 4-3. Unlocking stress as a function of temperature of stress application. Samples of medium oxygen content ($6.3 \times 10^{17} \text{ cm}^{-3}$) annealed at 730 °C for 15 min (squares) and 1.5 h (triangles) were used.

The linear variation of the unlocking stress with increasing unlocking temperature is predicted by a simplified theory of thermally activated release of dislocations from impurities, frequently used by Sumino and Yonenaga³ to explain their experimental results. According to this theory, the expression of the unlocking stress for a pinned dislocation segment is given by

$$\tau = \frac{N}{b^2} \left[\Delta G - kT \ln \left(\frac{LN\nu}{\Gamma} \right) \right] \quad (4.4)$$

where L is the dislocation length, N is the number of impurities (locking points) along a unit length of dislocation, ΔG is the maximum interaction energy between an impurity and the dislocation, ν is the vibration frequency of the dislocation, Γ is the release rate of the locked dislocation, k is the Boltzmann constant, T is the absolute temperature and b is the magnitude of the Burgers vector of the dislocation. Unfortunately, there are several parameters in Equation (4.4) for which it is not possible to estimate accurate experimental values. However, if the unlocking data is extrapolated to a temperature of 0 K, the equation predicts

$$\tau_{0^\circ} = \frac{N\Delta G}{b^2}.$$

The extrapolation of the low temperature experimental data in Fig. 4-4 was then

fitted using a value of $\Delta G = 0.74$ eV, as deduced by Senkader *et al.*⁴ from dislocation locking experiments (see Chapter 1, Section 8), and the number $N = 8.8 \times 10^6 \text{ cm}^{-1}$, which is equivalent to oxygen atoms separated from each other by a distance given by three Burgers vectors $\mathbf{b}$ along the dislocation line. It is noted that this value for N is in fair agreement with the value which will be obtained in Section 3.2 using the numerical simulation. It is reassuring that these two different approaches to analysing the data (Equation 4.4 which uses the dependence of τ_u on unlocking temperature and the numerical analysis of Section 3.2 using the dependence on annealing temperature) give such closely similar results. The data up to 550°C

shown in Fig. 4-4 were fitted by assuming $\frac{L\nu}{\Gamma} = 20 \mu\text{m}$ (dashed line), but it is difficult to say

whether or not this is physically reasonable. However, in Fig. 4-3, the fact that the gradient by

which the unlocking stress decreases is much lower at high temperatures indicates that the number N in Equation (4.4) must be much smaller at high temperatures and larger at low temperatures. For temperatures over 600°C the data show a considerably decreased gradient that perhaps is due to oxygen clustering or even precipitation, as shown, for example, in Fig. 5-4 of next chapter. In support of this hypothesis, if at high temperature the density N is taken equal to $2.5 \times 10^5 \text{ cm}^{-1}$, such that the pinning points along the dislocation are separated by a longer distance ($\sim 40 \text{ nm}$), the calculation carried out using Equation (4.4) gives a binding energy $\Delta G = 1.5 \text{ eV}$. Such values seem physically reasonable, although because of the assumptions involved, many others combinations of N and ΔG would also fit the data.

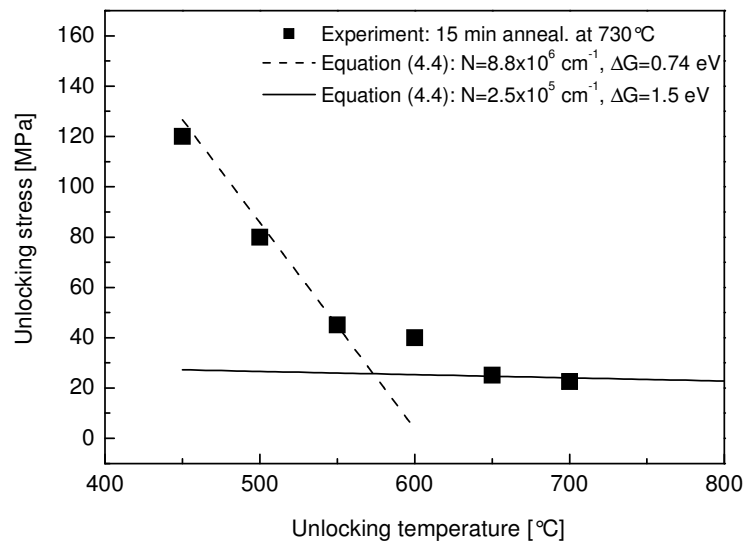


Figure 4-4. Calculation of the unlocking stress as a function of temperature according to Equation (4.4). For a fixed value of $L\nu/\Gamma$, a change in the gradient involves a variation in the number N of pinning points (impurities) per unit length of dislocation and a different binding energy ΔG . The smaller value of N and the bigger value of ΔG needed at high temperatures to simulate the experimental data suggest that clustering or precipitation of oxygen might occur above 600°C .

Interestingly, the clustering/precipitation process is the one that would dominate the locking effect at high temperatures, but because of the experimental difficulties described earlier, it was not investigated further. However, in Fig. 4-3, the data referring to 1.5 hours experiments

show (on the basis of only two data points) slightly more locking effect and this would be consistent with more clustering/precipitation having occurred.

3. Discussion of experimental results and modelling

3.1 The oxygen-dislocation binding energy

The behaviour of the unlocking stress during regime 2 is governed by the thermodynamics that control the oxygen concentration at the core. The expression of the unlocking stress τ_u when oxygen in the bulk is at thermodynamic equilibrium with that at the dislocation is given by Equation (3.1). Thus, data shown in Fig. 4-1 taken during the saturation regime can be plotted as a function of temperature to deduce the binding enthalpy of the interaction between an oxygen atom and a dislocation (Fig. 4-4). In the temperature range 650-850°C, binding enthalpy measurements deduced from low oxygen specimens are in very good agreement with other data obtained by Senkader *et al.* from specimens with higher oxygen content. In addition, since the unlocking stress produced in a sample with low oxygen content is not as high as that for larger concentrations of oxygen for the same annealing conditions, the low oxygen concentration of the specimens used in this work has allowed measurements of the unlocking stress during regime 2 at much lower temperatures than those achieved with samples with medium and high oxygen concentration. Surprisingly, data in the low temperature range of 450-650°C show a markedly different behaviour compared to that at higher temperatures. In this low temperature range a binding enthalpy of 0.23 ± 0.03 eV has been found. This result would suggest that, at temperatures below 650°C, oxygen shows a smaller activation energy with respect to binding at dislocations.

The exact explanation for the different value obtained for the apparent binding enthalpy below 650°C is still not completely clear. However, the change in binding enthalpy occurs at

the same temperature as the change in behaviour of the oxygen transport, as shown in Fig. 1-27. This would suggest the existence of a species other than the oxygen monomer (that dominates at high temperatures) which is responsible for both dislocation locking and oxygen transport for temperatures less than 650°C.

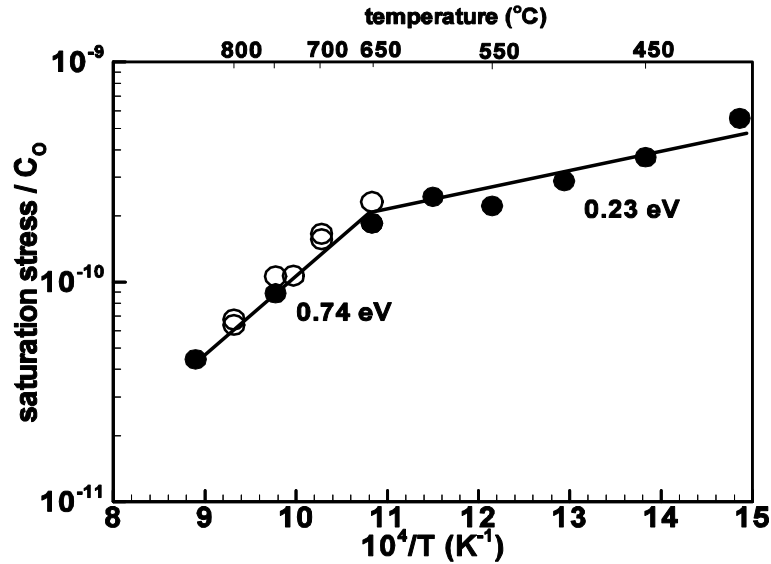


Figure 4-5. The saturation stress normalised by the oxygen concentration as a function of reciprocal temperature. The binding enthalpy of oxygen to a dislocation can be deduced from this graph. Closed circles indicate the results obtained using low oxygen samples. Data obtained by Senkader *et al.* using samples with high and medium oxygen concentration (open circles) are also shown.

3.2 Oxygen transport in silicon at low temperatures

The difficulty of measuring the oxygen diffusion coefficient at low temperatures was described in Chapter 1. During this work, taking advantage of the locking effect produced by oxygen atoms, it was possible to use well characterised dislocations, to obtain quantitative information on oxygen transport in silicon samples with low oxygen content. This was achieved for a broad temperature range and the method used was described in Chapter 3, Section 2. The calculation used to simulate oxygen transport is mainly based on Equation (3.6) which defines the oxygen flux.

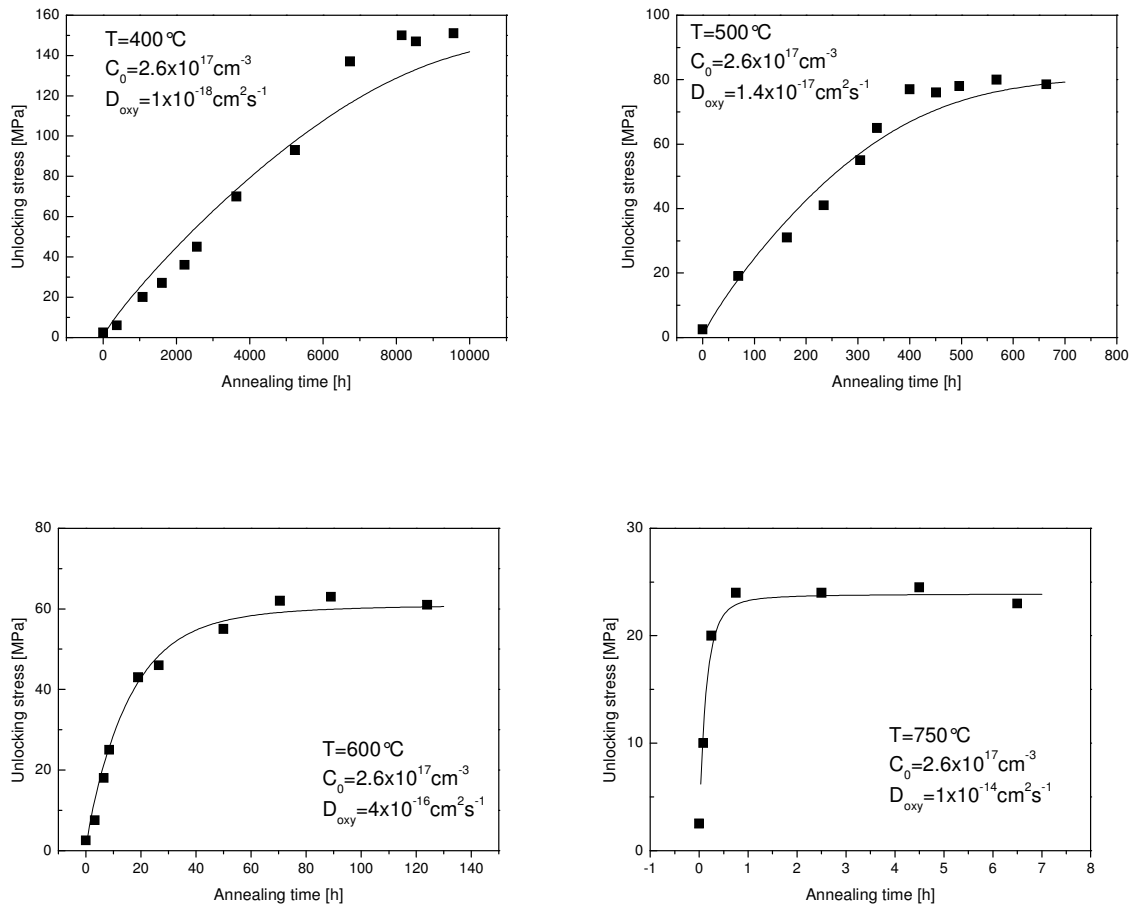


Figure 4-6. Examples describing the simulated behaviour of the unlocking stress (solid lines), according to the model described in Chapter 3. The best fit to the experimental data was achieved using the parameter values described in the text and considering the oxygen diffusivity as a fitting parameter.

The parameters used in Equation (3.6) and Equation (3.7) to simulate the results shown in Fig. 4-1 are:

- The unlocking stress due to a single oxygen atom per unit length of dislocation $\tau_0(550^\circ\text{C}) = 7 \text{ Pa}\cdot\text{cm}$,
- The concentration of available interstitial sites in the bulk for oxygen atoms $C_a = 5 \times 10^{22} \text{ cm}^{-3}$,

- The entropy $\Delta S = 7.6 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$, which is approximately the constant k , although the calculation was not very much affected by this parameter.

The oxygen diffusivity D_O was treated as a fitting parameter. Examples of the best fit to the experimental data shown in Fig. 4-1 are presented in Fig. 4-6. Using this method, the oxygen diffusivity was deduced for each temperature investigated. Moreover, according to simulations, the number N of oxygen atoms along a unit length of dislocation was found in the range 2×10^6 - $2 \times 10^7 \text{ cm}^{-1}$ for the temperature investigated (400-850°C).

Fig. 4-7 shows all the oxygen diffusivity data obtained during this work (diamonds, *Low-C_O*) together with data taken from the literature. Error bars were not drawn in the graph of Fig. 4-6 because errors bars for diffusivity would be practically invisible in the logarithmic scale. The results confirm that below 700°C, the effective diffusivity is controlled by an activation energy of about 1.5 eV while the magnitude of the diffusivity becomes dependent on oxygen concentration. In particular, for low oxygen content samples it was found:

$$D_O^{L-C_O} = 2.04 \times 10^{-7} \exp\left(-\frac{1.51 \text{ eV}}{kT}\right) \quad [\text{cm}^2 \text{ s}^{-1}] \quad (4.5)$$

which can be compared with the expressions (1.18) and (1.19) obtained by Senkader *et al.* with higher oxygen concentrations and also shown in Fig. 4-7 (*Medium-C_O* and *High-C_O*).

Comparison of the binding enthalpy data from Fig. 4-4 with the diffusivity data suggests that below 650-700°C the movement of oxygen in silicon is by a species other than the single oxygen atoms and this also results in dislocation locking by a species different from that at high temperatures. At low temperatures, where diffusivity data for single oxygen jump is available in the literature, dislocation unlocking experiments showed a three orders of magnitude “enhancement” in oxygen transport. Thus, the possibility that the transport might be dominated by fast diffusing single oxygen atoms has been discarded due to this experimental evidence.

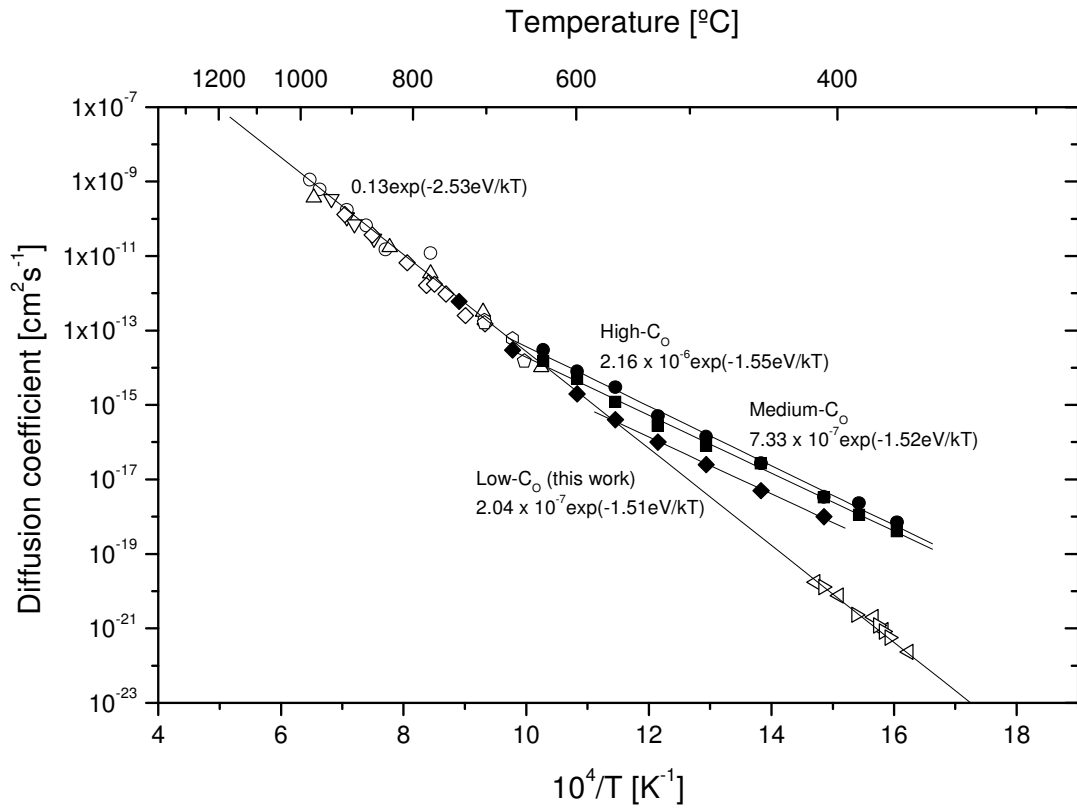


Figure 4-7. Oxygen diffusivity as a function of reciprocal temperature. Open symbols are previous data from the literature (Mikkelsen). Closed symbols are either values obtained in this work (diamonds) or measured by Senkader *et al.* in samples with different oxygen content. The oxygen concentrations were: $2.6 \times 10^{17} \text{ cm}^{-3}$ (Low- C_0 , diamonds); $6.3 \times 10^{17} \text{ cm}^{-3}$ (Medium- C_0 , squares); $10.4 \times 10^{17} \text{ cm}^{-3}$ (High- C_0 , circles). Best fit to each data group is also given.

In this work, it was also found experimentally that the transport of oxygen in samples with different point defect concentrations does not show any variation. Hence, any hypothesis connecting fast oxygen transport with oxygen-point defect complex would be unsubstantiated. Similarly, the effect of any hydrogen related complexes with oxygen is excluded since the samples investigated were practically hydrogen-free. Therefore, within the oxygen complexes, oxygen dimers are major candidates for a fast diffusing species⁵. It has been shown that analysis of generation kinetics of thermal donors would require a dimer diffusion

with an activation energy of about 1.3 eV ⁶. Furthermore, several theoretical studies concluded that the oxygen dimer in Si is stable and can diffuse with an activation energy of about 1.5 eV ⁷.

On the assumption that oxygen can be incorporated in silicon in the form of monomers or dimers at different concentrations and since both can be responsible for oxygen transport, the total flux J of oxygen atoms should be written as

$$J = -D_o \frac{dC_o}{dx} - 2D_{O_2} \frac{dC_{O_2}}{dx} \quad (4.6)$$

where D_{O_2} is the diffusivity of oxygen dimers and C_{O_2} is the concentration of oxygen dimers (similarly, D_o and C_o represent those of monomers). However, C_{O_2} is not known and is assumed to be much smaller than C_o . Thus, it is possible to define an approximate value for the total flux J given by

$$J = -D_o^{eff} \frac{dC}{dx} \quad (4.7)$$

where C is the total oxygen concentration and D_o^{eff} is the “effective” oxygen diffusivity, defined as

$$D_o^{eff} = \frac{C_o D_o + 2C_{O_2} D_{O_2}}{C_o + 2C_{O_2}} \quad (4.8)$$

For $C_o \gg C_{O_2}$, Equation (4.8) becomes

$$D_o^{eff} = D_o + 2 \frac{C_{O_2}}{C_o} D_{O_2} \quad (4.9)$$

If oxygen dimers are in equilibrium with single oxygen atoms, then their concentration will be

$$C_{O_2} \propto C_o^2 \exp\left(\frac{\Delta H_{b2}}{kT}\right) \quad (4.10)$$

where ΔH_{b2} is the binding enthalpy of the oxygen dimer. From equations (4.9) and (4.10) it can be deduced that if oxygen dimers are the species responsible for “enhanced” oxygen

transport, then the effective diffusivity at lower temperatures has to be proportional to the oxygen concentration, that is

$$D_o^{eff} \propto C_o, \quad \text{when } D_o \ll D_{o_2}. \quad (4.11)$$

The experimental results, and in particular those obtained in this thesis work, have shown that at lower temperatures diffusivity is in fact concentration dependent. Moreover, a simple analysis of the experimental values of diffusivity (shown in Fig. 4-7) measured at temperatures between 400 and 650°C for three different oxygen concentrations (10.4, 6.3 and $2.6 \times 10^{17} \text{ cm}^{-3}$) shows the diffusivity to increase on average (over six data points) by a factor of **1.61**, **5**, and **3.3** as the oxygen concentration increases by a factor $10.4/6.3=1.65$, $10.4/2.6=4$, and $6.3/2.6=2.42$ respectively.

The linear variation of the diffusivity with oxygen concentration is also shown clearly in Fig. 4-8 in the case of diffusion measurements between 450 and 600°C. This is consistent with the above analysis and shows that the dimers are capable of explaining the observed increase in the effective diffusivity. However, at lower temperatures, the linear variation of oxygen diffusivity with oxygen concentration is less clear because data are still missing and further investigation is needed, possibly using samples with even lower initial content of oxygen in the bulk.

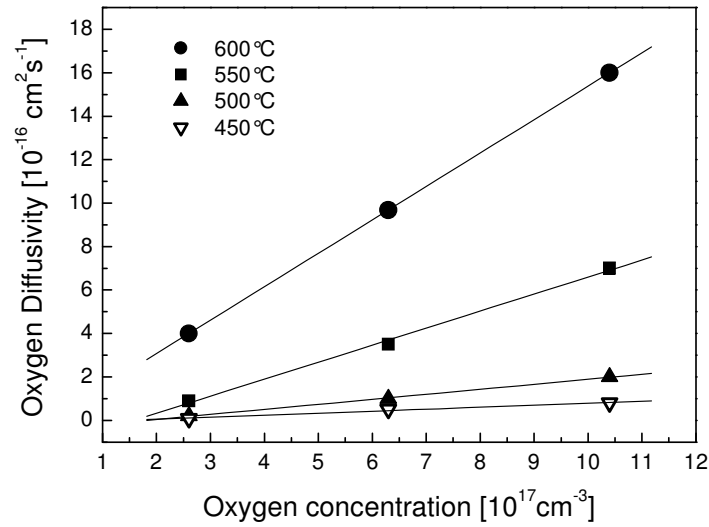


Figure 4-8. The graph shows the linear variation of the oxygen diffusivity measured at 600°C in samples with different initial oxygen concentrations.

