

Potassium ions in SiO₂: electrets for silicon surface passivation

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Abstract- This manuscript reports an experimental and theoretical study of the transport of potassium ions in thin silicon dioxide films. While alkali contamination was largely researched in the context of MOSFET instability, recent reports indicate that potassium ions can be embedded into oxide films to produce dielectric materials with permanent electric charge, also known as electrets. These electrets are integral to a number of applications, including the passivation of silicon surfaces for optoelectronic devices. In this work electric field assisted migration of ions is used to rapidly drive K⁺ into SiO₂ and produce effective passivation of silicon surfaces. Charge concentrations of up to $\sim 5 \times 10^{12}$ e cm⁻² have been achieved. This charge was seen to be stable for over 1500 days, with decay time constants as high as 17,000 days, producing an effectively passivated oxide-silicon interface with SRV < 7 cm/s, in 1 Ω cm n-type material. This level of charge stability and passivation effectiveness has not been previously reported. Overall, this is a new and promising methodology to enhance surface passivation for the industrial manufacture of silicon optoelectronic devices.

Key words: ionic conductivity, dielectric coating, silicon surface passivation, potassium ion electret, field effect.

1 Introduction

The presence of charged ions in thin oxide films was first reported in the mid and late 1960s when Bell Labs, Fairchild and IBM engaged in the study of thermal silicon dioxide (SiO₂) for the production of field-effect transistors (FET) [1]. The work of Snow *et al.* [2–4] showed that the ionic conductivity in thin SiO₂ films, as also reported by Yamin [5–7] and Kerr [8–10], was largely due to the presence of sodium and potassium ions. Moreover, they showed that these ions were responsible for the instability problems leading to failure in Metal-Oxide-Semiconductor field effect transistors (MOSFETs), as also thoroughly studied by Hofstein [11–13]. Extensive work was carried out in the decades following these reports showing that charged ions in SiO₂ were of important scientific interest [14]. This significance, however, was mainly related to eliminating the unwanted presence of charge in MOSFETs caused by ions mobile under a gate bias. This problem was later solved by eliminating all sources of ionic contamination in semiconductor processing and thus ionic species in SiO₂ were not further researched. This has recently changed as dielectrics exhibiting permanent charge have become an integral part of other semiconductor devices, especially for their surface passivation [15–18] and electrostatic operation [19,20]. In fact, charged dielectrics are often referred to as *electrets* since they represent the electrostatic equivalent of a magnet, and are used in a number of applications including sensors, actuators and optical fibres [19,21–23]. Dielectric films where the electrostatic charge arises from ions inside the film, here termed ion-charged dielectrics, have only recently been reported, most prominently in the application of alkali ions in SiO₂ for surface passivation [24,25], potassium charged SiO₂ for actuators [26,27], transformers [28], and energy harvesters [29], and new strontium silicate glass electrets [30]. In this manuscript we study these recently reported potassium charged SiO₂ electrets, with focus on their application to field effect passivation (FEP) of semiconductor surfaces for solar cells. We describe a theoretical model for the transport of charged ions in SiO₂ in the absence

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of the metal contact required for MOSFET devices. Such a model has not been previously reported since the interest in ion charged dielectrics was previously only related to MOS structures.

In the past two decades, thermally grown SiO_2 has not only been shown to be a suitable gate material for MOSFETs, but also a remarkable surface passivation dielectric [31–33]. The passivation of the silicon surface is a key requirement to achieve high performance optoelectronic devices, like for example solar cells. While this requirement has been commonly achieved using a dielectric coating either thermally grown, as for SiO_2 , or chemical vapour deposited (CVD), the possibility to improve passivation effectiveness using post processing of the dielectric has only been exploited in recent years. In particular, FEP can be largely controlled by adding charge extrinsically to the dielectric while maintaining its chemical and optical properties [34–36]. This has been demonstrated previously using corona charge [37] and K ions [24] yet the issue remains to make such improvements in passivation stable for the life-span of a solar cell. The use of embedded ionic charge to produce a permanent electric field (electret) has been previously demonstrated to passivate silicon surfaces [25,38]. This has been termed ionic extrinsic FEP and only moderate passivation was reported. A simplified model for ionic transport was then used, and a brief examination of the stability was reported. In this work ionic charge purposely driven into a dielectric at raised temperature is optimally exploited for passivation of silicon solar cells. The principal advantages of such a method are: (1) the charge can be controlled separately from that introduced during dielectric growth, (2) the rate of transport of ions into the dielectric can be made sufficiently fast to make it compatible with industrial solar cell manufacture, and (3) since the charge is produced by ions sessile at room temperatures and located within the dielectric, it has the potential to be very stable. In this work we use potassium ion charged SiO_2 to demonstrate a potential and new method to produce SiO_2 electrets, and thus of independently exploiting FEP in practical silicon solar cells. In what follows, a model of ion transport mechanisms in SiO_2 will be given, the experimental details and the main characteristics of the physical system described, and the observed results on the K ion dynamics and passivation effects presented, together with a discussion of its potential for long term passivation of silicon surfaces.