4. Direct application of the numerical model to wafer processing

The dislocation locking effect induced by intrinsic impurities present in silicon wafers, most notably oxygen atoms, could be used during device processing to reduce wafer warpage and thus to increase the device yield. The main advantage of using oxygen is that oxygen atoms are already present in Cz-grown material as intrinsic impurities and no further doping is needed. The other important advantage is that the immobilisation of dislocations due to oxygen segregation to their core would occur naturally during specific thermal treatments at high temperatures typical of device fabrication. Thus, no other particular processes would be needed other than opportune heat treatments of sufficient duration such that oxygen can rapidly segregate to the dislocations and lock them. In this section, the model described in Chapter 3 is used in practical applications to predict the unlocking stress for dislocations and

thus the critical stress, which if exceeded, would lead to wafer warpage during a certain thermal process.

It should be noted that the model described in Chapter 3 and used in the previous section to calculate the unlocking stress and other parameters has been developed for isolated, straight dislocations. However, in many practical situations this model may not be appropriate. In the case of dislocations associated with oxide precipitates, the interstitial oxygen concentration is locally depleted and thus the value for C_0 would be lower than that measured for the wafer as a whole. Similarly, if dislocations are present in a surface layer fully depleted of oxygen atoms, then a negligible locking effect can be expected. In some circumstances, where dislocation tangles are developed, the dislocation spacing may be sufficiently small that each dislocation segment can compete in the process of oxygen gettering and this should be considered in a more complicated analysis. Nevertheless, even if the values predicted in the case of straight isolated dislocations are not quantitatively accurate when applied to other particular situations, it is likely that the general trend as to how wafers can be strengthened or weakened according to processing will still be valid. For example, in the case of Cz-silicon wafers containing oxide precipitates, the qualitative indication that oxygen is able to improve the mechanical strength is clearly given by data described in Chapter 6, Fig. 6-14.

The numerical simulation described in Chapter 3 can be used to calculate the dislocation unlocking stress, given by Equation (3.7), during a particular heat treatment. The stress necessary to unlock the dislocations varies with the duration of thermal treatments and with temperature depending on the amount of oxygen atoms segregated to the dislocation core. The prediction of the evolution of unlocking stress during a specific heat treatment will provide information about the strength of the wafers throughout the processing. In practice, time-temperature profiles are often modified to minimise spatial temperature profiles and thus the thermo-mechanical stresses in wafers being processed. As is shown below, the present

analysis demonstrates that such modifications affect not only the stresses applied to wafers but also the mechanical resistance of wafers to such stresses. The strength of a wafer depends very sensitively on its thermal history; in some cases, different thermal treatments can be proposed to increase the mechanical strength of wafers and hence reduce their susceptibility to warpage. If (time dependent) external stresses are kept below the (time dependent) unlocking stress then plastic deformation of wafers could be prevented. This represents an additional, potentially very useful, independent process control variable.

A computer program was developed to simulate oxygen transport to the dislocations during real thermal processes. This program is similar to that shown in Appendix C, but in the extended version used for this purpose several heating and cooling ramps can be added in sequence. Moreover, the temperature dependence of the unlocking stress is taken into account in this simulation, as Equation (4.3) is implemented in the program. The numerical model allows the input of several parameters like the initial oxygen concentration, temperature and duration of the annealing steps; by changing these parameters it is possible to simulate the effect of different treatments on the mechanical properties of wafers. Simple examples of different heat treatments are given below. However, the numerical model could easily be applied to the more complicated treatments used in real device fabrication and would then give an indication of the strength of wafers at any time during their processing. In the following simulations, where not specified, it is assumed that Cz-Si wafers have an initial oxygen concentration equal to $6.3 \times 10^{17} \text{ cm}^{-3}$, although this parameter can be changed and given as input to the model. The graph in Fig. 4-9a shows the simulated behaviour of the unlocking stress in a wafer which has been subjected to a particular thermal sequence: this consisted of an increasing temperature ramp ($20^\circ\text{C}/\text{min}$ up to 950°C) followed by a constant temperature step (5 min at 950°C) and a final cooling step ($20^\circ\text{C}/\text{min}$ down to 25°C).

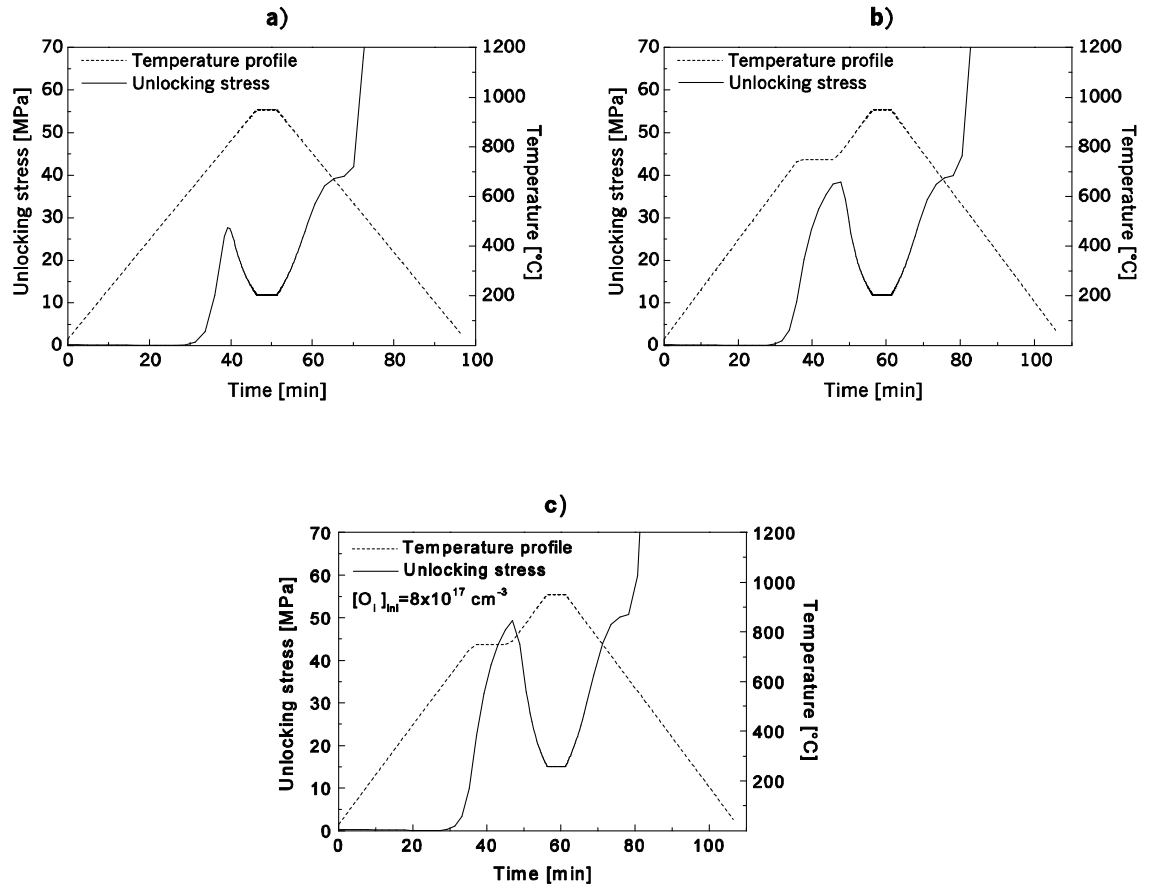


Figure 4-9. a) Unlocking stress behaviour during a specific thermal treatment. b) Enhancement of the unlocking stress is achieved by introducing an additional annealing step at 750°C. c) The dislocation locking can also be improved by simply increasing the initial oxygen concentration in the wafer, for example, to $8.0 \times 10^{17} \text{ cm}^{-3}$.

According to calculations the results of which are shown in Fig. 4-9a, during the increasing temperature ramp the value of the unlocking stress is initially negligible because the oxygen atoms at low temperatures move very slowly and do not have time to reach the dislocation core in significant numbers. The unlocking stress then increases steeply as the wafer temperature is raised from 700°C to 800°C and diffusion becomes much more rapid; it subsequently decreases with almost the same slope until the constant temperature step at 950°C takes place. The decrease is due to the enhancement at higher temperatures of the emission of oxygen atoms from the dislocation core which dominates over the absorption process. In the final temperature step, during the wafer cooling, the unlocking stress starts increasing again, as more oxygen is absorbed to the core, and rises until room temperature is

reached. Therefore, the unlocking stress profile shown in Fig. 4-9a suggests that at a given stress, for this particular heat treatment, plastic deformation is more likely to occur during the heating of wafers rather than during the cooling when the unlocking stress is larger.

In another sequence shown in Fig. 4-9b, a pause in the heating ramp has been introduced at 750°C. In this case the calculation shows that the additional annealing treatment at 750°C for 10 minutes allows the unlocking stress to reach a maximum value during the heating which is approximately 11 MPa higher than the previous value obtained.

This is an important result if we consider that thermal stresses during device processing are in general not very high and the increase in the unlocking stress of even a few MPa is important because it could lead to a significant reduction of mobile dislocations. Moreover, the unlocking stress can also be substantially increased when a higher oxygen concentration is initially present in the wafers as shown in Fig. 4-9c. The simulated behaviour of the unlocking stress during repeated thermal cycles is shown in Fig. 4-10.

Three sequential equal heat treatments are shown in Fig. 4-10a; the same treatments are shown in Fig. 4-10b where additional rapid thermal annealing (RTA, up to 1100°C in 1 minute) treatments have been performed. Comparing the two different data plots of the unlocking stress, it was found that the RTA treatment results in a detrimental effect on the wafer strength.

Fig. 4-10a shows that the unlocking stress calculated during the heating ramp in cycle 2 is much higher than that calculated for the same ramp in cycle 1: this is due to the oxygen atoms gathered at the dislocation core during the wafer cooling at the end of cycle 1. Hence, the wafer strength during the heating ramp in cycle 2 will be higher than in cycle 1 (Fig. 4-10a) for temperatures below 750°C. This improvement in the strength, obtained during the wafer cooling, is largely lost when a RTA is applied just after cycle 1 and before cycle 2 (Fig. 4-10b). Despite the short duration of RTA, the significant loss in the magnitude of the unlocking stress is due to the rapid emission of oxygen atoms from the dislocation core at

high temperatures. Therefore, according to calculations, during sequential thermal treatments silicon wafers are more susceptible to plastic deformation when subjected to heating ramps which are preceded by a RTA treatment.

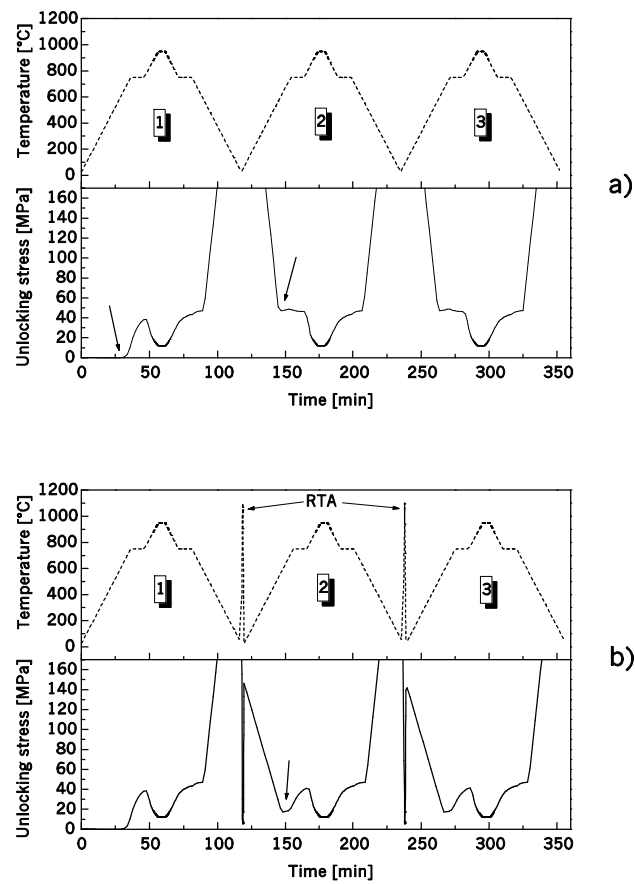


Figure 4-10. Variation of the unlocking stress during repeated thermal cycles when a RTA is inserted in between two identical sequences. Arrows indicate the region in the heating ramps where the unlocking stress changes significantly.

5. Summary

The dislocation unlocking experiments shown in this chapter and carried out using silicon samples with low oxygen content have produced new and interesting results. At high temperatures ($>650^{\circ}\text{C}$), the data produced in the present investigation overlap those achieved in previous work carried out using wafers with higher oxygen concentrations. At low temperatures ($<650^{\circ}\text{C}$), a different binding energy of oxygen to the dislocations has been found in these specimens and a new value of the concentration-dependent oxygen diffusivity has been deduced from the experimental data. Interestingly, the transition between the two different values of binding energy and the two different values of diffusivity (one per each temperature regime) occurs at the same temperature, which is approximately 650°C . This suggests the existence of an oxygen species other than monomers which becomes dominant at low temperatures and thus is responsible for transport and also for dislocation immobilisation. It is proposed that the dominant species for transport at low temperature are oxygen dimers which would account for the linear dependence of diffusivity on oxygen concentration.

The intrinsic dependence of the unlocking stress on unlocking temperature has been investigated experimentally and the results have been used to simulate the effects of real thermal processing on the mechanical behaviour of wafers. It is hoped that this study will be directly applied in wafer manufacturing to reduce wafer warpage and improve the device yield.

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Chapter 5:

Dislocation locking by nitrogen impurities

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1. Introduction

Despite the increasing interest in nitrogen as a beneficial impurity which might be added to silicon crystals, there is still a serious lack of fundamental and practical information about its properties when present. For example, as described in Chapter 1, there is an open debate about the magnitude of the nitrogen diffusion coefficient and the species (monomers, dimers, etc.) responsible for nitrogen transport at different temperatures^{1,2,3,4}. The research described in this chapter aims to investigate the properties of nitrogen in the purest silicon crystals that can be fabricated, that is FZ-grown silicon wafers. FZ-silicon, although technologically superior to Cz-silicon in some applications, is more susceptible to wafer warpage due to the low concentration of oxygen present in the material. Thus, the introduction of nitrogen impurities into FZ-silicon and their interaction with harmful dislocations could lead to a significant improvement in the mechanical stability of wafers during device processing at elevated temperatures. It is hoped that by studying nitrogen in such ideal material, an understanding of its behaviour will be obtained; this knowledge might then be applied to more complex systems such as N-doped Cz-silicon.

The work presented in this chapter represents the first detailed investigation of the interaction of nitrogen and dislocations in FZ-silicon and thus not only provides information on the diffusivity of nitrogen in silicon and how it binds to the dislocations, but also gives an indication of the extent to which the mechanical properties of FZ-silicon may be improved by nitrogen doping.

2. Experimental results

2.1 Unlocking stress measurements

The N-doped Floating-Zone (NFZ) silicon samples used in this investigation were described in Chapter 2, Section 8.2 and contained $\sim 2 \times 10^{15} \text{ cm}^{-3}$ nitrogen. In these specimens, the locking of dislocations by the nitrogen impurities was investigated as a function of annealing time (0-1500 hours) in the technologically important temperature range 550-830°C. High purity FZ-silicon specimens, not intentionally doped with nitrogen (control samples), were also tested to investigate any possible variation of the unlocking stress in samples with low nitrogen content. In these samples, no appreciable dislocation locking effect was detected using the dislocation unlocking experimental procedure. This confirms that the oxygen and nitrogen concentrations (and those of other impurities) in pure FZ-grown silicon are too low to produce a significant dislocation locking and also indicates that our experimental apparatus is sufficiently contamination-free such that any locking measured is due to intentionally introduced impurities.

The investigation began with the collection of unlocking stress data measured at 550°C in NFZ-silicon samples as a function of annealing duration at 700°C (see Fig. 5-1); the first important observation was that nitrogen has a strong locking effect on dislocations, despite its low concentration in the silicon wafers. These initial experiments gave an indication of the magnitude of locking achievable in NFZ samples and the rate of increase with time during annealing at 700°C. At this temperature, it was found that the saturation regime of the unlocking stress is reached after approximately 20 hours of annealing. These were the first such measurements ever made on NFZ material and this work is the first to indicate a saturation regime for the unlocking stress in NFZ-silicon. It was observed that the locking behaviour is similar to that found in Cz-silicon where oxygen atoms are responsible

for pinning the dislocations. In Cz material, a second increase in unlocking stress after some time in the saturation regime was also observed (Fig. 1-25) probably due to precipitation of oxygen along the dislocations. However, experiments carried out with NFZ samples subjected to more than 250 hours of annealing at 700°C did not show any further increase in the unlocking stress after the saturation regime and in this respect the behaviour is different to Cz-silicon.

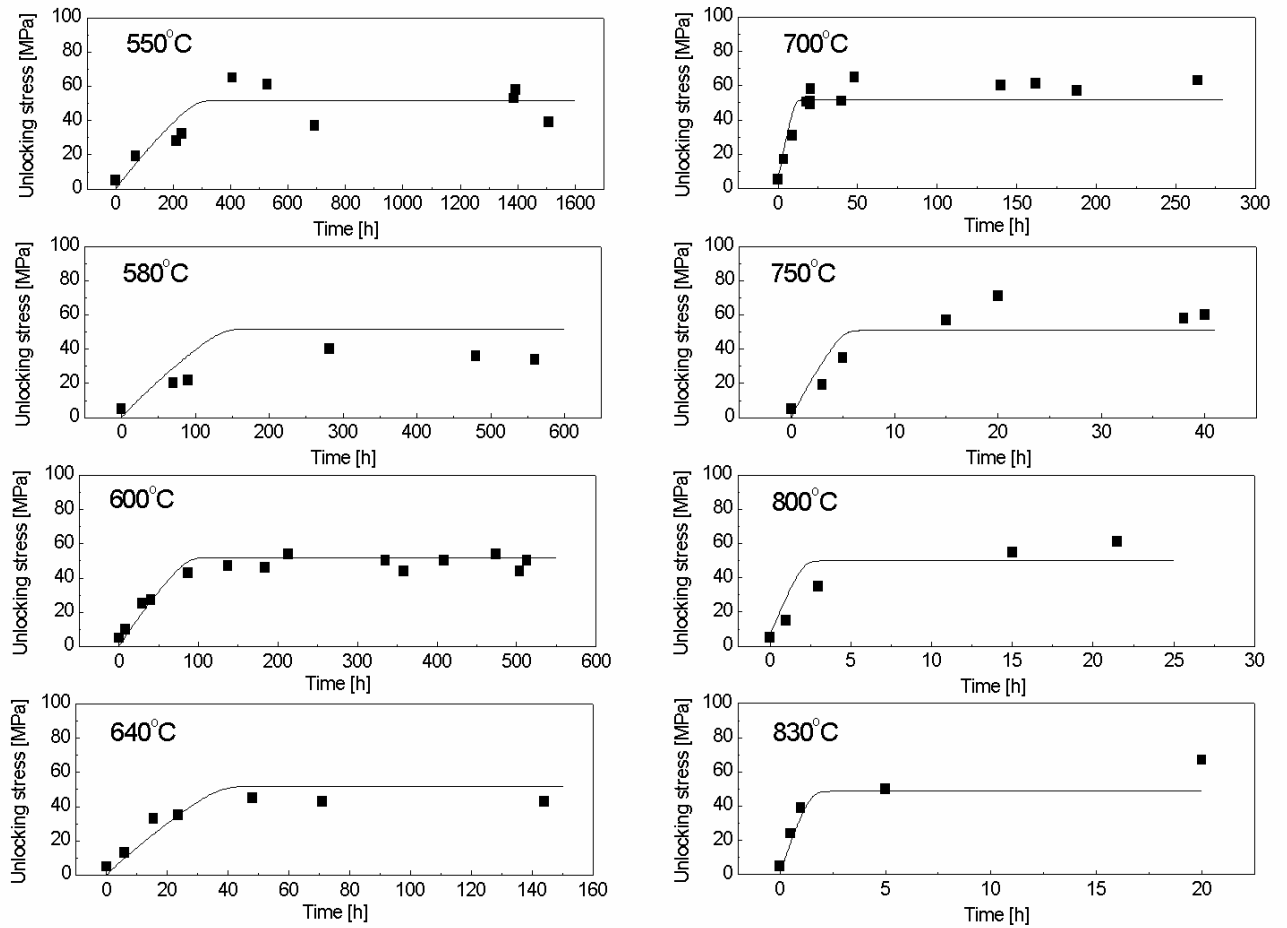


Figure 5-1. Data points (squares) represent the unlocking stress measured at 550°C in N-doped FZ-silicon samples subjected to different annealing times (0-1500 hours) and annealing temperatures (550°C-830°C). Values obtained by using a numerical simulation with fit parameters as described in this chapter (Section 3.4) are also shown in the figures (lines).

During the collection of data, it was clear that NFZ samples were producing a more scattered distribution of data points in the graphs compared to those obtained in the case of oxygen in Cz-silicon samples. The explanation for this is still not clear, but different possible causes are suggested: the first reason could be that the concentration of nitrogen within the NFZ wafers was not as uniform as the concentration of oxygen in Cz wafers, since the latter was more regularly distributed after the specific homogenization treatment (*tabula rasa*) at 1000°C. It is rather likely that the outer regions of the NFZ wafers used in these experiments contained nitrogen impurities in larger concentration than that incorporated in their central area, since the external part of the ingot was more directly exposed to the nitrogen/argon mixture during the crystal growth⁵. The second reason for the larger scatter of these data (when compared with similar data obtained from Cz-silicon specimens) could be the different dimensions of each NFZ sample used in the experiments. Although the dimensions were accurately measured in each sample, the shape of NFZ specimens was not always as regular as that of samples cleaved from mirror polished Cz-silicon wafers. In fact, since NFZ wafers were initially thick and rough, as-cleaved samples were then subjected to polishing and etching steps which may have altered the original shape of the bar (for example, the sample edges were unavoidably rounded after planar etching). This may have influenced the stress distribution calculated for a perfect rectangular bar and thus may have affected the determination of the unlocking stress. A third reason for the increased scattering could be the (111) orientation of the samples itself. (111) specimens were not used previously for unlocking experiments since in this geometry the dislocations travel obliquely in respect to the direction of the applied stress, causing a more difficult measurement of the stress required to unlock dislocations. Consequently, this increases the error in the determination of the unlocking stress.

Fig 5-1 shows the whole set of data regarding the unlocking stress measured at 550°C using NFZ-silicon samples annealed under different time and temperature conditions. It

should be noted that each data point was achieved by following all the processing steps described in Chapter 2, Section 8.2 and also that the anneals ranged in duration up to 62 days. In many cases, several attempts were needed to achieve a single data point without the NFZ-silicon bar breaking. Thus, the data presented in Fig. 5.1 represents a considerable portion of all the experimental work produced for this thesis. In addition, the experiments carried out used up all the nitrogen-doped material available for this work and in some cases this limited the number of data points which could be obtained, for example at 830°C.

In NFZ samples, the unlocking stress for dislocations increases with annealing time and its rate of increase depends on the annealing temperature. After the initial increase (*regime 1*), the unlocking stress (measured at 550°C) saturates to a value (*regime 2*) approximately equal to 50 MPa for all the annealing temperatures investigated. This was another striking and unexpected observation: contrary to oxygen in Cz-silicon for which the unlocking stress decreases dramatically with increasing annealing temperature, in NFZ-silicon the unlocking stress measured during the saturation regime is constant up to at least 830°C (Fig. 5-2), over a range of approximately 300°C. One likely explanation for this is that during regime 2, the dislocations are probably fully decorated by nitrogen impurities, thus the unlocking stress is only limited by the annealing time needed for nitrogen to occupy all the available sites along the dislocation, as will be explained in Section 3.2 of this chapter. Furthermore, data in Fig. 5-2 indicate that above ~750°C, nitrogen at a concentration of approximately $2 \times 10^{15} \text{ cm}^{-3}$ gives more effective locking than oxygen at a concentration of $6.3 \times 10^{17} \text{ cm}^{-3}$ in the Cz-silicon wafers studied. This is an important new result since it shows that nitrogen should be very beneficial to reduce wafer warpage, especially when oxygen is not present in the material (like in FZ-silicon) or when the locking ability of oxygen is reduced by thermodynamic effects present at high temperatures. Unfortunately, measurements at temperatures above 830°C were not possible because during the few experiments carried out at higher temperatures, the formation of glide dislocations from sources other than the indents was

observed at the sample surface after bending and this precluded accurate measurements of the unlocking stress for dislocations intentionally introduced into the specimens by indentation. It is thought that the new dislocations were probably generated during rapid cooling of the specimens from such elevated temperatures to room temperature. This operation was performed by taking the sample out of the furnace and laying it down on a cold quartz surface within a very short time (< 20 s). Originally, this fast cooling of the samples was introduced during the experiments with oxygen to avoid the impurity segregation to the dislocation core during relatively slow cooling, especially at high temperatures when oxygen diffusion is fast. This procedure was also maintained for the investigation of nitrogen in FZ-silicon since at the beginning of the work, little was known about the nitrogen diffusivity and behaviour at the temperatures of interest. Another possible cause of the presence of dislocations at the silicon surface after annealing at very high temperatures could be the formation of a silicon nitride layer on top of samples: this induces a certain stress field at the silicon/nitride interface that in turn might induce the formation of glide dislocations.

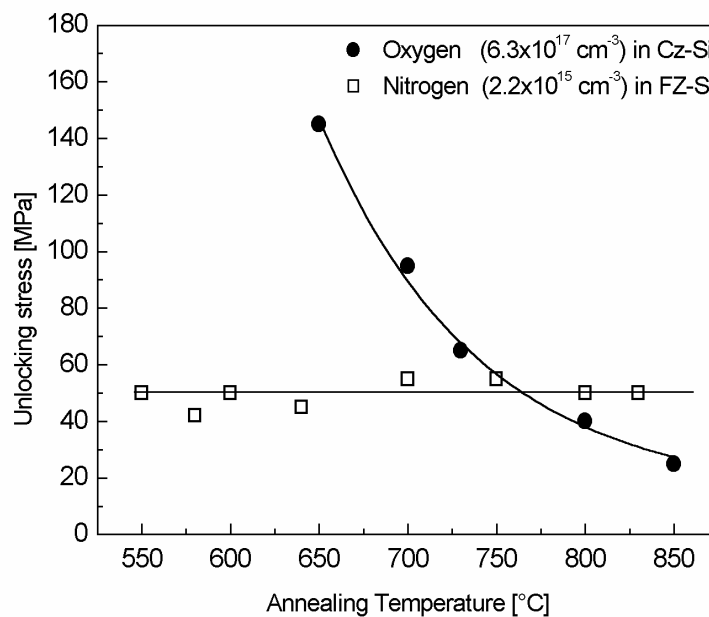


Figure 5-2. The saturation unlocking stress (regime 2) measured at 550°C as a function of anneal temperature for Cz and NFZ-silicon.

2.2 The activation energy of the locking process

During regime 1, the unlocking stress τ_u increases linearly with anneal time t and the rate of this increase, $\frac{d\tau_u}{dt}$, increases with increasing temperature. From the data presented in Fig. 5-1, quantitative values for $\frac{d\tau_u}{dt}$ may be obtained for each anneal temperature investigated. An Arrhenius plot of these values is shown in Fig. 5-3. From this, an activation energy for the locking process of 1.45 ± 0.09 eV can be inferred using the method of least squares fitting (straight line in Fig. 5-3). If it is assumed that the unlocking stress depends on the number of nitrogen atoms at the dislocation core and that in regime 1 this is limited by the transport of atoms to the core, the activation energy measured for the locking process will be that for nitrogen transport itself. Thus, with these assumptions, a value of 1.45 ± 0.09 eV is inferred for the activation energy for nitrogen transport to the dislocations in the temperature range 550-830°C.

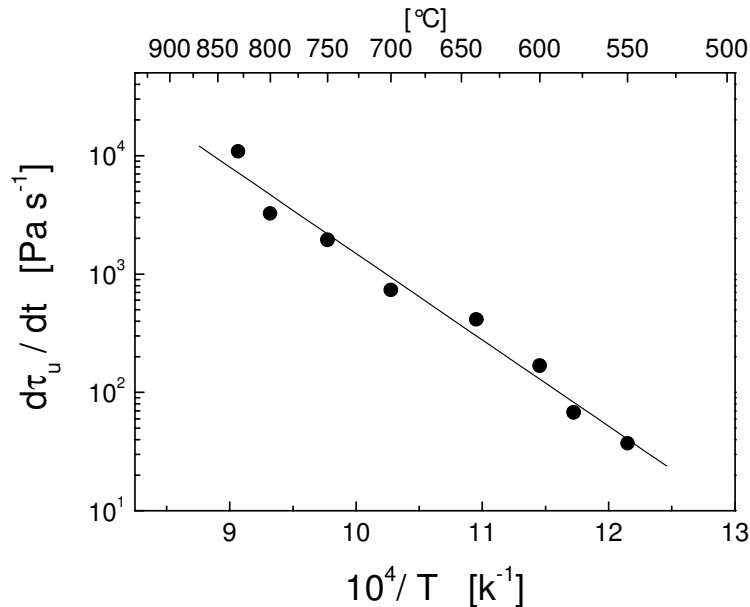


Figure 5-3. An Arrhenius plot of the ratio $d\tau_u/dt$ at different temperatures. The linear fit to the data gives an activation energy for the locking process of 1.45 ± 0.09 eV.

3. Discussion of experimental results

In the case of nitrogen in FZ-silicon, it is known that both nitrogen monomers and dimers maybe present in the crystal and their relative concentration is dependant on temperature. This was already described in Chapter 1, Section 4.1. In principle, since it is assumed that the dislocation unlocking stress depends on the number of impurities collected at the core, in NFZ samples the locking effect can be caused by segregation of both nitrogen dimers and monomers to the dislocation core. In particular, the following three possibilities are considered in this section:

- 1) nitrogen accumulation at the dislocations followed by precipitation, the precipitates resulting in locking;
- 2) nitrogen dimers segregating to the dislocations to produce locking;
- 3) nitrogen monomers segregating to the dislocations to produce locking.

Nitrogen-oxygen complexes were not considered as a candidate species for dislocation locking since these are thought to form at temperatures higher than those investigated in this thesis⁶.

The possibility of nitrogen precipitation is described in the next paragraph, whereas the other two options are discussed further before being considered separately.

3.1 Possibility of locking produced by nitrogen precipitation at the dislocations.

The work of Yonenaga⁷ has shown that in silicon, the precipitation of oxygen at high temperature along a dislocation can lead to the immobilization of the dislocation. When this occurs, the stress required to unlock the dislocation depends on the spacing of the precipitates along the dislocation line and can depend on their size. The spacing of the precipitates

depends on the temperature at which they are nucleated and it increases after prolonged annealing (Fig. 5-4). This in turn reduces the unlocking stress (Fig. 5-5). Thus, the unlocking stress for dislocations pinned by precipitates is expected to depend on the temperature and duration of the anneal during which they are formed.

In the case of nitrogen in silicon, little is known about precipitation at a dislocation. However, the saturation unlocking stress measured in this work is practically constant for a wide range of temperatures and times and this strongly suggests that nitrogen precipitates along the dislocation core are not responsible for the locking observed.

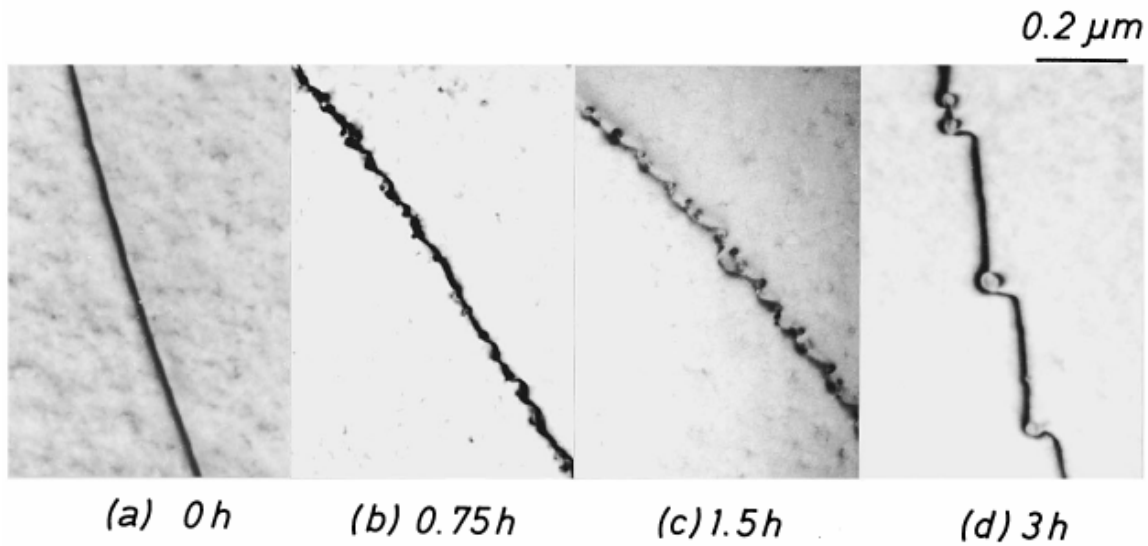


Figure 5-4. Variation in the configuration of a dislocation decorated by oxygen precipitates in Cz-silicon for increasing annealing time at 900°C. (after Yonenaga⁷)

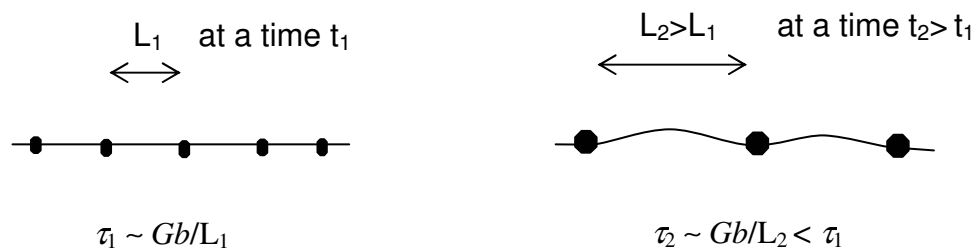


Figure 5-5. The length of the dislocation segments delimited by two adjacent precipitates depends on annealing duration t . Therefore, the stress τ to activate a Frank-Read source should be lower in the configuration on the right (after ripening). The quantities G and b in the expressions of τ_1 and τ_2 represent the shear modulus and the Burgers vector of silicon respectively.

3.2 Binding energy of nitrogen to a dislocation

One of the new results shown in this chapter for NFZ-silicon samples was the effective invariance of the saturation unlocking stress (regime 2) as a function of the annealing temperature. It is suggested that regime 2 takes place when all (or nearly all) of the available sites at the dislocation core are fully occupied and thus no further increase of the unlocking stress can be observed because the nitrogen concentration at the dislocation is then independent of time and temperature. Previously in this thesis, the equilibrium concentration of an impurity at the dislocation core C_{core} during regime 2 was assumed to follow a Maxwell-Boltzmann distribution, thus

$$C_{core} = C_{\infty} \exp\left(\frac{\Delta H - T\Delta S}{kT}\right) \quad (5.1)$$

where C_{∞} is the impurity concentration at the far field of diffusion. Although the concentration of nitrogen in FZ-silicon is at least two orders of magnitude lower than that of oxygen in Cz-silicon, the experimental results show that during regime 2, nitrogen is able to produce a dislocation locking effect comparable to that caused by oxygen. It then follows from Equation (5.1) that the enthalpy of interaction between a nitrogen species and a dislocation has to be significantly larger than that due to the oxygen-dislocation interaction ($\Delta H=0.74$ eV) in order to achieve a sufficient nitrogen concentration at the core to produce an appreciable locking. This is shown schematically in Fig. 5-6. However, if the enthalpy of interaction of an impurity with a dislocation is sufficiently high, then a large fraction of the available sites at the core will be occupied and Maxwell-Boltzmann statistics will no longer be accurate. In this situation, Fermi-Dirac statistics should be used and the probability p that a site is occupied is then given by

$$p = \frac{1}{1 + \frac{1}{C} \exp\left(\frac{\Delta S}{k}\right) \exp\left(-\frac{\Delta H}{kT}\right)} \quad (5.2)$$

where $C=[C_{\text{impurity}}]/[C_{\text{silicon}}]$ is relative concentration of the impurity. It is noted that the numerical model discussed in Chapter 3 (Section 2), which is used in this thesis to describe impurity locking of dislocations, accurately reproduces the Fermi-Dirac occupation probability for sites at the core. This is because the flux of atoms to the dislocation, in this model, depends on the concentration of unoccupied sites at the dislocation core.

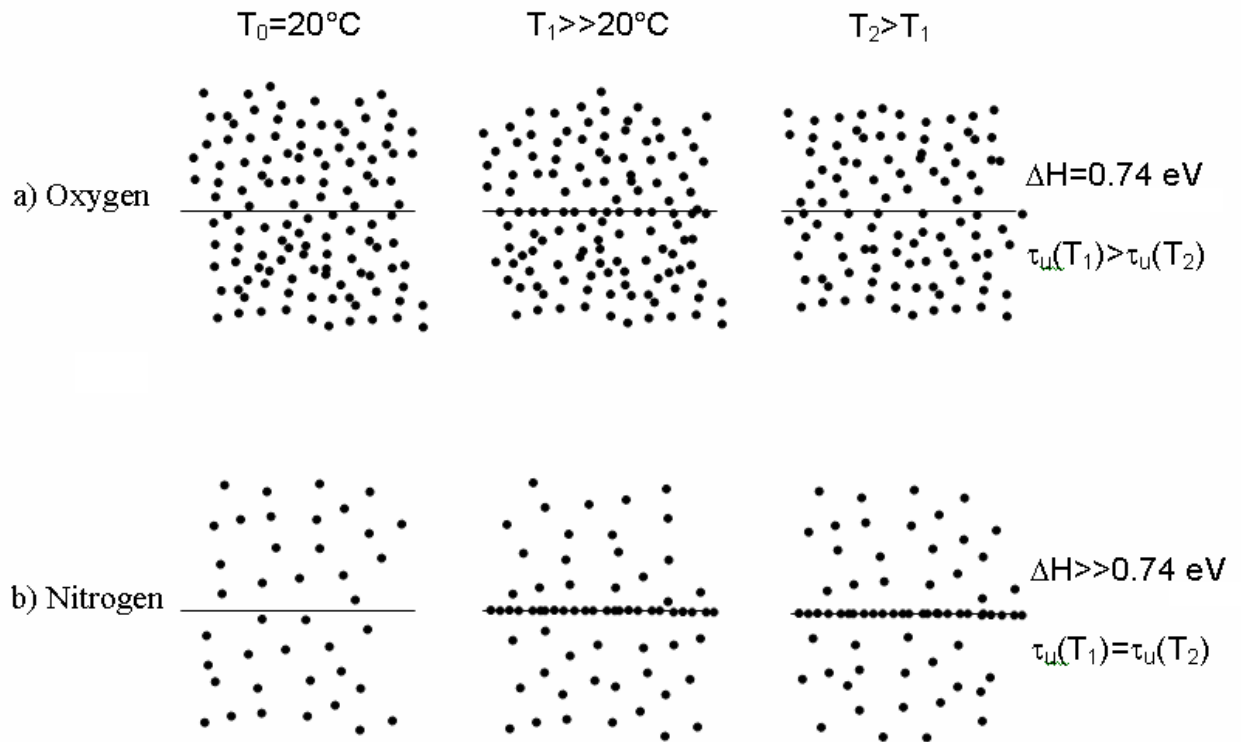


Figure 5-6. Dislocation (solid line) decoration at thermodynamic equilibrium in the case of oxygen (a) and nitrogen (b) impurities. The bulk concentration of oxygen is 100 times that of nitrogen, but the interaction enthalpy of oxygen (0.74 eV) is assumed to be lower than that of nitrogen. Thus, according to Equation (5.1), after sufficient annealing at a temperature T_1 , it may be possible to trap enough nitrogen atoms at the dislocation core (b) such that these would produce a locking effect similar to that obtained with oxygen (a), despite the difference in concentrations. At higher temperatures, whilst most of the oxygen atoms boil-off the dislocation core due to their low binding energy, nitrogen atoms are able to remain bonded to the core. In this way nitrogen is capable of fully decorating the dislocation without leaving any empty sites along the core. The observed saturation of the unlocking stress is then a consequence of all the available sites being occupied and is independent of the anneal temperature.

How large does the interaction enthalpy have to be in order to decorate fully the dislocations? The experiments indicate that the nitrogen impurities do not “boil-off” the dislocations at least up to 830°C during regime 2 and thus the probability of occupation p will be close to unity. Fig. 5-7 shows p plotted as a function of temperature for a series of different interaction enthalpies with the entropy concentration assumed to be negligible. This shows that, within the sensitivity of the experimental data obtained in this work, a binding enthalpy of approximately 1.7 eV or higher would account for the measured constant value of the saturation unlocking stress. The value of 1.7 eV deduced with the above analysis was used as the interaction enthalpy in the numerical simulation which will be described in the following sections.

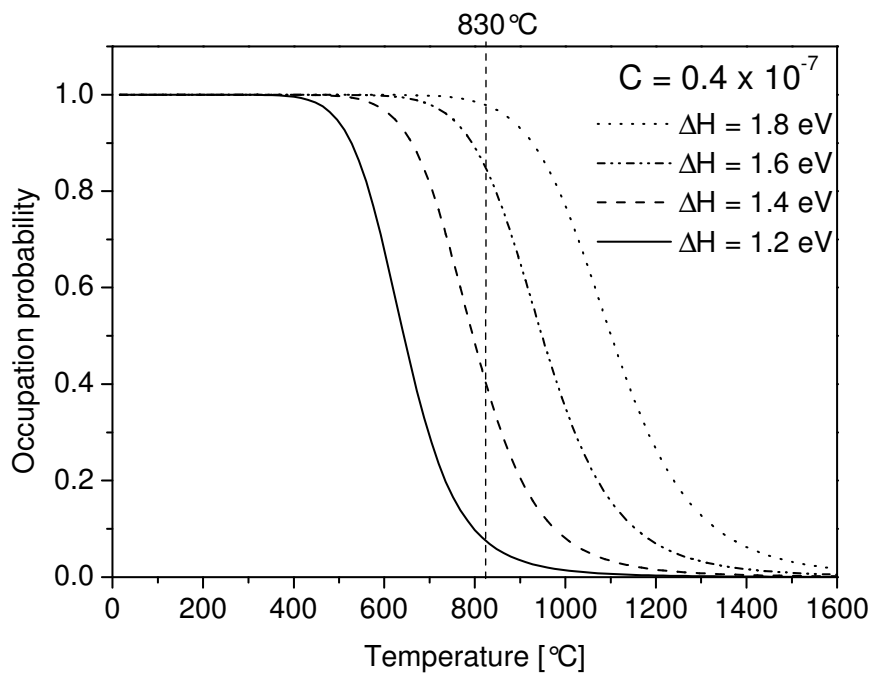


Figure 5-7. Probability for a dislocation site to be occupied by an impurity species (given by Equation 5.2) as function of temperature and different values of binding enthalpy. The relative bulk concentration of impurities was taken as $C = [2 \times 10^{15} \text{ cm}^{-3}] / [5 \times 10^{22} \text{ cm}^{-3}] = 0.4 \times 10^{-7}$.

3.3 Transport of nitrogen in silicon

It is known that nitrogen in silicon can exist in the form of monomers and dimers. Thus, in general the unlocking stress τ_u could be due to the accumulation of nitrogen monomers and dimers along a dislocation, so that τ_u can be written as

$$\tau_u = n_1 \tau_1 + n_2 \tau_2 \quad (5.3)$$

where n_1 and n_2 are respectively the number of nitrogen monomers and nitrogen dimers accumulated along a unit length of dislocation, τ_1 and τ_2 are respectively the unlocking stress for a dislocation pinned by a single monomer and a single dimer per unit length. The number of nitrogen dimers or monomers at the dislocation core is limited by:

- a) the transport of nitrogen to the core during annealing at a certain temperature;
- b) the number of sites at the core available for occupation n_{total} (which in general is different for the each of the two species, $n_{total1} \neq n_{total2}$);
- c) when steady state is reached, the equilibrium concentration at the core.

For most of regime 1, the unlocking stress τ_u increases linearly with time and, under these conditions, the rate of increase in τ_u is proportional to the transport of nitrogen to the dislocation. Since both nitrogen monomers and dimers may be present in the silicon crystal, the value of the diffusivity for each of the two species can be written in the form

$$D_i = D_{0i} \exp\left(-\frac{E_{diff}^{(i)}}{kT}\right) \quad (5.4)$$

where $i=1$ or 2 in the case of monomers or dimers respectively. Thus, the variation of the unlocking stress during regime 1 can be written as

$$\frac{d\tau_u}{dt} \propto \frac{dn_i}{dt} \propto D_{0i} \exp\left(-\frac{E_{diff}^{(i)}}{kT}\right) \quad (5.5)$$

where $i=1$ or 2 depending on the dominant species locking dislocations at the specific temperature T . According to Equation (5.5), the activation energy deduced in Fig. 5-3 could be associated with either monomers or dimers depending on which is the dominant nitrogen species for locking between 550°C and 830°C . In the most general case, assuming that the nitrogen monomers (with concentration C_1) are in dynamic equilibrium with the dimers (with concentration C_2), the effective transport of nitrogen in silicon can be written as:

$$D_N^{\text{eff}} = \frac{C_1 D_1 + 2C_2 D_2}{C_1 + 2C_2} \quad (5.6)$$

where D_1 is the diffusivity of the nitrogen monomers and D_2 is that of dimers.

At the temperatures of the experiments, however, the concentration of dimers C_1 is much greater than that of monomers C_2 [see Ref. 8-11], thus equation (5.6) can be rewritten as

$$D_N^{\text{eff}} = \frac{1}{2} \frac{C_1}{C_2} D_1 + D_2. \quad (5.7)$$

The diffusivity D_1 of nitrogen monomers is large at high temperatures⁴ and considering the temperature dependence of the monomer concentration, which can be written as

$$C_1 = \sqrt{C_2} \exp\left(-\frac{1}{2} \frac{E_{\text{bind}}}{kT}\right) \quad (5.8)$$

where E_{bind} is the (positive) binding energy of a dimer, Equation (5.7) becomes

$$D_N^{\text{eff}} = \frac{1}{2\sqrt{C_2}} \exp\left(-\frac{1}{2} \frac{E_{\text{bind}}}{kT}\right) D_1 + D_2 \quad (5.9)$$

or, more explicitly:

$$D_N^{\text{eff}} = \frac{1}{2\sqrt{C_2}} \exp\left(-\frac{1}{2} \frac{E_{\text{bind}}}{kT}\right) D_{01} \exp\left(-\frac{E_{\text{diff}}^{(1)}}{kT}\right) + D_{02} \exp\left(-\frac{E_{\text{diff}}^{(2)}}{kT}\right) \quad (5.10)$$

Fig. 5.3 shows that locking data is well described by a single activation energy over the complete experimental temperature range (550°C - 830°C), whereas if the first and second terms of Equation (5.10) were comparable at some temperature in the measured range, the term with

the larger activation energy would be expected to dominate at higher temperatures and that with the smaller energy at lower temperatures such that the data in Fig. 5-3 would exhibit a “kink”. Since a straight line is observed throughout, it is inferred that one or other of the two terms of Equation (5.10) is dominant for all the experimental data and the analysis will now be continued in these terms.

3.4 Locking dominated by segregation of monomers to dislocation core

Even though the monomer concentration is expected to be a small fraction of the dimer concentration, particularly at low temperatures, it could still dominate locking effects if the diffusivity of the monomers was orders of magnitudes higher than that of the dimers. The situation would then be that most of the nitrogen is in the form of essentially immobile dimers⁴ with a very small proportion of highly mobile monomers responsible for diffusing to the dislocations and subsequent locking. In this section, an analysis is performed on the basis that monomers are responsible for dislocation locking. With this assumption, the first term of Equation (5.10) dominates such that

$$D_N^{eff} \propto \exp\left(-\frac{E_{bind}/2 + E_{diff}^{(1)}}{kT}\right) \quad (5.11)$$

and the measured activation energy (1.45 eV, Fig. 5-3) will then be the sum of the activation energy for monomer diffusion $E_{diff}^{(1)}$ and half the monomer binding energy E_{bind} . The smallest value which can be found in the literature for E_{bind} is 1.7 eV [see ref. 11], thus the maximum value for $E_{diff}^{(1)}$ would be $E_{diff}^{(1)} = 1.45 - \frac{1.7}{2} = 0.6$ eV, which seems remarkably small. In addition, the binding energy to a dislocation core, which was found to be approximately 1.7

eV from the experimental data (Section 3.2), becomes $(1.7 \text{ eV} + \frac{E_{bind}}{2}) = 2.55 \text{ eV}$ in the case of locking produced by nitrogen monomers. This value of the binding energy to a dislocation seems very large for a nitrogen monomer and more difficult to explain from the theoretical point than that deduced for nitrogen dimers (see next section).

3.5 Locking dominated by segregation of dimers to dislocation core

To understand which is the species responsible for nitrogen transport in the temperature range investigated, a numerical simulation was used to deduce important parameters such as the unlocking stress τ_0 due to a single nitrogen species pinning a unit length dislocation, the transport of nitrogen and the binding enthalpy of the interaction between nitrogen and the dislocations. In this section, the data is analysed assuming dimers are responsible for dislocation locking and hence the first term of Equation (5.10) dominates. The section also includes a discussion as to which of the two analyses performed here and in the previous section is most likely to represent the physical processes actually occurring.

The same numerical simulation that was used in the previous chapter to model the interaction of oxygen with dislocations is used here to analyse the nitrogen locking data. Thus, in the presence of a dislocation stress field, the equation for diffusion of a nitrogen species i is¹²

$$\frac{\partial C_i}{\partial t} = D_i \nabla \left[\nabla C_i + \frac{C_i \nabla (\Delta G_i)}{kT} \right] \quad (5.12)$$

where C_i is the concentration of the active nitrogen species, D_i is its diffusivity, k is Boltzmann's constant, T is the absolute temperature, ΔG_i is the Gibbs free energy (binding energy) of the interaction between a nitrogen impurity and a dislocation and t is the annealing

time. The values of both the bulk concentration of nitrogen and the concentration of sites available for occupation by the locking species at the dislocation core are needed in order to perform the analysis of the experimental data using Equation (5.12) with appropriate boundary conditions - see Equation (3-10).

As mentioned above, in this section it is assumed that it is the nitrogen dimer which diffuses to the dislocations and then locks them. Thus $C_2 \gg C_1$ and also $n_2 \gg n_1$ in Equation (5.3). In addition, the dimer concentration $C_2 = \frac{C_N}{2} = 1.0 \times 10^{15} \text{ cm}^{-3}$ is half the total atomic nitrogen concentration $C_N = 2.0 \times 10^{15} \text{ cm}^{-3}$ measured by FT-IR. The density of available sites for dimers along the dislocation, n_{total2} , was taken to be $1.3 \times 10^7 \text{ cm}^{-1}$, which is equivalent to the individual nitrogen atoms of the dimers aligned along a perfect dislocation and accommodated in interstitial sites separated by a Burgers vector ($3.8 \text{ \AA}$) each from the other. The numerical simulation is based on the solution of Equation (5.12), which gives the number of nitrogen dimers at the dislocation core, and Equation (5.3) which describes the total unlocking stress due to dimers when $n_1 \ll n_2$. The simulation is able to fit all the experimental data of Fig. 5-1 using τ_0 , D_{0dimer} , ΔS and ΔH as fit parameters, where ΔS and ΔH are the entropy and enthalpy change due to the interaction between a nitrogen dimer and the dislocation. The value of the activation energy for dimer diffusion $E_{diff}^{(2)}$ used in the simulation was taken from the Arrhenius plot in Fig. 5-3. Fig. 5-1 shows the calculated curves (solid lines) that best fit the experimental data over the temperature range of interest; each curve was obtained using the same set of parameters, which is the following:

$$D_{dimer} = 6.8 \times 10^{-6} \exp(-1.45 \text{ eV} / kT) \text{ cm}^2 \cdot \text{s}^{-1}, \quad (5.13)$$

$$\tau_0 = 4 \text{ Pa} \cdot \text{cm} \text{ (for a dimer),}$$

$$\Delta H = 1.7 \text{ eV},$$

$$\Delta S = 8.6 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$$

The simulation is rather insensitive to the particular value chosen for ΔS ($\Delta S \ll \Delta H$); for example, a variation by a factor 2 in ΔS affects the calculated unlocking stress by less than 1%.

The numerical simulation can provide a good fit to the experimental data, as shown in Fig. 5-1. During regime 1, the observed behaviour of the unlocking stress can be understood in terms of an increasing concentration of nitrogen at the dislocation core, as the anneal progresses, with transport of nitrogen to the dislocation being faster at high temperatures. Regime 2 takes place when all (or nearly all) of the available sites at the dislocation core are fully occupied, as explained in Section 3.2.

The error in the pre-factor of D_{dimer} deduced from the simulation can be up to an order of magnitude, whereas the inaccuracy in the activation energy for diffusion (1.45 eV) is approximately ± 0.1 eV. This is in agreement with the possible range of values deduced from the data in Fig. 5-3 using the method of the least squares. Diffusivity measurements are also affected by the error in the nitrogen concentration which was not known with an accuracy better than a factor of two. In addition, as D_{dimer} describes the diffusivity of nitrogen dimers, the transport of single nitrogen atoms would be twice as fast. However, the small value of pre-factor in D_{dimer} compared to the usual range of values for monomer diffusion in silicon suggests that either the value obtained in this investigation is inaccurate or that dimers have different pre-factors to those of the more normally investigated monomer species, although this possibility has not been explored further in the present work. Other errors in D_{dimer} may come from the estimation of the number of available sites for occupation at the core n_{total2} ; although the dislocations are assumed to be straight in the model, n_{total2} can vary by a factor of two if perfect dislocations are effectively split into partials.

The rather large value of enthalpy (1.7 eV) deduced for the interaction of a single nitrogen dimer with a dislocation is physically reasonable especially if compared to the 0.74

eV binding energy associated to oxygen monomers. In this case, ΔH for nitrogen dimers should be roughly double the binding enthalpy already deduced for oxygen monomers at dislocations, as described in Chapter 4. The large binding energy of nitrogen dimers allows the dislocations to be fully decorated at temperatures up to 830°C, such that nitrogen atoms occupy all the sites available along the linear defect.

The value $\tau_0 = 4 \text{ Pa}\cdot\text{cm}$ of the unlocking stress per nitrogen dimer is lower than that for oxygen monomers (7 Pa·cm). Although this could appear strange, the above value of τ_0 for nitrogen dimers is not unrealistic especially if the different possible reconstruction of the atomic bonds for monomers and dimers at a dislocation are considered. Therefore, it is believed that the values associated to the parameters deduced from the simulation are best explained on the basis that nitrogen dimers are responsible for transport and accumulation at the dislocation core in significant concentration. Consequently, the accumulation of nitrogen dimers produces the observed dislocation locking effect. Thus, if the active nitrogen species at the temperatures investigated is thought to be dimers, then the experimental data can be modelled using the above physically reasonable values for the different parameters involved.

However, it should be noted that in the temperature range investigated, if dislocation locking is due to segregation of dimers, this does not imply that all nitrogen transport is dominated by dimers in this range. In fact, it is possible that the concentration of monomers in the bulk is so small that the equilibrium concentration of monomers at the dislocation core would be insufficient to give a significant locking stress (the saturation stress in regime 2). Thus, even if the transport of monomers was faster than that of dimers, the dislocation unlocking experiments would only be sensitive to the behaviour of the dimers.

The nitrogen dimer diffusivity deduced in this work (Equation 5.13) is plotted in Figure 5-8 together with out-diffusion data¹ reported by Itoh *et al.* obtained at higher

temperatures. Recent theoretical studies have suggested that Itoh's data describe the behaviour of nitrogen monomers rather than dimers³.

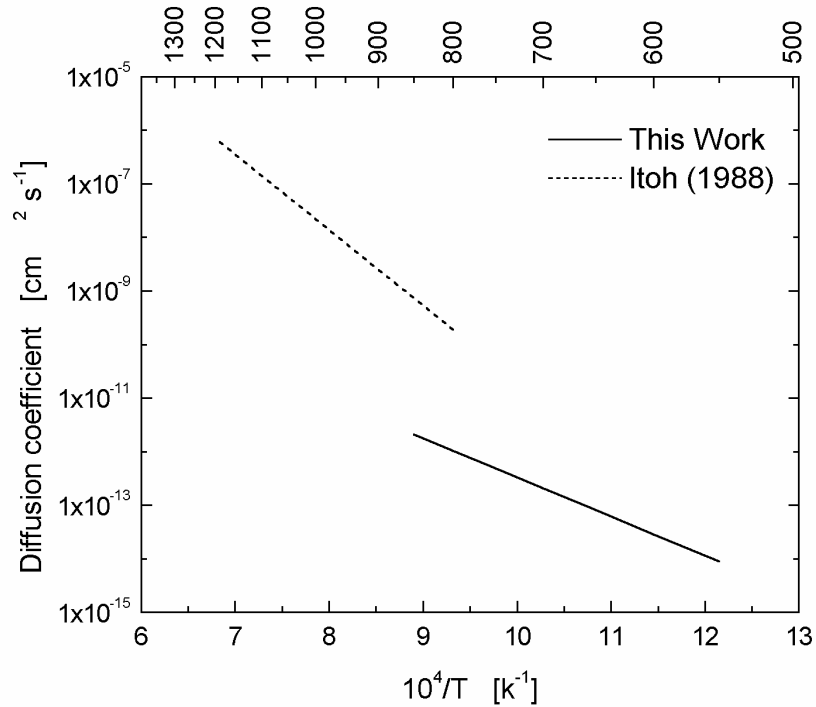


Figure 5-8. Diffusion coefficient of nitrogen in silicon. The solid line represents the results obtained in this work, whereas the dotted line refers to out-diffusion data obtained at higher temperatures by Itoh in 1988.

Thus, it is proposed that the results presented in this chapter are consistent with those of Itoh being due to fast diffusing monomers (to which out-diffusion measurements are sensitive), and that any monomer segregation to dislocation cores is too small to produce significant locking. From this point of view, nitrogen and oxygen in silicon behave similarly in that dimer transport dominates at low temperatures, but monomers become important at higher temperatures.

4. Conclusions

The locking of dislocations by nitrogen impurities in nitrogen-doped FZ-grown silicon crystals was investigated as a function of time in the temperature range 550–830°C. It was found that nitrogen impurities induce a strong locking effect on stationary dislocations after a sufficiently long anneal. The locking is similar in magnitude to that observed for oxygen atoms in Cz-grown crystals, although the nitrogen concentration in the NFZ samples ($\sim 2 \times 10^{15} \text{ cm}^{-3}$) is two orders of magnitude lower than the usual oxygen concentration in Cz silicon. For the first time, it was observed that the unlocking stress (measured at 550°C) due to accumulation of nitrogen at a dislocation initially increases with annealing time and then saturates to a value of approximately 50 MPa for all the anneal temperatures investigated. As no other regimes were observed in the behaviour of the unlocking stress as a function of annealing time, it was suggested that nitrogen precipitation at the dislocation core did not occur during the experiments. From the analysis of the experimental data, information concerning the binding energy of a nitrogen impurity to a dislocation ($> 1.7 \text{ eV}$) was deduced. In addition, using a numerical simulation of the experimental results and by making certain physically realistic assumptions, quantitative data is inferred regarding the nitrogen diffusion coefficient and the dislocation pinning force per nitrogen atom at the dislocation core (2 Pa·cm). Although nitrogen dimers are believed to be the dominant species at the temperatures of the experiments, an analysis has been carried out with the hypothesis that nitrogen diffusion and binding to the dislocations were governed by monomers. The results of this analysis showed that the value of the activation energy for monomer diffusion deduced from the experimental data would be rather small ($< 0.6 \text{ eV}$) and, in addition, the binding energy of a monomer to a dislocation would be large (2.55 eV), particularly if compared with the binding energy of oxygen monomers (0.74 eV). Thus, it is considered more likely that dimers are responsible for nitrogen transport and for dislocation locking in the temperature range

investigated. Assuming that the nitrogen dimer is the dominant species, the values obtained for the activation energy for dimer transport (1.45 eV) and the binding energy of a dimer to a dislocation (>1.7 eV) appear physically reasonable. However, fast diffusing monomers probably dominate at temperatures higher than those considered in the present work; this hypothesis is supported by the out-diffusion measurements of nitrogen diffusivity performed by Itoh *et al.*

According to the diffusivity data deduced from unlocking experiments, nitrogen transport due to dimers is faster than that due to oxygen dimers in Cz-silicon, but the difference is only about one order of magnitude (or a little more in the case of low oxygen concentration). In Fig. 5-10, the expressions deduced for the transport of nitrogen and that of oxygen are plotted over a wide range of temperatures for both dimers (unlocking experiments) and monomers (out-diffusion data from the literature).

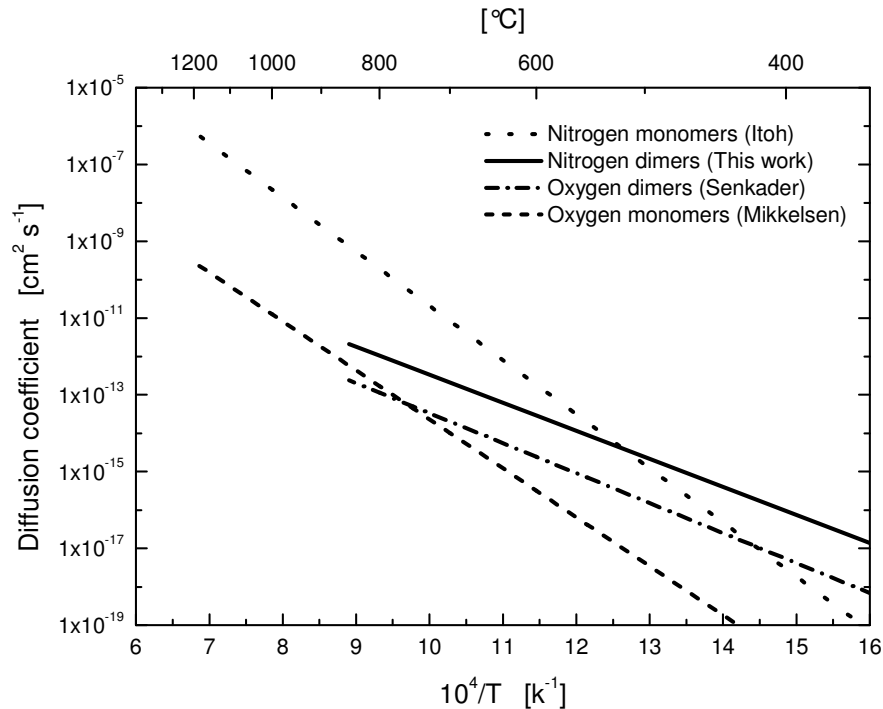


Figure 5-10. Diffusivity of oxygen and nitrogen with distinction between monomer diffusion and dimer diffusion.

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Chapter 6:

Generation of dislocation glide loops by oxide precipitates

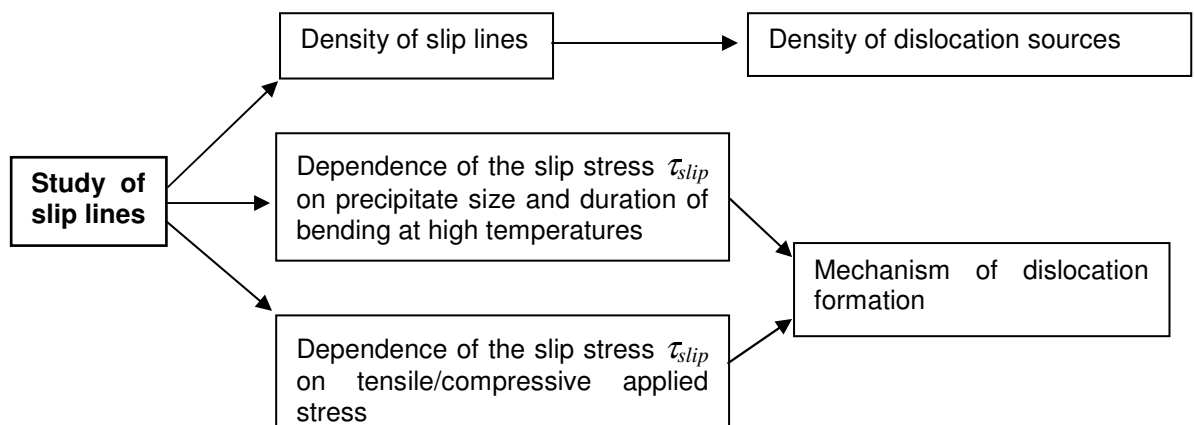
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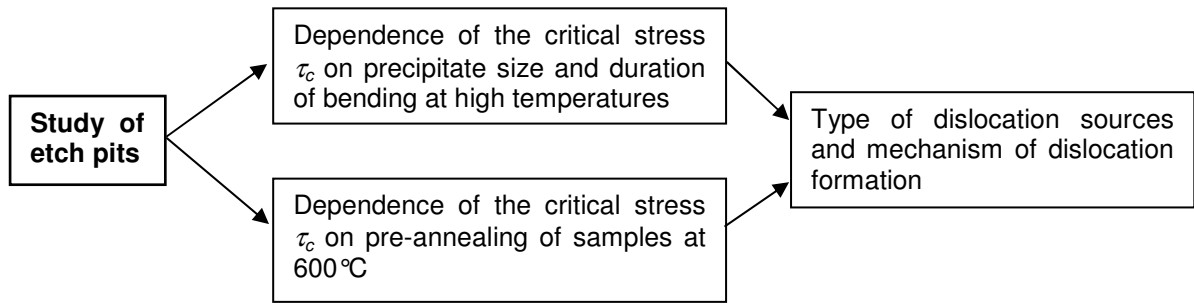
1. Introduction

As described in Chapter 1, if a certain stress is applied on a silicon crystal, then a “glide” dislocation loop (Fig. 1-19) is able to expand conservatively in the glide plane which contains the loop and its Burgers vector, whereas a “prismatic” dislocation loop can only move conservatively along the glide prism (Fig. 1-21). Glide dislocation loops intersecting the wafer surface are potentially catastrophic for semiconductor devices. In this chapter, the mechanism by which these glide dislocations are generated in Cz-silicon wafers containing a controlled distribution of oxide precipitates is investigated by means of mechanical tests at high temperatures. Although some authors believe that glide dislocations in a silicon wafer originate directly from every single oxide precipitate present in the crystal¹, the new results presented in this chapter allow the role of other dislocation sources to be considered. In fact, it is known that large precipitates cause the formation of induced defects such as prismatic dislocations or more complex dislocation tangles⁹, which in turn can originate dislocation multiplication processes. In this work, the role of such defects in the generation of glide dislocations is investigated in several silicon samples containing oxide precipitates with different sizes. Modern technology requires silicon wafers which can combine a very small density of dislocations with an efficient internal gettering of impurities to achieve higher performance. Thus, the present study is important in order to develop better quality silicon-based materials for device manufacturing. In particular, it will be shown that if the precipitate size is controlled and kept under a critical size, then the number of active dislocation sources and hence the plastic deformation of wafers during processing could be reduced.

Before presenting the experimental results in detail, an overview is given of all the experiments performed and how these were chosen to give the required information.

Experiments have been carried out to investigate the distribution of slip lines at the wafer surface after the application of an external stress under different experimental conditions. It was found that the occurrence of slip in silicon (at a given temperature, for a certain duration of stress application) is limited by a critical value of the applied shear stress. The resolved shear stress needed to observe (using an optical microscope operating in Nomarski mode) a slip line at the surface is called the “slip” stress τ_{slip} . The occurrence of slip is still a problem in wafer manufacturing and device fabrication, thus the results obtained from the experiments described in this chapter are of importance to the semiconductor industry. However, the study of slip lines did not provide direct information on single dislocation generation because usually tens of dislocations are needed to form a slip line which can then be detected under an optical microscope. For this reason, further experiments were performed to detect the distribution of chemical etch pits, rather than slip lines. In fact, with chemical etching techniques, every pair of pits could be associated with a single glide dislocation emerging at the surface during stress application at high temperatures. In particular, the study of etch pits allowed the determination of the critical shear stress τ_c necessary to produce and detect a single glide dislocation loop under specific conditions. The different experiments that are described in this chapter and the information deduced from the analysis of the experimental data are schematically listed below.





The experiments described in the following sections are divided in two different groups, depending on the specific bending geometry used to apply the stress on the samples: annular bending or three-point bending.

2. Annular bend tests

2.1 Dependence of slip line density on precipitate size and shear stress

Slip lines can appear at the wafer surface after processing at high temperatures and are mostly responsible for degrading microelectronic devices. The dependence of the slip stress τ_{slip} on precipitate size and density was initially studied by Senkader *et al.*², as described in Chapter 1, Section 9. The technique used by Senkader to produce slip lines in silicon wafers involved annular bending of fixed duration (20 min) at 635°C, in argon atmosphere. However, the variation of the slip stress with duration of the applied stress and the relationship between applied stress, precipitate size and density of slip lines has not been fully investigated before.

Annular bending was used in these experiments to apply the external stress on the samples at elevated temperatures. The slip lines produced during this thermal treatment were then observed with an optical microscope. In the present study, a correlation between the number of precipitates and the number of slip lines was found, although in some specimens it was difficult to measure the actual density of slip lines, particularly in heavily dislocated areas. It was found that, under same stress conditions, the density of slip lines, σ_{slip} , can vary considerably with the density of dislocation sources within the material (in the case of Cz-Si, the number of sources is essentially the number of “active” oxide precipitates and/or associated defects). For example, the pictures in Fig. 6-1 show the increase in the number of slip lines when the precipitate density in the material changes from 2×10^9 to $8 \times 10^{10} \text{ cm}^{-3}$. Precipitate size and loading conditions were the same for both the samples shown in the figure. For this particular case, it can be observed that, due to the large numbers of slip events, it is practically impossible to count the number of slip lines at the surface when the precipitate density is $8 \times 10^{10} \text{ cm}^{-3}$ or higher. Hence, this difficulty in measuring the slip lines in heavily dislocated areas represented an experimental limit for the determination of the slip line density.

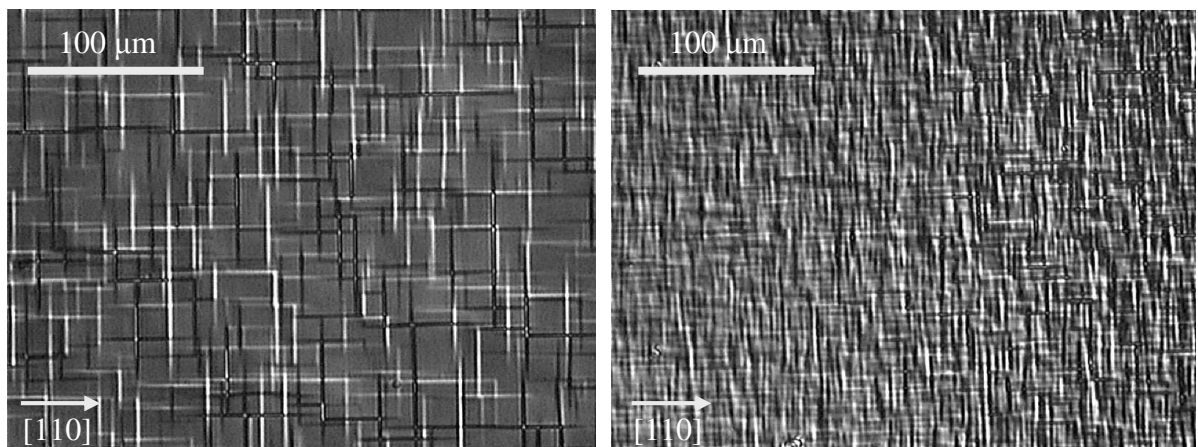


Figure 6-1. The two pictures above refer to the area over the ball contact, during annular bending, for samples with precipitate concentrations of 2×10^9 (left) and $8 \times 10^{10} \text{ cm}^{-3}$ (right). Precipitate size ($\sim 200 \text{ nm}$) and loading conditions (annular bending, $\sim 70 \text{ N}$ applied load at 635°C) were approximately the same for both the samples.

The graph in Fig. 6-2 shows the variation of the slip line density σ_{slip} (measured with DIC optical microscopy) as a function of the applied stress and precipitate size. The external stress was applied on all the specimens for 3 minutes at 635°C by using the annular bending technique. The temperature of 635°C was the highest temperature easily achievable for the furnace used in this work and is at the lower end of the temperature range for which wafer deformation is an issue for manufacturing. The load applied directly on the annular knife edge (Fig. 2-19) was typically 100 N. The density of slip lines was measured counting the number of slip lines in a well defined area (generally a circle of radius $\sim 200\mu\text{m}$) under a DIC microscope. The measurements were reproducible within a percentage error of approximately $\pm 5\%$; this was deduced by using different samples having same specifications and subjected to same experimental conditions. The precipitate sizes shown in Fig. 6-2 were calculated using Equation (2.8), according to the thermal history of the wafers which is reported in the specifications received from the manufacturer³ (8 hours nucleation at 650°C followed by precipitate growth at 1000°C for different times).

It can be observed in Fig. 6-2 that the density of slip lines in samples with small oxide precipitates (approximately 60 nm) does not show a strong dependence on the applied stress, whereas in sample containing large oxide particles ($> 100\text{ nm}$) the slip line density increases steeply with increasing stress. Moreover, a lower limit for the detection of slip lines is shown in Fig. 6-2 because it was not possible to measure accurately densities lower than approximately $5 \times 10^3\text{ cm}^{-2}$. Similarly, an upper limit also exists for the experimental data in Fig. 6-2 since for heavily dislocated regions it was rather difficult to measure the slip line density, as shown in Fig. 6-1 (picture on the right).

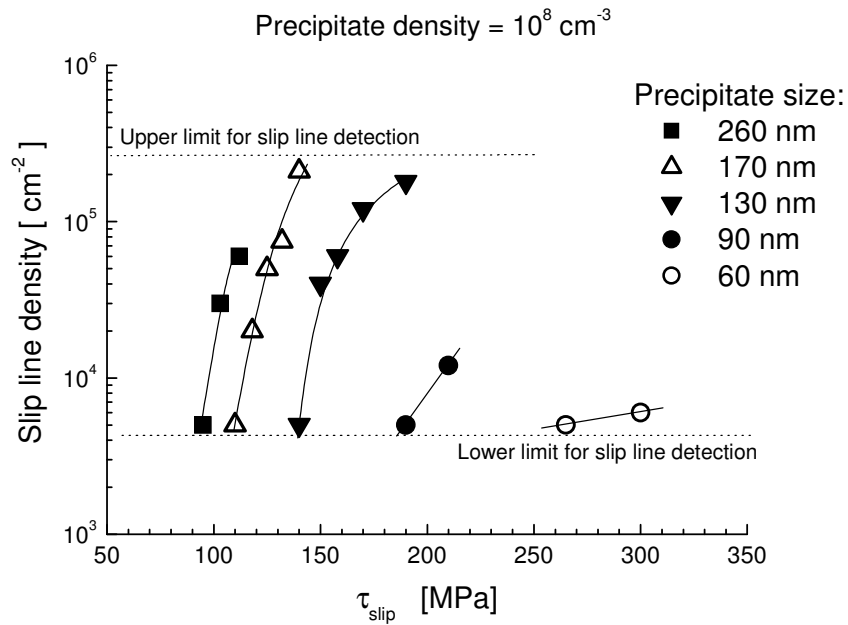


Figure 6-2. Slip line density as function of the slip stress τ_{slip} in Cz-silicon samples containing oxide precipitates of different sizes. The density of precipitates was approximately 10^8 cm^{-3} . External stresses were applied for 3 minutes at 635°C by using the annular bending technique.

The slip line density shown in Fig. 6-2 was measured at the silicon surface after 3 minutes of applied stress at 635°C . However, most of the dislocations forming the slip lines were not generated at the surface, but rather they were nucleated in some deeper portion of material. The volume of this portion becomes larger (for constant time of stress application) with increasing applied stresses because the velocity by which the dislocations glide to the surface increases. In order to explain this more clearly, Fig. 6-3 shows a schematic cross-section of a region underneath the silicon sample surface. The resolved shear stress distribution in the specimen, when this is subjected to a load of 100 N, is calculated and shown in Fig. 6-3 (dashed contour lines, units are MPa).

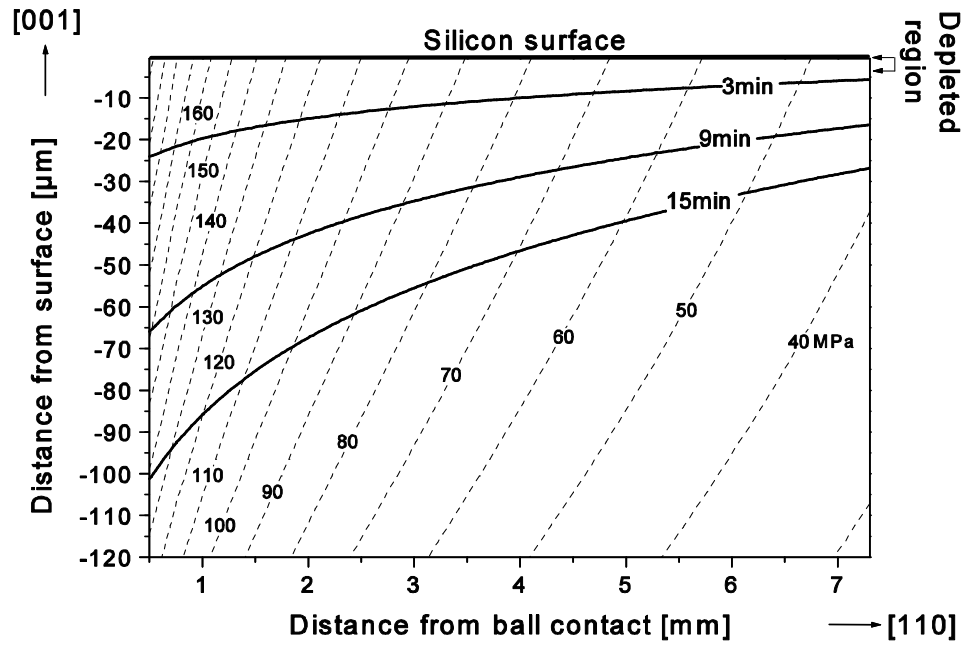


Figure 6-3. Cross-sectional view of the stress distribution (dashed lines, MPa) in silicon samples when subjected to a load of 100 N under annular-bending conditions. Contour solid lines represent the time needed for a dislocation to appear at surface (at $T=585^{\circ}\text{C}$). The precipitate-free zone (a few microns deep) typical of silicon wafers used in VLSI is indicated as “depleted region” in the graph.

Similarly, in the same graph, each point forming the solid contour lines indicates the time needed for a dislocation (generated at that point by a stress-activated precipitate) to reach the surface under applied stress at 585°C . The calculation of the time was carried out numerically considering the dislocation moving by steps in the (111) plane with velocity given by Equation (1.13) and taking into account the local value of applied shear stress at each step. For a given time t , it is possible to define an “active” volume for the wafer that is the portion of crystal for which all the dislocations generated by the active precipitates present in this portion can finally appear at the surface after a time t . Since the dislocations move with a well known velocity (depending on the applied stress), it is clear that the active volume changes as time progresses. These active crystal portions are delimited by the solid contour lines of Fig. 6-3 and depend on the duration of applied stress. Therefore, only a

fraction of activated precipitates within the material will be responsible for the formation of dislocations intersecting the surface at a given time t . For example, according to Fig. 6-3, dislocations that are generated from precipitates in regions deeper than 10 microns cannot emerge at the surface within 3 minutes (at 585°C) if the applied stress is not very large (<70 MPa).

2.2 Use of the slip line density to measure the slip stress τ_{slip}

Measurements of the slip stress τ_{slip} were carried out by observing the slip line distribution at the wafer surface (Fig. 2-21) and calculating the local applied shear stress, with the method described in Chapter 2, Section 9. It is noted that the slip line density data in Fig. 6-2 were measured at constant time t of applied stress and constant precipitate density (10^8 cm^{-3}). For these conditions, if the proportion of active precipitates in the material is independent of stress, then the slip density at the surface, σ_{slip} , is limited (for a given t) only by the dislocation velocity, which in turn depends linearly on the applied shear stress. Thus, for $t=\text{const}$ and precipitate density= const , the slip density σ_{slip} can be written as

$$\sigma_{slip} = a \tau_{slip} \quad (6.1)$$

where a is a constant [$\text{cm}^{-2} \text{ MPa}^{-1}$]. Fig. 6-4 shows lines referring to Equation (6.1) for different values of a . Thus, if a specimen contains a certain constant density of active dislocation sources and is subjected to increasing stress, the slip line density measured at the surface would increase according to the lines shown in Fig. 6-4. This increase is entirely due to the increasing volume of material from which dislocations can be detected (within 3 minutes) as the applied stress, hence the dislocation velocity, is increased.

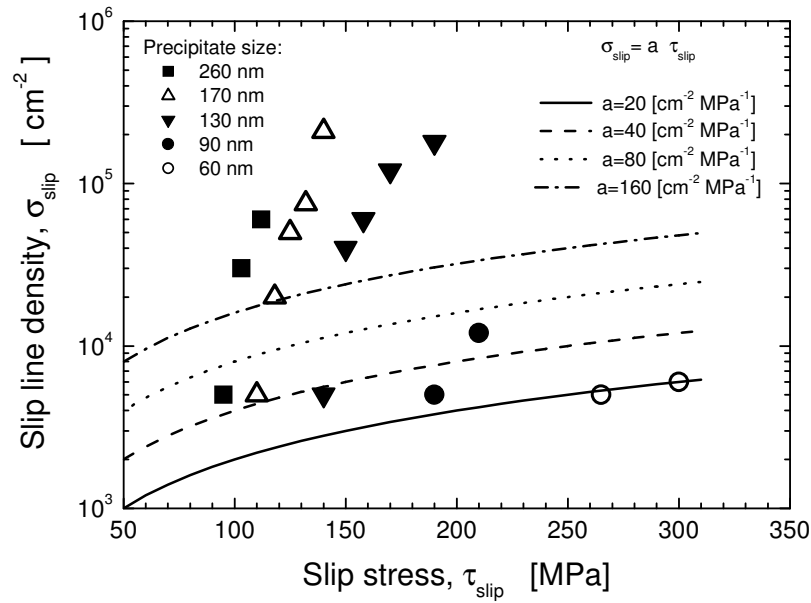


Figure 6-4. Same slip line density data as in Fig. 6-2 together with lines referring to Equation (6.1) and obtained using different values of a . The precipitate density in the samples was approximately 10^8 cm^{-3} .

Data in Fig. 6-4 suggest that the density of activated dislocation sources is, in most cases, stress dependent. In other words, each particular source needs to be subjected to a given stress level in order to be operative and release glide dislocation loops within a given wafer. Large precipitates induce the formation of prismatic dislocations or dislocation tangles, which in turn can originate dislocation multiplication processes. Hence, each of these potential dislocation sources can in principle have a different value of the activation stress because of their different morphology. Thus, for a specimen containing large precipitates, the fraction of these precipitates which act as dislocation sources increases, as they are subjected to higher stresses. This would explain the steep increase in the number of active sources as the applied stress increases. On the other hand, Fig. 6-4 shows that in the case of small oxide precipitates, dislocations can only be detected at the surface if very high stresses are applied and when the stress is increased further, the density of activated precipitates

remains constant. This is probably because each small oxide precipitate is morphologically very similar to each other, with perhaps only one small dislocation loop associated and not completely detached from the precipitate. Hence, these small defects need approximately the same activation stress to operate as dislocation sources. Surely the activation stress must be very large for small oxide precipitates, as more than 200 MPa applied shear stress is required to detect slip lines in samples containing small precipitates (Fig.6-2). It is believed that this must be due to the higher stress required to activate, for example, a Frank-Read source of small length or to expand a dislocation loop with small radius. Moreover, the slip line density may be characterised in relation to the volume of material which can produce dislocations capable of reaching the surface in the three minutes of applied stress using an analysis like that used to produce Fig. 6-3. In this way, a surface density of slip lines can be related to a volume density of sources (within the active region).

In the case of samples containing small precipitates (60 nm), it is found that only approximately 1 in 1000 precipitates generates dislocations at applied stresses of 260-300 MPa. This supports the hypothesis that not all the oxide precipitates are responsible for the generation of glide dislocations, but there must be some particular defects in the crystals that are more likely to nucleate glide dislocation loops for a given value of the applied stress. The active dislocation sources could be associated with prismatic dislocation loops punched-out from oxide precipitates. Alternatively, the active sources may consist of precipitates that are abnormally large or differently shaped or with a special dislocation configuration, as will be discussed in Sections 3, 4 and 5 of this chapter. On the other hand, for the larger precipitates at the highest slip line densities measured, it appears that at least 90% of all the precipitates have produced gliding dislocations, but at high densities it is possible that slip lines intersect with each other generating new secondary dislocation sources.

In the next sections, surface slip lines are investigated as a function of precipitate size, magnitude of applied stress and duration of applied stress. In each case, a value for the

slip stress is given, which is the stress required to produce the minimum detectable slip line concentration at the surface (approx. $5 \times 10^3 \text{ cm}^{-2}$). In experiments where the stress is applied for different lengths of time, the active volume of material investigated will depend on time, hence different numbers of precipitates will be activated depending on the duration of applied stress. For example, considering Fig. 6-3, a 15 minute experiment is sensitive to five times as many active precipitates as a 3 minute experiment, because the dislocations have more time to reach the surface. However, the minimum detectable slip line density remains the same in each case. Thus, the 15 minute experiment gives the stress required to activate only 1/5 the precipitates which are activated in the 3 minute experiment.

2.3 Dependence of the slip stress τ_{slip} on precipitate size and stress conditions

Extensive experiments carried out during this work confirmed that the applied stress needed to detect dislocation movement (as slip lines) depends mainly on the mean precipitate diameter and on the morphology of precipitates (Fig. 6-5). This is in agreement with the results from other authors⁴. The investigation, results of which are shown in Fig. 6-5, was performed by using silicon wafers containing $\sim 10^{10}$ precipitates per cm^3 with size ranging from 30 nm to 500 nm (see Tab. 2-4, 32 hours nucleation time) for this experiment. The precipitate size was deduced from TEM investigation. The external stress was applied at 635°C for 3 minutes on square silicon samples of 20mm×20mm by using the annular bending technique already described Chapter 2.

The data show a decrease of the slip stress with increasing precipitate size. It is possible that the last point in the graph (at precipitate size=300 nm) includes the effect of dislocation locking produced by the segregation of oxygen during wafer cooling. In this case, the magnitude of the stress required to unlock the dislocations pinned by oxygen atoms

is comparable with the applied stress needed to generate glide dislocations in these samples containing large precipitates.

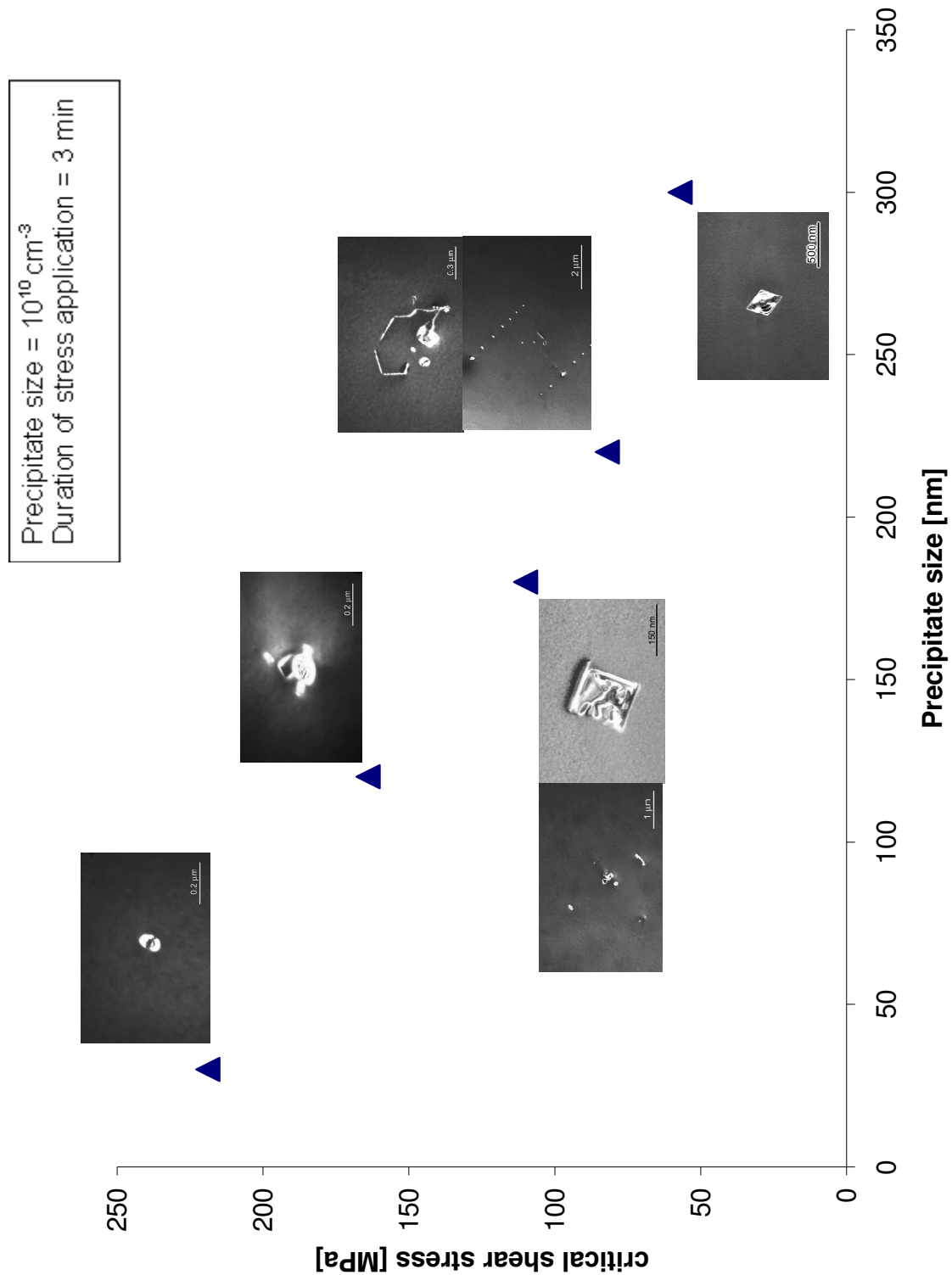


Figure 6-5. Data (triangles) representing the variation of slip stress with precipitate size (measured with TEM) in Cz-silicon samples with precipitate density of 10^{10} cm^{-3} . The external stress was applied at 635°C for 3 minutes. Every TEM image (produced by Dr. Reznik in Moscow) refers to a sample taken from the same wafer as that used for the mechanical test.

Further experiments carried out with samples containing precipitates with different sizes and different densities (10^8 and 10^{11} cm^{-3}) showed a strong dependence of the slip stress on bending duration. Data in Fig. 6-6 shows the behaviour of the slip stress as a function of duration of applied stress for four different wafers. The precipitate sizes were calculated by solving Equation (2.8) according to the specific thermal treatment to which each wafer was subjected. The dependence of τ_{slip} on duration of applied stress was found in all the different specimens investigated. However, the graph in Fig. 6-6 shows a little dependence of τ_{slip} on precipitate density in samples containing precipitates with size of 50 nm, whereas there is a significant variation in the slip stress when this is measured in samples containing precipitates of different sizes.

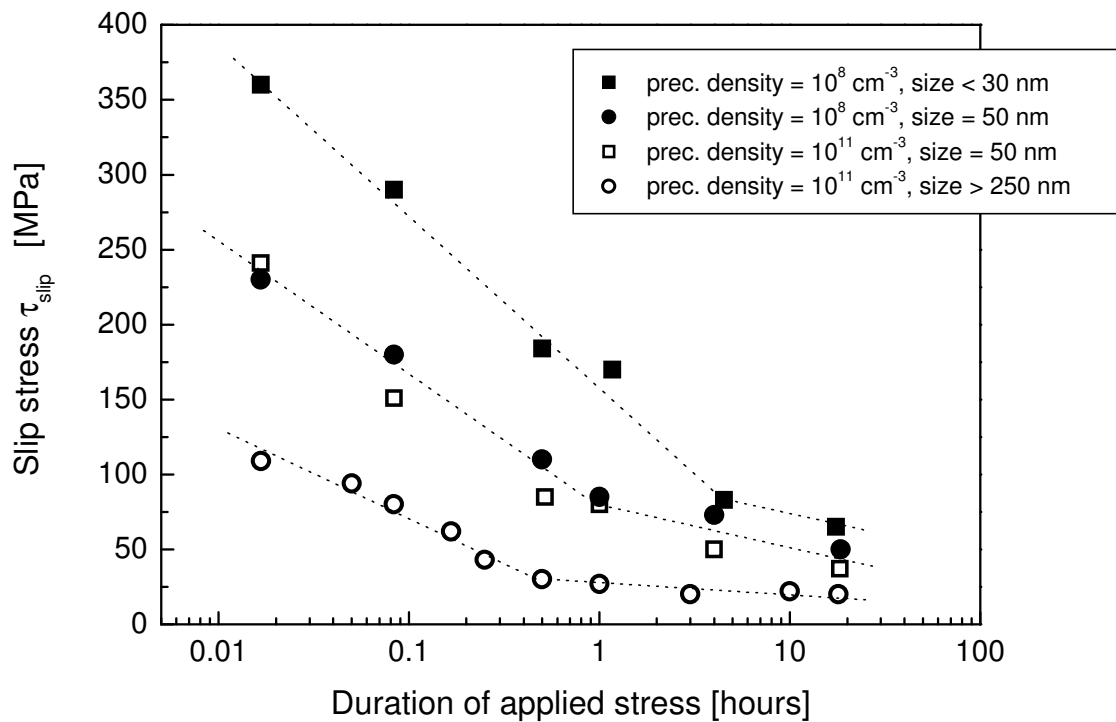


Figure 6-6. Variation of the slip stress with duration of applied stress. The slip stress was deduced from slip lines produced after annular bending at 635°C in samples having different precipitate concentrations and sizes.

In the case of small oxide precipitates, the critical resolved shear stress to generate a slip line at the surface was found to vary significantly when the sign of the applied stress changed from tensile to compressive conditions. Fig. 6-7 shows data collected using silicon samples containing oxide precipitates of different (calculated) sizes. The duration of bending was ~1 minute at the temperature of 635°C. The experimental evidence of Fig. 6-7 suggests that small dislocation loops close to small precipitates are more sensitive than large dislocation tangles to the misfit stress at the interface between the oxide particle and the silicon matrix.

As shown in Fig. 1-9, the stress-field surrounding a platelet precipitate rapidly decreases with increasing distance from the precipitate/matrix interface and it is practically negligible after a distance approximately equal to the precipitate size⁵. Let us assume for simplicity that the misfit strain at the precipitate site is purely compressive; this is approximately true in the direction of prismatic punching of dislocation loops generated from the precipitate (Fig. 1-9). It is also assumed that punched-out prismatic dislocation (PPD) loops will stop moving at the position where the misfit stress caused by the oxide precipitate equals the Peierls stress or other pinning forces arising from the presence of impurity atoms at the dislocation core. Therefore, in the case of a crystal containing very small oxide precipitates producing a short-range misfit stress field, the PPD loops should stop relatively close to the precipitate/matrix interface or probably remain pinned to the precipitate and not detach completely from it. If an external compressive stress is applied to the crystal, the strain energy at the oxide precipitate surface will increase and thus it is possible that the PPD loops (or parts of them) near the oxide particle will be subjected to a higher shear stress than that before applying the compression. In this case, the higher shear stress will be able to start the dislocation multiplication mechanism typical, for example, of a Frank-Read source. On the contrary, when an external tensile stress is applied, the misfit strain at the oxide/silicon interface will be relaxed and the PPD loops will be subjected to a minor shear stress than in the case of compressive stress application. As a consequence, a

larger external stress has to be supplied in the case of tensile stress application in order to start dislocation glide and multiplication processes.

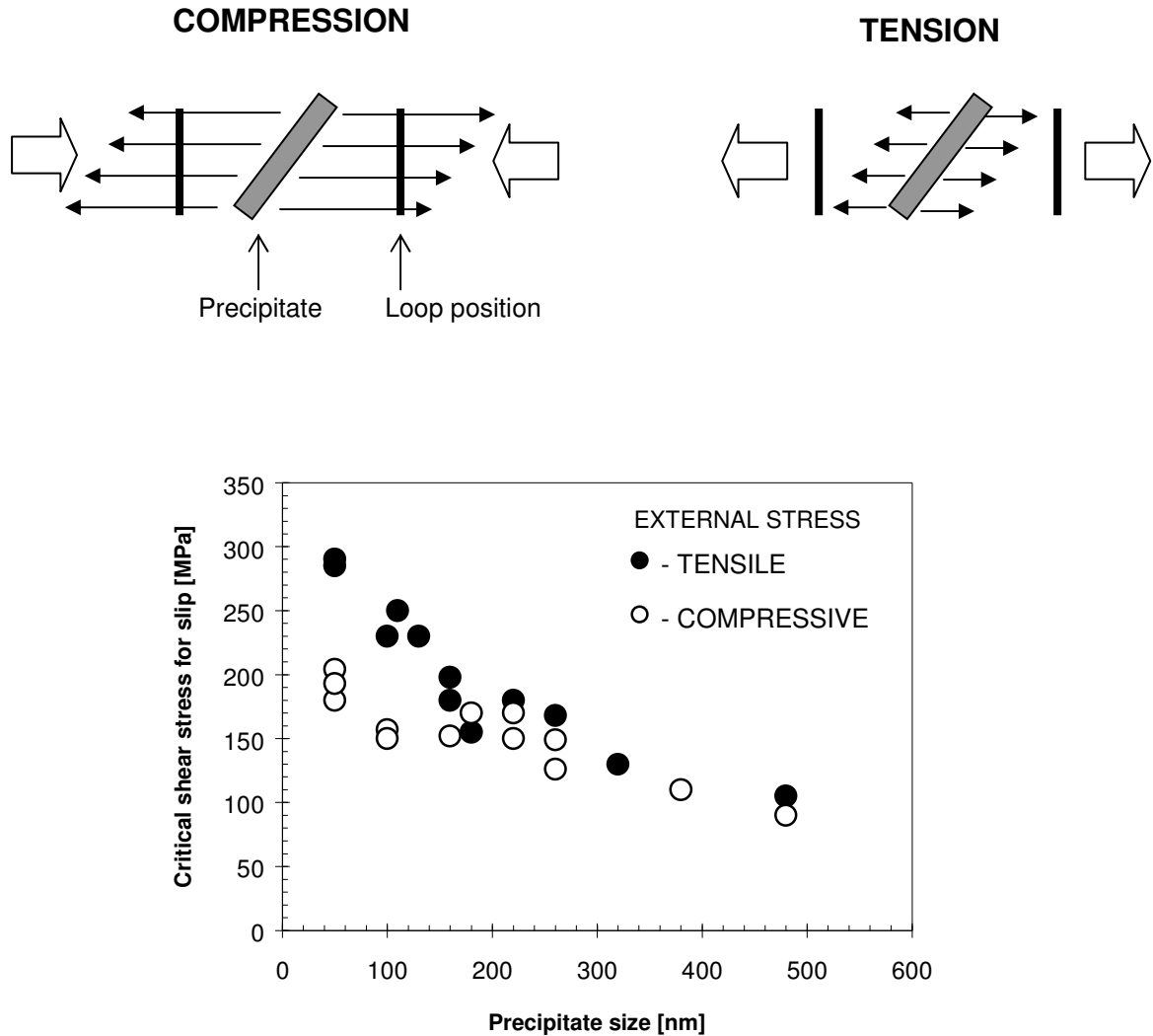


Figure 6-7. *Top:* schematic representation of an oxide precipitate (grey colour) and related changes in the stress magnitude (represented by black arrows of different length) at the precipitate/matrix interface when a compressive or tensile force is applied. Thick black lines represent the dislocation loops. *Bottom:* the graph shows the critical shear stress for the generation of slip lines (slip stress) at the silicon surface, measured using annular bending at 635°C for 1 minute. Slip lines were detected by using a differential-interference-contrast (DIC) optical microscope. In the case of small precipitates there is a significant difference in the slip stress when samples are subjected either to compressive or tensile external stresses.

According to the discussion above, for precipitates with smallest size, Fig. 6-7 indicates that the precipitate stress field to which the PPD loops are subjected is approximately $(300-200)/2 = 50$ MPa. The difference between tensile and compressive stress disappears as soon as the oxide precipitate size is larger. In fact, with increasing precipitate size during growth at high temperatures, the PPD loops can glide for a longer distance away from the precipitate stress field and/or may interact with other PPD loops forming dislocation tangles with long segments. Dislocation segments belonging to tangles formed near large precipitates can extend for a few hundreds of nanometers (see for example Fig. 2-24). Since the stress required to activate a Frank-Read source is inversely proportional to the segment length⁶, a lower shear stress is generally needed to activate the motion and the multiplication process of longer dislocation segments. These can easily expand under low stress application, but their motion is not affected by the precipitate stress-field, as in this case the dislocation lines are outside the stress field associated with the precipitate/matrix misfit and then their behaviour does not depend on the sign of applied stress.

2.4 Observation of single dislocations using chemical etch pits

A more accurate study of the behaviour of single dislocations rather than slip lines was needed to measure and analyse properly the dependence of the critical shear stress for dislocations on the duration of applied stress. It is noted that slip bands are generated by the motion of several dislocation loops emerging at surface, thus the technique described in the previous sections was not suitable to understand the fundamental generation mechanism of a single glide dislocation. However, since the formation of slip lines is frequently observed on wafer surface after heat treatments typical of VLSI and since slippage represents a real

problem for device processing, the data reported in Fig. 6-5 and Fig. 6-6 might be extremely important from the technological and industrial point of view.

Many details of the following experiments have been already given in Chapter 2, section 10.4. The observation of dislocation etch pits (rather than slip lines) formed at silicon surface confirmed that the mechanical behaviour of samples containing precipitates varies according to precipitate sizes, as shown in Fig. 6-8. The individual etch pits are not resolved in Fig. 6-8, but give rise to the dark grey contrast in the images. The samples used in this experiment were cleaved from the wafers described in Tab. 2-4 and Tab. 2-5, row 4, 32h nucleation time. All samples appearing in the figure were stressed under the same conditions (10 kg applied load at 585°C for a duration of 3 minutes) and were subsequently etched to reveal the dislocations at the surface. The stress distribution in the sample was similar to that shown in Fig. 2-28. The dislocated area was found to be larger in samples with bigger precipitates. Therefore, under the same experimental conditions, the critical resolved shear stress to produce dislocations intersecting the sample surface (such that etch pits could be formed) was found to be lower in samples containing large precipitates. The critical shear stress τ_c was defined (Chapter 2, Section 10.4) as the critical resolved shear stress to generate a single dislocation glide loop, which can be detected in the form of an etch pit under an optical microscope.

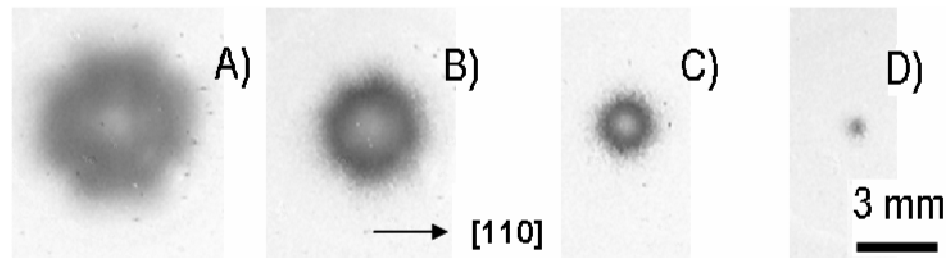


Figure 6-8. Dislocated area in different samples containing precipitates of size equal to A) 300 nm, B) 220 nm, C) 180 nm, D) 120 nm, according to TEM examination. The duration of load application (10 kg) was 3 minutes for all the samples. Precipitate density was $\sim 10^{10} \text{ cm}^{-3}$, bending temperature was 585°C.

As shown in Fig. 6-9, the shear stress τ_c decreases with increasing duration of the application of stress. This effect is more evident in samples containing small oxide precipitates, as larger stress values are required to expand the dislocation loops away from the smaller precipitates. Similarly to what was described in the previous section, the lower value of τ_c measured in samples with large oxide precipitates can be explained in terms of dislocation segments belonging to tangles which form near large oxide precipitates; this is because a lower shear stress is usually required to activate the motion and the multiplication process of longer dislocation segments. However, in the case of small precipitates, the growth mechanism of small-radius prismatic loops remains mostly unclear, as the huge stresses predicted by the theory for small loop expansion do not match the experimental results, as will be shown in Section 4.

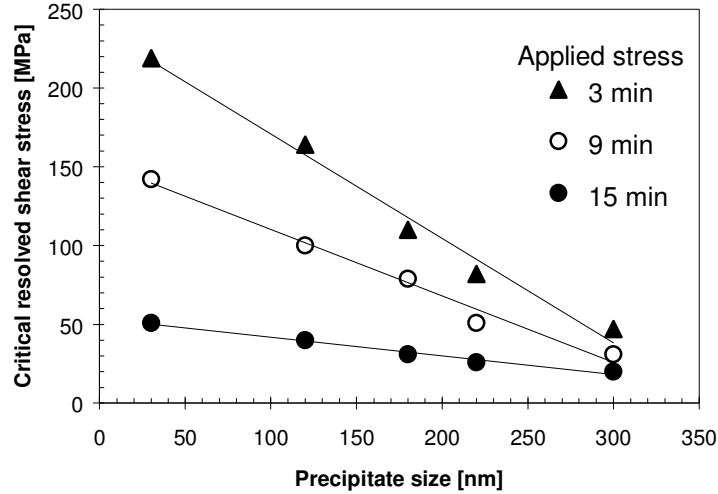


Figure 6-9. The critical resolved shear stress τ_c as a function of precipitate size and different duration of stress application (annular bending). Samples are those described in Tab. 2.4 and Tab. 2.5, row 4, 32h.

3. Three-point bend tests

According to the results discussed in the previous paragraphs, the sources of glide dislocations in Cz-silicon seem to be related to defects of a “special” kind present in the crystal rather than simple oxide precipitates. Direct TEM observation (by Dr Reznik in Moscow) revealed the presence of different defect types in samples subjected to annealing of different durations at 1000°C (Fig. 6-10): these defects consisted of either isolated oxide precipitates, or precipitates with PPD loops, or larger precipitates surrounded by tangled dislocations. The prismatic dislocation loops associated with the precipitates could have been nucleated during precipitate growth or on cooling the wafer, but the exact mechanism of nucleation was not investigated in this thesis. However, Fig. 6-10b and Fig. 1-21 suggest that the PPD loops are generated during precipitate growth, as the very first loop punched out from the precipitate is always the smallest loop in the pile, whereas the last loop generated (closest to the precipitate) is always the biggest.

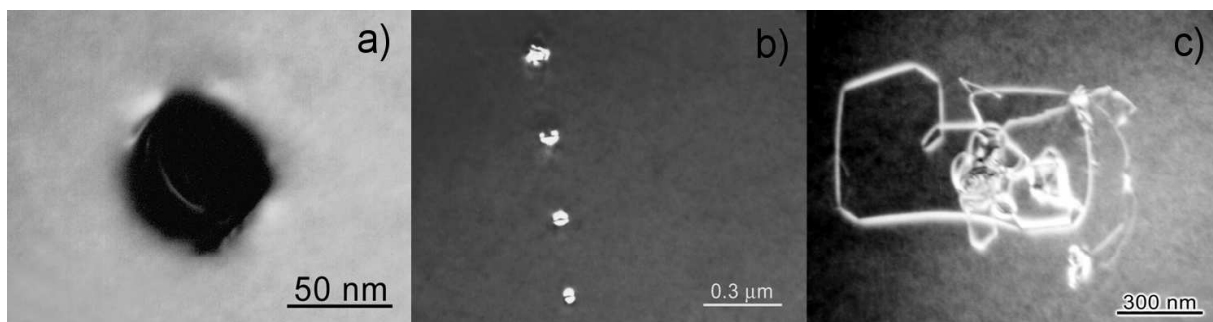


Figure 6-10. Different types of defects in samples with different annealing time at 1000°C: a) After 1 hour annealing, precipitates are smaller than 50 nm and they may have only one prismatic loop attached. b) Precipitates grow to a size of 100-150 nm after 4 hours annealing and punch-out several prismatic loops that can travel a few microns away from the precipitate. c) After 16 hours, precipitates have grown up to 300 nm or more, thus punched-out loops are bigger, interact each other and form tangles of dislocations (*after Reznik*).

Most of the experimental details and the technique used to achieve the following results were described in Chapter 2, section 10.4. As expected from previous results obtained with other techniques, the critical resolved shear stress τ_c measured with three-point bending experiments decreases with increasing precipitate size and defect morphology, as shown in Fig. 6-11. As discussed before, this is because the external stress required to activate a Frank-Read source is inversely proportional to the dislocation length. Thus the stress to activate a long dislocation segment belonging to a large complex defect, such as that in Fig. 6-10c, is lower than the stress required to expand a regular prismatic loop with short radius, generated from a small oxide precipitate. Therefore, dislocation tangles are more likely to move, cross-slip and multiply even when a low shear stress is applied. Moreover, the experimental data in Fig. 6-11 confirm that the stress τ_c decreases with increasing duration of stress application. This effect is more evident in samples with smaller precipitates (Fig. 6-10a) where initially the application of high external stresses is needed to detect the dislocation loops at sample surface.

Surface flaws are inevitably introduced during sample preparation for three-point bending. However, surface effects are not solely responsible for the nucleation of glide dislocations since in the experimental data there is a clear dependence of the critical stress on the precipitate size, which cannot be explained in terms of surface irregularities because these are expected to be approximately the same, independent of precipitate size. On the other hand, tests carried out by using high purity FZ-silicon samples showed that also in precipitate-free crystals the critical shear stress τ_c is indeed dependent on the duration of stress application (Fig. 6-11).

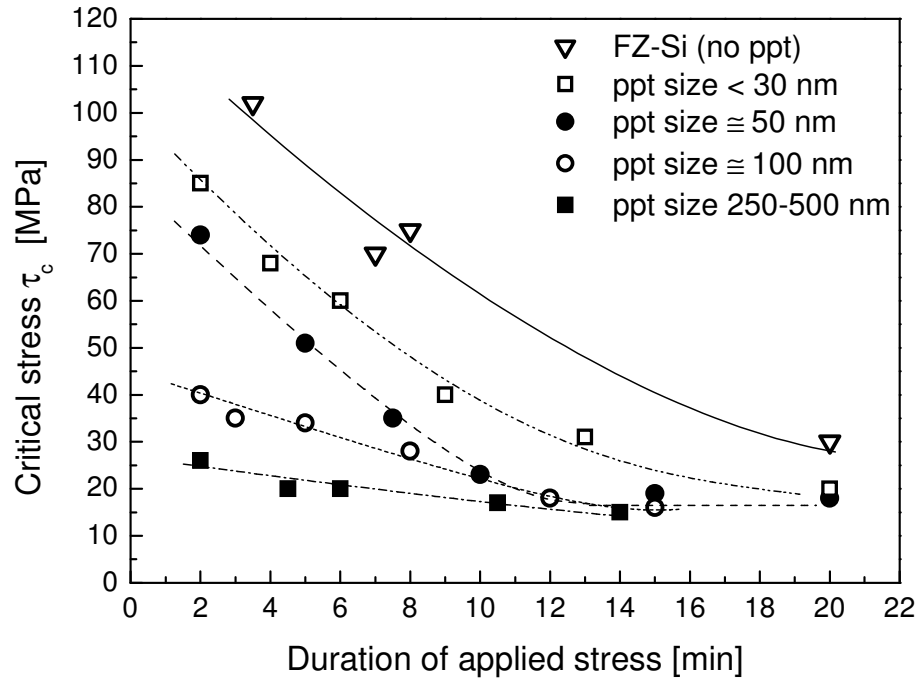


Figure 6-11. Time-dependence of the critical shear stress τ_c for samples containing oxide precipitates of different sizes. For comparison, data concerning the behaviour of FZ-silicon samples is also shown in the graph. The external stress was applied on all the samples at 585°C.

Since the FZ specimens were precipitate-free and although every possible care was taken with handling and preparing the samples, it is probable that very small amount of surface damage was unintentionally introduced at some point during specimen preparation and these surface flaws acted as dislocation sources. The stress needed to produce surface damage and the possibility to generate dislocated regions beneath the silicon surface is considered in the following. The stress to which a unit volume of silicon wafer is subjected when a load is applied on a circular surface area of radius R can be calculated by using elasticity theory⁷ and considering the cylindrical coordinates shown in Fig. 6-12.

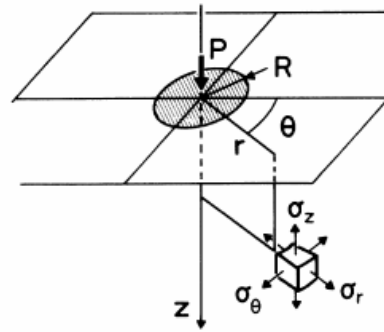


Figure 6-12. Geometry used for the calculation of the stress when a load P is applied on the surface (after Minowa⁷).

As an example, considering a load $P=2$ g and $R=0.7$ μm , the maximum value of the resolved shear stress τ is found to be ~ 4.5 GPa. This huge stress can induce the generation of hairpin dislocations and phase transformation from crystalline to amorphous silicon beneath the loaded silicon surface.

It is known that amorphous silicon starts to recrystallise at 500°C and hence the stress-induced amorphous regions can re-transform to a crystalline structure during heat treatments⁸, but the recrystallised area will contain tangled dislocations that might propagate and multiply under applied stress at high temperatures. Evidence for this was given by Minowa *et al.*; Fig. 6-13 shows a cross-sectional micrograph of a scratched region of silicon that was subjected to annealing at 600°C for 1 hour. The original amorphous region generated during scratching at room temperature disappeared after heat treatment and tangled dislocations are found along the scratch in a region 0.15 μm deep beneath the surface. Longer dislocations (about 1 μm) introduced simply by surface scratching are also visible in Fig. 6-13.

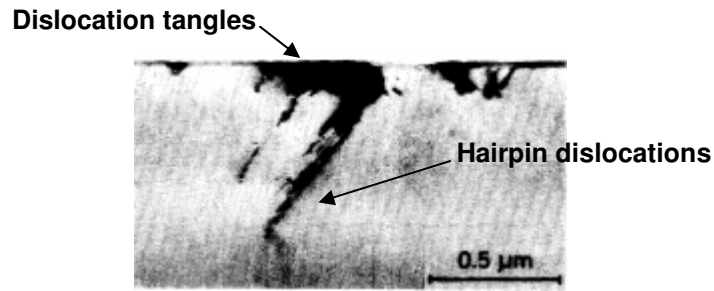


Figure 6-13. Cross-sectional TEM micrograph of a scratched region annealed at 600°C for 1 hour (after Minowa⁷).

Thus, it is believed that surface effects due to microscopic damage were not completely suppressed during the three-point bending experiments. However, this effect is not thought to be significant as it does not explain the observed dependence of τ_c on precipitate size. Necessarily there must be a different activation mechanism for the dislocation sources which should depend on defect size.

Importantly, the time-dependence of the critical shear stress was also observed in the case of pure FZ-silicon, where oxide precipitates are not present in the material. A possible explanation would be that FZ-silicon contains a very small concentration of defects which can be activated by stress to produce dislocation glide loops. These defect have not been observed by TEM because their concentration is small, but their effects on the mechanical properties of wafers are detectable with the present technique. However, such an explanation is viewed as unlikely since FZ material is well studied and no other techniques have indicated such defects either. Thus, it is believed that, in the case of experiments carried out with FZ-silicon samples, the glide dislocations were generated by surface damage introduced during sample preparation.

Considering the critical stress data shown in Fig. 6-11, for large precipitates the glide dislocations are likely to be generated from dislocation tangles (Fig. 6-10c). However, for smaller precipitates, the glide loops may originate from pre-existing dislocations such as the

small PPD loops. As described in the following section, a model was developed to investigate if PPD loops might be responsible for the production of glide dislocations.

4. Origin of the dislocation glide loops

4.1 Introduction

In the previous paragraphs it was suggested that the sources of glide dislocations might be probably PPD loops rather than regular oxide precipitates. Thus, it might be possible to explain the time-dependence of the critical shear stress (shown in Fig. 6-11) by considering the motion and subsequent cross-slip of the prismatic loops generated from the precipitates. An experiment was carried out to investigate the possibility of locking the PPD loops by segregation of residual oxygen to the core. In fact, on the basis that PPD loops can be responsible for the generation of glide dislocations, if PPD loops are immobilised by oxygen and no other glide dislocation sources are present in the material, then the glide dislocations should not be produced. A model was also developed to investigate if PPD loops might act like glide dislocation sources and the stress required to activate this dislocation multiplication mechanism was deduced from the simulation. A discussion will follow the results presented in these sub-sections.

4.2 Locking of punched-out prismatic loops by residual oxygen atoms

The experiment presented in this section is similar to those described in Fig. 6-11. In this study, some Cz-silicon specimens containing oxide precipitates with size of approximately 50 nm were annealed at 600°C for 5 hours before being tested. The graph in Fig. 6-14 shows

that after annealing of the Cz-silicon samples, τ_c was found to be roughly 20 MPa larger than that for the same non-annealed samples. This is thought to be due to accumulation of oxygen atoms at the core of prismatic dislocation segments, which are then locked. The behaviour shown in Fig. 6-14 cannot be explained by considering oxide precipitates as direct sources of glide dislocations that are produced only on application of an external stress. Rather the glide dislocations are likely to originate from pre-existing dislocations produced by the precipitates at an earlier stage and which can be locked by subsequent anneal.

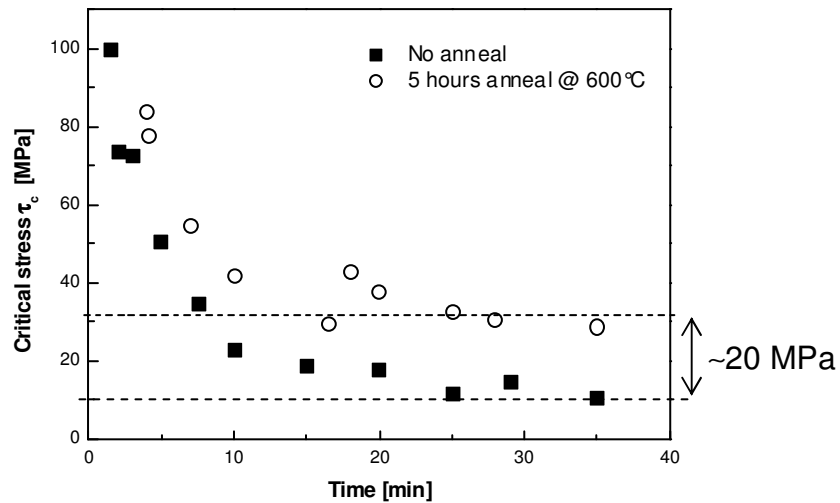


Figure 6-14. Critical shear stress τ_c measured as function of time at 585°C in specimens containing small oxide precipitates (approx. 50 nm). Data represented by open circles show the increase in τ_c (more than 20 MPa) after anneal at 600°C for 5 hours.

4.3 Model: formation of dislocation dipoles from PPD loops

A simplified model was developed to simulate the behaviour of a PPD loop when an external stress is applied in the geometry of the three-point bending experiments. In silicon, PPD loops move on {111} planes and each segment of the loop is edge in character. When

precipitates are platelets, no punching is possible along directions lying in the platelet habit plane. The habit planes of precipitates are $\{100\}$ with their sides oriented along $[110]$ directions. Each of the four segments forming the prismatic loop lies on a different $\{111\}$ glide plane. Therefore, the base of the glide prism is actually a rhomb with 54.7° internal angle.

For simplicity, the case of a single prismatic loop, punched-out from a precipitate and gliding along a square-based prism is considered (Fig. 6-15a). It is assumed that this loop moves away from the precipitate until the residual stress field of the precipitate is equal to the sum of the Peierls stress and the stress required to move the dislocation against the effect of impurity dragging. As in the experimental situation, the external stress (for example, that produced in the three-point bend experiments) was considered to be along the $[110]$ direction. In this geometry, the resolved shear stress can be zero in two (parallel) planes of the glide prism and non-zero in the other two “activated” planes. These different values of resolved shear stress over the loop planes stretch the loop (Fig. 6-15b). The TEM picture in Fig 6-16 is evidence of the deformation to which prismatic loops are subjected when the above stress conditions are applied⁹.

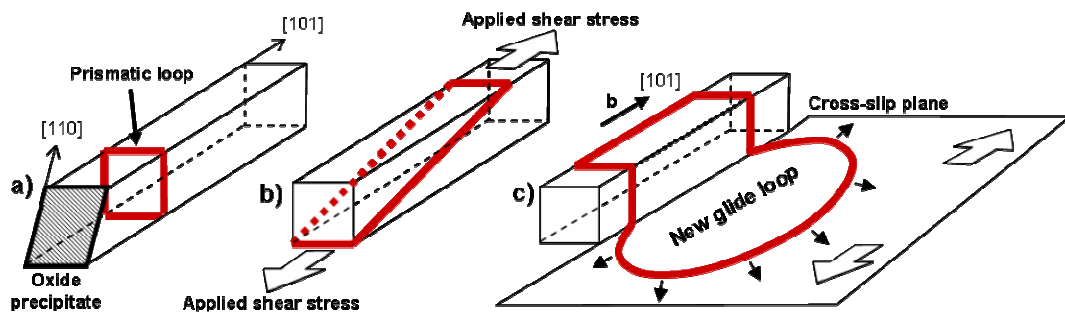


Figure 6-15. a) Schematic of a punched-out loop moving along the glide prism b) Schematic of a dipole stretched by two driving segments subjected to shear stress. c) One segment of the dipole cross-slips once it reached the screw character.

The loop expands to form a glide dipole where the two end segments are in opposite motion due to their opposite sign. The segments lying in the other two parallel planes, with no resolved shear stress applied, are pulled only by line tension provided by the gliding segments. If the segments or parts of them become screw in character, they can cross-slip in another plane, as this is energetically more favourable, and generate new glide dislocations (Fig. 6-15c).

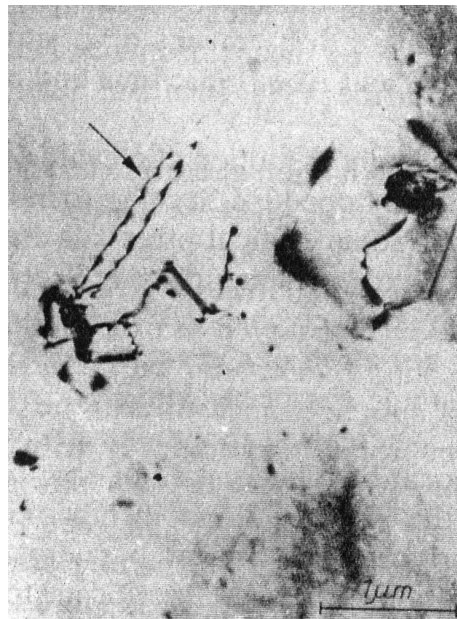


Figure 6-16. TEM picture of a dipole formed at the precipitate site after low stress application at high temperatures (after Yasutake⁹).

Referring to Fig. 6-17, let L be the length of one side of the prism. The two segments lying on the activated planes move by a relative distance x .

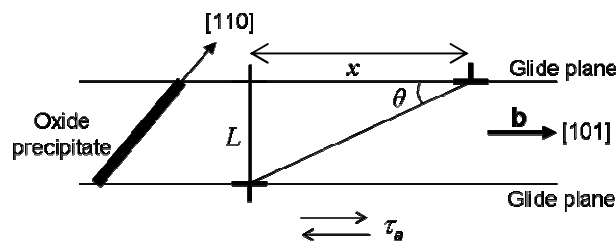


Figure 6-17. Geometry used for the calculation of the cross-slip stress. A certain stress τ_a is needed to stretch the dipole for a distance greater than x .

The elastic energy per unit length of an edge dislocation with core radius r is⁶

$$E_{edge} = \frac{Gb^2}{4\pi(1-\nu)} \ln \frac{R}{r} \quad (6.1)$$

where R is the radius of a cylinder with axis given by the dislocation line, G is the shear modulus for silicon, b is the Burgers vector and ν is the Poisson's ratio. Similarly, the elastic energy for a mixed dislocation can be written as

$$E_{mixed} = \frac{Gb^2(1-\nu \cos^2 \theta)}{4\pi(1-\nu)} \ln \frac{R}{r} = E_{edge} \left(1 - \nu \frac{x^2}{x^2 + L^2} \right) \quad (6.2)$$

where θ is the angle between the line of the mixed dislocation and its Burger vector. The elastic energy for the four segments of the dipole stretched at a position x (Fig. 6-17) can then be written as

$$E_{el} = 2E_{edge}L + 2E_{mixed}\sqrt{x^2 + L^2} \quad (6.3)$$

Edge segments on the two glide planes attract each other and the shear stress on the glide plane resulting from this interaction is given by

$$\tau_i = \frac{Gb}{2\pi(1-\nu)} \frac{x(L^2 - x^2)}{(x^2 + L^2)^2} \quad (6.4)$$

To balance τ_i , an opposite shear stress τ_e is needed to keep the dipole at rest in position x .

The work done by both these stresses is

$$E_\tau = -(\tau_e - \tau_i)bLx \quad (6.5)$$

and then the total energy of the dipole at a position x can be written as

$$E(x) = E_{el} + E_\tau \quad (6.6)$$

The equilibrium value of $\tau_e(x)$ can be deduced from Equation (6.6) considering the condition

$$\frac{\partial E(x)}{\partial x} = 0 \quad (6.7)$$

At equilibrium, a stress value τ_a larger than $\tau_e(x)$ has to be applied to stretch the dipole for a distance greater than x .

Data in Fig. 3-8 show that dislocations can be produced in Cz-Si containing small precipitates even for applied stresses of approximately 20 MPa. However, according to the model above, the calculation of τ_a considering 50 nm precipitate size would predict a value of 1.5 GPa as the critical shear stress necessary to let the dipole elongate and cross-slip. According to the model, an applied shear stress of 20 MPa would only elongate PPD loops with size of the order of 1 μm . Moreover, each segment L of a prismatic loop cannot even act as a usual Frank-Read source because this would require an activation stress τ_{crit} given by

$$\tau_{crit} \simeq \frac{Gb}{L} \quad (3.11)$$

which gives $\tau_{crit} \simeq 500$ MPa when $L \simeq 50$ nm. Therefore, the critical shear stress τ_c measured in samples containing small precipitates must be associated to glide dislocations generated either by surface flaws or by other special defects, since the very large stresses needed to elongate the PPD loops and form dipoles were not applied during the experiments.

The multiplication process described above would better work in the case of larger prismatic loops generated from precipitates with size >200 nm where the stress needed for dipole formation becomes of the same order of that observed experimentally. Evidence for this is also shown in Fig. 6-16.

4.4 Discussion of the origin of the glide dislocation loops

Several experiments have demonstrated that the critical shear stress necessary to detect the formation of glide dislocation loops depends on oxide precipitate size. Thus, it is inferred that the observed dislocations originate directly or indirectly from the oxide precipitates.

A pre-anneal of the silicon samples at a given temperature and for sufficient time increases the critical shear stress τ_c . This is consistent with the dislocation sources being pre-existing loops which are then locked and inconsistent with the source being the oxide precipitate itself.

To investigate this further, an analysis of the stress required to grow dislocation glide loops from pre-existing dislocation segments was performed. The conclusion of this investigation shows that in the case of loops of small diameter (~ 50 nm), the elongation mechanism of PPD loops to form dipoles similar to that shown in Fig. 6-16 would require a shear stress of 1.5 GPa. Thus, whilst this mechanism is probably responsible for glide dislocation generation in samples containing large precipitates (>200 nm), the same mechanism cannot be considered in sample with small precipitates because huge stresses are required. In addition, a simple Frank-Read source consisting of a 50 nm pinned dislocation segment cannot be activated by the stresses used in the experiments because this type of dislocation source requires approximately 500 MPa to start the multiplication process for such short dislocation segments. Therefore, neither of the two mechanisms involving dipoles or simple Frank-Read sources can explain the generation of glide dislocations in specimens containing small oxide precipitates.

The stress field surrounding a precipitate cannot affect much the PPD loops because these glide away from the precipitate. In fact, compression/tension measurements indicate that the maximum stress produced by a small precipitate, to which a PPD loop must be subjected, is only approximately 50 MPa.

In conclusion, experiments show that the presence of glide dislocations is most likely due to pre-existing prismatic dislocation loops which can be as small as 50 nm in diameter. However, modelling shows that glide dislocations cannot be generated until long dislocation segments or dislocation tangles of the order of 1 μm are produced in the material. This only occurs when precipitates as large as 200-300 nm are generated. In the present work, no way of resolving this apparent contradiction was found, unless very occasionally, special defects are present in specimens containing small precipitates and these can generate 1 μm size dislocation tangles, although this seems unlikely. It is noted that the analysis of the number of precipitates producing glide dislocations (Section 2.1) showed that for the smallest precipitates only about 1 in 1000 was active.

5. Summary

Although this study was not conclusive (a definitive proof demonstrating the mechanism of dislocation generation has not been given), quantitative information concerning the critical stress for glide dislocation reaching the wafer surface was presented as a function of precipitate size, density and duration of stress application. Such data regarding these mechanical properties of silicon crystals at high temperatures are of substantial importance in wafer processing and VLSI technology. Thermal stresses which arise from temperature gradients during device fabrication should not exceed the critical values presented here for dislocation generation and motion. In addition, the dislocation locking effect produced by segregation of oxygen atoms to the core can be used as a method of strengthening wafers containing oxide precipitates.

Experimental data suggested that in the case of silicon crystals containing small precipitates, only a very small fraction of these precipitates is responsible for the generation

of glide dislocation loops. However, the analysis showed that for glide dislocations to be produced at the stresses observed, the specimens with very small precipitates must contain larger defects, although no direct evidence of them has been found.

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Chapter 7: Summary and conclusions

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1. Summary of dislocation locking by oxygen and nitrogen

1.1 The dislocation locking effect

During silicon wafer processing, the activity of those dislocations which are harmful for the electronic devices has to be suppressed or reduced. This can be achieved either by eliminating the sources of glide dislocations in the silicon wafers or by decorating the dislocations with certain impurities present in the crystal, as these are known to hinder the dislocation motion. The latter approach was used in the present work.

In the previous chapters, it was experimentally demonstrated that oxygen and nitrogen impurities in silicon can have a strong immobilization effect on stationary dislocations after annealing at high temperatures. However, the duration of the thermal treatment has to be sufficiently long to allow the diffusion of a significant number of impurities to the dislocation core which then act as pinning points. The magnitude of this locking effect depends on the particular properties of the impurities present in the material.

In Cz-grown silicon, oxygen is present in a large concentration in the form of interstitial impurity atoms and thus no further doping is necessary to observe the dislocation locking effect upon appropriate annealing conditions. In pure FZ-silicon, the concentration of oxygen or other impurities is so low that no appreciable dislocation locking effect can be observed and thus intentional doping of the FZ crystals with appropriate impurity species is needed to stop the dislocation motion. Nitrogen doping of high-purity FZ-silicon was investigated in this work to determine whether nitrogen impurities can lock the dislocations effectively. It was found that the locking effect of nitrogen on stationary dislocations in FZ-silicon is comparable to that of oxygen in Cz-silicon, despite the much lower concentration of nitrogen compared to oxygen. In addition, the unlocking stress due to nitrogen in FZ-silicon showed the same two distinct regimes observed for oxygen (increase followed by saturation), although the other regimes observed in Cz-silicon and associated with oxygen precipitation

were not found in N-doped FZ samples. It is believed that the information contained in this thesis concerning the dislocation unlocking stress due to nitrogen in silicon as a function of annealing time and temperature represents the most complete set of data yet obtained.

Assuming that the unlocking stress is proportional to the concentration of impurity atoms at the core, the main general results achieved during this study and valid for both oxygen and nitrogen in silicon are the following:

1. The unlocking stress is initially limited by impurity diffusion (kinetic effects).
2. After sufficient time, the unlocking stress depends on the equilibrium concentration of impurities at the dislocation (thermodynamic effects).

The two results above suggested the possibility of determining some key parameters such as the diffusion coefficient of oxygen and nitrogen and their binding energy to the dislocations using dislocation unlocking experiments. These important parameters were deduced either directly from experimental data or by simulating the diffusion processes in order to fit the data. After that, the same parameters were used to calculate the number of impurity atoms accumulated at the dislocation core at each time during a certain thermal treatment. Since the unlocking stress is assumed to be proportional to the number of impurities at the core, if the proportionality factor is known, then it should be possible to predict the effective unlocking stress necessary to start dislocation motion during thermal treatments of wafers typical of device fabrication. A numerical model was developed for this purpose and this was used to simulate the mechanical behaviour during real thermal processes of wafers. In the case of oxygen in Cz-silicon, it was shown that modifications to heat treatments can lead to a significant improvement of the mechanical properties of wafers and thus should lead to an increase in device yield. On the other hand, an incorrect use of particular thermal treatments such as, for example, rapid-thermal-annealing (RTA), can weaken the silicon wafers, making their plastic deformation more likely.

1.2 Behaviour of oxygen and nitrogen in silicon

During the unlocking stress experiments carried out in this work, it was found that oxygen and nitrogen impurities behave differently in silicon single-crystals, although some similarity between the two chemical species can also be observed. In particular, due to the low nitrogen solubility in silicon, the concentration and then the number of nitrogen atoms available for dislocation decoration is usually very small if compared with that of oxygen atoms in Cz-silicon crystals.

The nitrogen unlocking data obtained in this work was analysed in terms of either monomers being responsible for the dislocation locking or dimers. Although the experimental data could not be used to prove that the species responsible was dimers, the values obtained for the activation energy for diffusion and binding of dimers to the dislocations were more physically reasonable than those obtained if monomers were responsible. It is thus assumed that dimers are the species responsible for locking the dislocations and on that basis, the main findings of the work are summarised below.

- 1. Binding energy to the dislocations:** the value of the binding enthalpy to a dislocation for the nitrogen species ($\Delta H > 1.7$ eV) is more than twice that deduced for oxygen ($\Delta H = 0.74$ eV). Since the binding energy of nitrogen to a dislocation is far larger than that of oxygen, nitrogen sticks to the dislocation core easily even at high temperatures. For this reason, once thermodynamic equilibrium is reached, the amount of nitrogen at the dislocation core can be even larger than that of oxygen, despite the fact that the initial bulk nitrogen concentration is much lower than that of oxygen. In principle, nitrogen is able to fully decorate the dislocation and take place in all the sites available for occupation along the core. This does not happen in the case of oxygen for the experiments performed in this work since its binding energy to the dislocation is only

0.74 eV. In addition, at temperatures over 850°C the concentration of oxygen atoms at the core (and thus the resulting unlocking stress) is practically negligible.

The difference in the locking ability at high temperatures of oxygen and nitrogen is clearly visible in Fig. 5-2 where data indicate that above ~750°C, nitrogen in concentration of $2 \times 10^{15} \text{ cm}^{-3}$ gives more effective locking than oxygen in concentration of $6.3 \times 10^{17} \text{ cm}^{-3}$ when measured at 550°C.

2. Diffusion coefficient: For both nitrogen and oxygen, it is generally accepted that transport can be dominated by either dimers or monomers depending on temperature. It is believed that the unlocking stress measurements carried out in this work using Cz and FZ silicon wafers provided information about dimer transport rather than diffusion of monomers. In standard Cz-silicon, evidence for oxygen dimer diffusion is given in this work by the direct dependence of oxygen diffusivity on initial oxygen concentration at temperatures below 700°C. In nitrogen-doped FZ-silicon, if nitrogen dimers are considered as the dominant species in the temperature range investigated (up to 830°C), the diffusivity of nitrogen dimers in silicon was found to be

$$D_{\text{dimer}} = 6.8 \times 10^{-6} \exp(-1.45 \text{ eV} / kT).$$

According to the data presented in this work, nitrogen should be able to reduce FZ-silicon wafer warpage during processing at temperatures up to 830°C or more, whereas the beneficial effect of oxygen atoms on mechanical properties becomes weak at these temperatures. From the technological point of view, if the ability of nitrogen to suppress dislocation movement holds up to very high temperatures (~1000°C), then nitrogen-doped FZ-silicon could have wider range of applications in microelectronics, since FZ materials could combine their well known high-purity (and high resistivity) with good mechanical reliability at high

temperatures, whereas at present, the poor resistance of FZ wafers against plastic deformation and warpage represents one of the main disadvantages of FZ-grown silicon.

2. Summary of dislocation generation at oxide precipitates

The critical stress to start plastic flow in a silicon wafer is very much dependent on the presence in bulk silicon of prismatic dislocation loops associated with oxide particles and/or the formation of dislocation tangles, which in turn depends on the precipitate size. The shear stress to cause the generation and subsequent expansion of glide dislocations from different sources was measured as a function of different parameters. It was found that the critical shear stress necessary to observe (at the surface) the motion of a single glide dislocation depends on

- Precipitate size;
- Duration of stress application;
- Thermal history of wafers.

Interestingly, experiments showed that the number of dislocation sources per unit volume in Cz-silicon wafers is in general far lower than the density of oxide precipitates within the wafer. This was observed for a wide range of oxide precipitate sizes although the effect is more marked for smaller precipitates. Experiments show that the presence of glide dislocations is most likely due to pre-existing dislocation loops which can be as small as 50 nm in diameter. However, modelling showed that glide dislocations must be generated from longer pre-existing dislocation segments or dislocation tangles of the order of 1 μm . In the present work, it was not possible to give an explanation to this apparent contradiction, unless it is assumed that special defects can be present at very low concentrations in samples containing small precipitates and these can generate 1 μm size tangles.

Although this study was not conclusive, as a direct proof of the mechanism of dislocation generation was not given, the quantitative information obtained about the critical stress for dislocations is of substantial importance for wafer processing and VLSI applications. In fact, thermal stresses generated during device fabrication should not ever exceed the critical value for dislocation formation in order to prevent wafer warpage. These critical values are presented in this thesis as a function of different parameters like oxide precipitate size, applied load and duration of thermal treatments.

3. Further work

The results achieved in this thesis are very encouraging and introduce several new matters of debate. It is particularly worth highlighting the importance of the technique used in this study as this not only provides information about the mechanical behaviour of silicon at high temperatures, but also allows the determination of fundamental parameters such as the diffusion coefficient of impurities, which would otherwise be difficult to measure with other more conventional techniques.

An interesting experiment to do would be that involving a set of silicon samples with oxygen (or nitrogen) concentrations very different from those already used to see whether the diffusivity measured in these samples scales with concentration, according to predictions. This is also important to clarify which of the monomers and dimers species is responsible for transport. For example, in the case of oxygen and according to the theory of dimers (Chapter 4, Section 3.2), the oxygen diffusivity should decrease linearly with decreasing oxygen concentration (Equation 4.11) at temperatures below 700°C. This linear dependence was demonstrated in this work for a small range of oxygen concentrations, but a more definitive

proof could be given if an oxygen concentration lower than 10^{17} cm^{-3} was used. Similar useful information could be achieved using nitrogen-doped FZ-silicon samples with different (and possibly more homogeneous) nitrogen concentration.

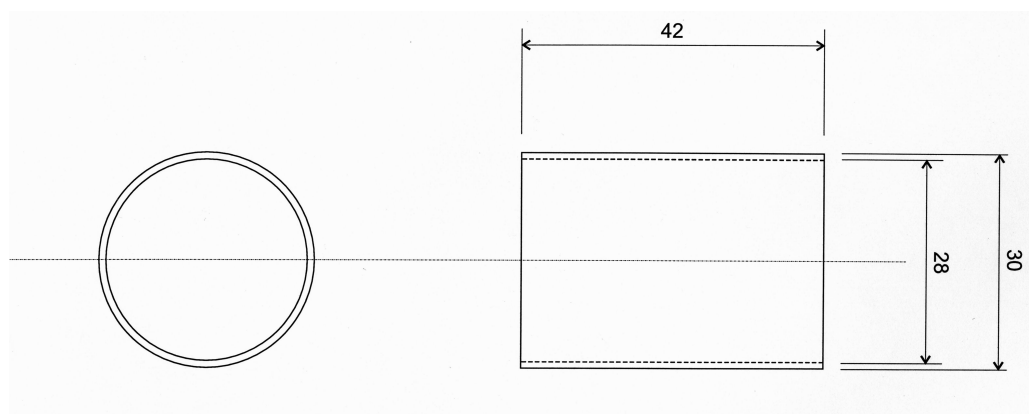
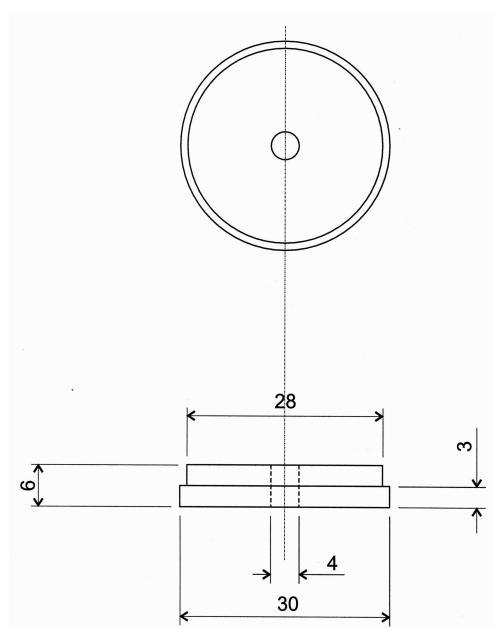
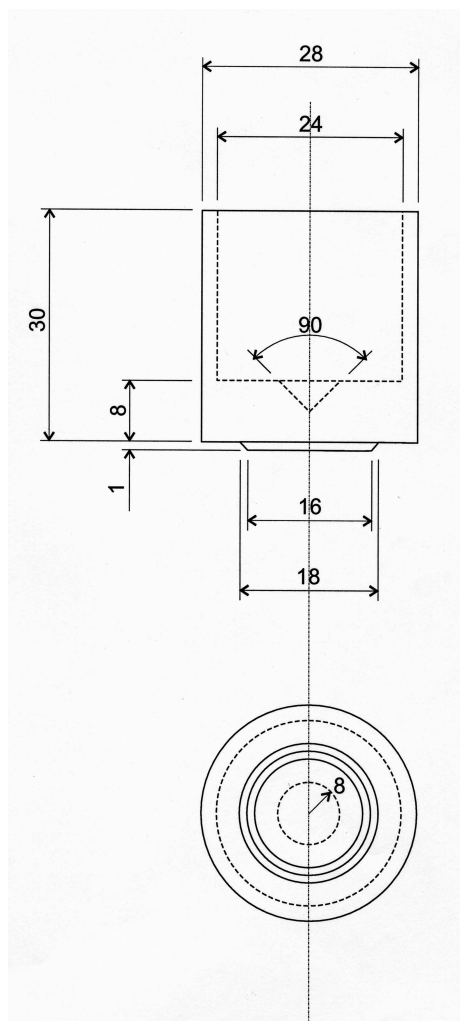
The other information which is missing in this work is the intrinsic temperature dependence of unlocking stress for nitrogen, as the unlocking stress data were only collected at a temperature of 550°C . This is important in order to predict the unlocking stress at each temperature and time in a typical thermal treatment of FZ-silicon wafers during device processing.

It is also important to note that nitrogen data were collected using a relatively simple system consisting of pure FZ-silicon doped with nitrogen. However, a more interesting material from the industrial point of view and for direct applications is nitrogen-doped Cz-silicon, where a strong interaction between oxygen and nitrogen impurities is expected (see for example Ref. 65, 66, 70 in Chapter 1). Once the interaction between nitrogen and linear defects in FZ-silicon is fully understood, it may be possible to study the combined effect of nitrogen and oxygen impurities on dislocations, for instance in nitrogen-doped Cz-silicon wafers. It is hoped that this combination of impurities in Cz-silicon will produce a more efficient dislocation locking and thus an increase in the mechanical stability of silicon wafers during thermal processing.

APPENDIX A

Annular bending rig

Mechanical drawing (dimensions are in mm)



APPENDIX B

Calculation of stress distribution during annular bending.

For any loading conditions, the differential equation governing the deflection w at a distance r from the centre of the plate is

$$\frac{1}{r} \frac{d}{dr} \left\{ r \frac{d}{dr} \left[\frac{1}{r} \frac{d}{dr} \left(r \frac{dw}{dr} \right) \right] \right\} = \frac{q(r)}{D} \quad (\text{b.1})$$

where $q(r)$ is the load intensity and D is the flexural rigidity of the plate given by

$$D = \frac{Eh^3}{12(1-\nu^2)} \quad (\text{b.2})$$

where h is the plate thickness and E and ν are the Young's modulus and Poisson's ratio respectively. During the bend test, the alumina ball is in physical contact with the silicon sample over a circular area of radius a . The parameter a must be estimated in order to obtain an expression for the load intensity $q(r)$ in Equation (b.1) and this can be done by using the theory of elasticity for the contact between two spherical bodies having radius R_1 and R_2 , where the approximation of $R_1 \rightarrow \infty$ is considered for one of the spheres. According to this theory, the relationship between the load intensity q and the total load P is given by

$$q(r) = \frac{3P}{2\pi a^2} \sqrt{1 - \left(\frac{r}{a}\right)^2} \quad (\text{b.3})$$

with

$$a = \sqrt[3]{\frac{3\pi P}{4} R(k_1 + k_2)} \quad (\text{b.4})$$

where

R = radius of alumina ball

ν_1, ν_2 = Poisson's ratios of Alumina and Silicon respectively

E_1, E_2 = Young's moduli of Alumina and Silicon respectively

$k_1 = (1-\nu_1^2)/(\pi E_1), \quad k_2 = (1-\nu_2^2)/(\pi E_2)$

Therefore, the Equation (b.3) can be substituted into Equation (b.1) which can be integrated in order to obtain the expression of dw/dr . Once Equation (b.1) has been solved for a given load and the quantity dw/dr has been deduced, the bending moment per unit length can be calculated from the following expressions:

$$M_r = -D \left(\frac{d^2 w}{dr^2} + \frac{\nu}{r} \frac{dw}{dr} \right) \quad (\text{b.4})$$

$$M_\theta = -D \left(\frac{1}{r} \frac{dw}{dr} + \nu \frac{d^2 w}{dr^2} \right) \quad (\text{b.5})$$

where M_r is the radial moment and M_θ is the tangential moment.

The corresponding radial and tangential stresses within the plate, σ_r and σ_θ , are related to the moments above by the following expressions:

$$\sigma_r = \frac{12 M_r z}{h^3} \quad (\text{b.6})$$

$$\sigma_\theta = \frac{12 M_\theta z}{h^3} \quad (\text{b.7})$$

where z is the vertical distance from the centre of the plate (the distance from the “neutral axis” of Fig. 2-21). Expressions (b.6) and (b.7) show that stresses are maximised at the surfaces of the plate, where $z = h/2$. The value dw/dr obtained from Equation (b.1) can be inserted into Equations (b.4) and (b.5) to evaluate the bending moments and, in turn, to calculate the stress components by using Equations (b.6) and (b.7). After some algebra, it is possible to achieve the following final expressions for radial and tangential stresses during annular bending:

$$\sigma_r = \frac{3P}{8\pi h^2} \left[4(1+\nu) \ln \left(\frac{X}{r} \right) + \frac{12}{5}(1-\nu) a^2 \left(\frac{1}{a^2} + \frac{1}{X^2} \right) \right] \quad (\text{b.8})$$

$$\sigma_\theta = \frac{3P}{8\pi h^2} \left[4(1+\nu) \ln \left(\frac{X}{r} \right) + 4(1-\nu) - \frac{12}{5}(1-\nu) a^2 \left(\frac{1}{a^2} + \frac{1}{X^2} \right) \right] \quad (\text{b.9})$$

where X is the radius of the annular knife-edge.

APPENDIX C

Fortran codes

1) Calculation of the major axis of a spheroidal precipitate and residual oxygen concentration in the crystal.

```

PROGRAM concentration

DOUBLE PRECISION t,tstep,y(5),PI,BOLTZ,CS,
dCP,RS,A,AR,ECC,rad,CBMD,CI,C0,r,r1,r2,RO,ocr,lam,c,fi
c N:number of equations, nsteps:number of steps, tstep:length of steps
INTEGER N, j, nstep, nsteps

write(*,*)'Calculation of the O2 residual concentration and'
write(*,*)'major axis for spheroidal oxide precipitates in Si'
write(*,*)'Temperature is 1000 °C'
write(*,*)'GROWTH TIME ? (hours - No fractions are allowed)'
read(*,*) nstep

N=1
nsteps=360*nstep
tstep=10.

write(*,*)'BMD ? (cm-3)'
read(*,*) ACBMD
write(*,*)'Initial Oxygen concentration ? (cm-3)'
read(*,*) ACI
CBMD=ACBMD
CI=ACI

c***** Init. Parameters *****
c See also parameters in the FUNCTION below
c*****
PI=3.14159265
BOLTZ=(8.6173E-5)*(1273.0)
CS=2.2E21*DEXP(-1.03/BOLTZ)
CP=4.6E22
AR=1.e-2
A=1.E-7
RS=(3./(4.*PI*CBMD))**(1./3.)
ECC=DSQRT(1.-AR**2.)
C0=CI-CS
c*****

y(N)=C0
OPEN(1, FILE='grow.dat')
OPEN(2, FILE='ox.dat')
WRITE (1,*) 0.0, C0, 2.*A*1.E7
DO 60 j = 1, nsteps
t=j*tstep

call rk4(t, y, tstep, N, CBMD, CI)

r1=(RS**3)*(C0-y(N))
r2=CP*((1-ECC**2)**(0.5))
rad=(r1/r2+A**3)**(1./3.)

WRITE (1,*) t/3600., y(N) , 2.*rad*1.E7

60 CONTINUE
CLOSE(1)
RO=y(N)+CS

WRITE(*,*)'***** RESULTS *****'
write(*,*)'ASPECT RATIO =',AR
WRITE(*,*)'TIME (h)'
WRITE(*,*) t/3600.
WRITE(*,*)'AVERAGE EXCESS O2 CONCENTRATION (cm-3)'
WRITE(*,*) y(N)
WRITE(*,*)'RESIDUAL O2 CONCENTRATION (cm-3)'

```

```

WRITE(*,*) RO
WRITE(*,*)'MAJOR AXIS (nm)'
WRITE(*,*) 2.*rad*1.E7
c=ECC*A
lam=DSQRT((3.*c)/(DASIN(ECC)*(RS**3)))
DO 70 i = 1,3000,10
  r=i*1.e-7
  fi=dsin(lam*(r-rad))/(lam*r)
  ocr=CS+y(N)*fi
  if(r.gt.rad) WRITE (2,*) (r-rad)*1.e7, ocr, RO
70 continue
close(1)
close(2)
  STOP
END

c  fourth-order Runge-Kutta subroutine
SUBROUTINE rk4(t, y, tstep, N, CBMD, CI)
  IMPLICIT none
  DOUBLE PRECISION DERIV, h, t, tstep, y(5), CBMD, CI
  REAL*8 k1(5),k2(5),k3(5),k4(5),temp1(5),temp2(5),temp3(5),rad
  INTEGER i, N

  h=tstep/2.0
  DO 10 i = 1,N
    k1(i) = tstep * DERIV(t, y, i, CBMD, CI)
    temp1(i) = y(i) + 0.5*k1(i)
10  CONTINUE
    DO 20 i = 1,N
      k2(i) = tstep * DERIV(t+h, temp1, i, CBMD, CI)
      temp2(i) = y(i) + 0.5*k2(i)
20  CONTINUE
      DO 30 i = 1,N
        k3(i) = tstep * DERIV(t+h, temp2, i, CBMD, CI)
        temp3(i) = y(i) + k3(i)
30  CONTINUE
        DO 40 i = 1,N
          k4(i) = tstep * DERIV(t+tstep, temp3, i, CBMD, CI)
          y(i) = y(i) + (k1(i) + (2.*(k2(i) + k3(i))) + k4(i))/6.0
40  CONTINUE
        RETURN
      END

c**** Function which returns the derivatives ***

  FUNCTION DERIV(t, temp, i, CBMD, CI)
    IMPLICIT none
    DOUBLE PRECISION D1,D2,D3,D4,DERIV,t,temp(5),PI,BOLTZ,D,CS,
    /CP,ECC,A,RS,AR,CBMD,CI,C0
    INTEGER i
c****PARAMETERS*****
    PI=3.14159265
    BOLTZ=(8.6173E-5)*(1273.0)
    D=0.13*DEXP(-2.53/BOLTZ)
    CS=2.2E21*DEXP(-1.03/BOLTZ)
    CP=4.6E22
    AR=0.01
    RS=(3./(4.*PI*CBMD))**(1./3.)
    C0=CI-CS
c*****

C**** Initial semimajor axis value (cm)
  A=1.E-7
  ECC=DSQRT(1.-AR**2.)

  D1=-(D*temp(i)*3.*ECC)
  D2=(CP**(0.33333333))*(RS**2)*(AR**(1./3.))*DASIN(ECC)
  D3=CP*(A**3)*AR/(RS**3)
  D4=(D3+C0-temp(i))**(0.33333333)
  DERIV=D1*D4/D2

  RETURN
  END

```

2) Calculation of the unlocking stress after annealing of certain duration at a given temperature (parameters are set for the case of oxygen in silicon).

```

program Oxygen

implicit double precision (a-h,o-z)
dimension flux(100),concentration(100),radi(100),deltaradi(100)
dimension area(100)

c *** UNITS ARE IN Cm *****

pi = 3.141592654
boltz = 8.6173E-5
cini = 6.3E17
rmax = 1.E-4
rmin = 5.E-8
cav = 5.E22
pirmin = pi * rmin * rmin
av = pirmin*cav
entropy = 7.6E-5
atlock = 7
actenergy=0.74
enterprob = exp(entropy/boltz)
totf=cini*pirmin

c *** Open output file *****
open(3,file='data.dat')

write(*,*)'Number of annuli? (MAX 100)'
read(*,*) n
write(*,*)
write(*,*)'Annealing Temperature [°C]?'
read(*,*) temperature
temperature=temperature+273.
write(*,*)
write(*,*)'Annealing duration (in hours)?'
read(*,*) time
time=time*3600.
write(*,*)
write(*,*)'Time STEP (milliseconds)?'
read(*,*) step
step=step*1.e-3

c *** SET THE NUMBER OF POINTS PER GRAPH (200)***
ndata=200
writestep=time/ndata

c *** DIFFUSIVITY AND ESCAPE PROBABILITY ***
escapeprob = exp(-actenergy/(boltz*temperature))
diffusivity = 0.13*exp(-2.53/( boltz * temperature ))
pidiff = 2 * pi * diffusivity

c *** SET THE RADIUS OF ANNULI AND INITIAL CONCENTRATION ***
i=1
do while (i.le.n)
radi(i)=dexp(dlog(rmin)+(i-1)*(dlog(rmax)-dlog(rmin))/n)
concentration(i)=cini
i = i + 1
end do
radi(n)=rmax

c *** SET THE DELTA-RADIUS AND DELTA-AREA ***
i=1
do while(i.le.n-1)
deltaradi(i)=(radi(i+1)-radi(i))/2
area(i)=pi*(radi(i+1)*radi(i+1)-radi(i)*radi(i))
i=i+1
end do

c *** START THE CALCULATION *****

```

```

t=0.

do while (t.lt.time)

c *** FLUX AT THE BOUNDARY (n=1) ***
flux(1)=pidiff*radi(1)*(concentration(2)*(1-totf/av)
--concentration(1)*escapeprob*enterprob)*step/deltaradi(1)

totf=totf+flux(1)

concentration(1)=totf/pirmin

c *** FLUX AT THE OTHER ANNULI (n=i) ***
i=2
do while (i.le.n-1)
flux(i)=pidiff*radi(i)*((concentration(i+1)
--concentration(i))/deltaradi(i))*step
c *** RECALCULATION OF THE CONCENTRATION AT THE ANNULUS i ***
concentration(i)=concentration(i)+(flux(i)-flux(i-1))/area(i)
i=i+1
end do

c**** CONTROL IF ***
if (totf.gt.av) then
write(*,*)
write(*,*) 'Please reduce the time step!'
endif
if (totf.gt.av) goto 1000
c*****

t=t+step

c *** WRITE THE DATA EVERY T=TIMESTEP ***
wstep=wstep+step
if (wstep.gt.writestep) then
write(3,*) t/3600, totf*atlock*1.e-6
write(*,*) 'Percentage done ',100*t/time
wstep=0.
endif

end do
write(*,*)
write(*,*) 'Data written on file every',writestep,'secs of anneal'

1000 end

```