2 Model for ion transport in the silicon-dielectric system

Dielectric layers on silicon are universal to the manufacture and operation of optoelectronic devices. Unless the semiconductor processing is performed under extreme cleanliness, a concentration of ions, typically alkali ions due to their abundance, will be present at the surface of the dielectric. Here the dielectric surface is interpreted as the dielectric-air interface which is often susceptible to this kind of contamination. In other instances, the ions can be purposely deposited on the dielectric with the aim of subsequently driving them into the film's bulk. The ions can either be in their neutral or charged states. For potassium ions the charged state is commonly a +1 state. Such ions tend to migrate into the dielectric film when sufficient energy is provided by subsequent elevated temperature processing. At high temperature the ions experience a substantial driving force resulting from gradients in concentration. Additionally, when the ions are present in a charged state, a second driving mechanism is established by their Coulombic attraction to mirror charges in the silicon, thus establishing an electric field. In some cases an externally applied electric field can also be used to provide an additional driving force for ion migration. Such driving forces bring ions from the surface into the dielectric film's bulk, and often accumulates them at the interface between the dielectric and silicon. Most importantly however, the migration of ions in oxide thin films is limited by the presence of traps. These can arise from the presence of low energy sites in the bulk of the amorphous film, or the surfaces and interfaces. In a silicon-dielectric system, both the surface and the interface have been reported to be the main trapping sites mediating the migration of ionic charge [39].

The oxide-silicon system is schematically pictured in Figure 1. Here a concentration of ions $[X]$, some of which are charged, are present both at the surface and in the bulk of the dielectric film. Those ionised produce a charge concentration Q in the dielectric, positive in this case, which is mirrored by a negative space charge region in the underlying silicon. This gives rise to an electric field \mathcal{E} directed from the dielectric towards the silicon, Figure 1.a. Trapping and de-trapping at the interfaces has been schematically pictured in Figure 1.b, including the effect of an electric field. Here ions are given enough energy either by thermal excitation to surmount the trap energy barrier and migrate across the film. An estimate for the timescale for the diffusion process can be drawn from the drift mobility of potassium ions in a SiO_2 matrix, reported as [40,41]:

$$\mu = 2.5 \times 10^{-3} \exp\left(-\frac{1.05 \text{ eV}}{kT/e}\right) [\text{cm}^2/(\text{V.s})], (1)$$

In Fickian diffusion, the average diffusion length is given by $2\sqrt{D\tau} = 2\sqrt{(\mu k_B T/e)\tau}$, which indicates that for ions to diffuse 100 nm, a time constant of only 10 s at 400 °C would be required. While concentration-gradient migration takes place in the order of seconds for sub-micron films, empirical reports have shown that transport of alkali ions from the surface to the oxide-silicon interface require much longer timescales [2,42].

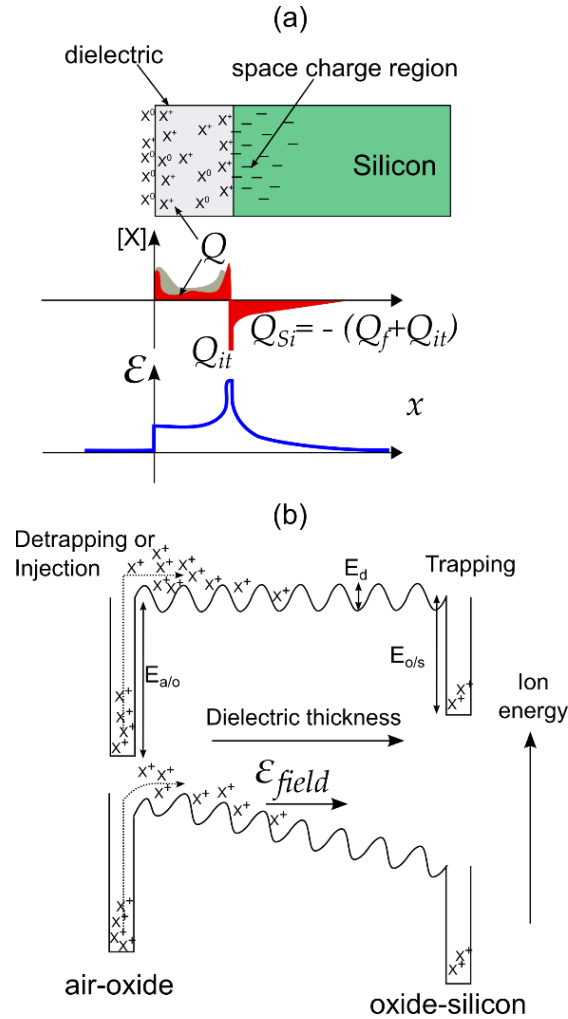


Figure 1. (a) Dielectric-silicon system where ionic charge inside of the oxide is assumed to be accumulated at the interfaces, and the charge is in turn mirrored at the semiconductor surface. (b) Energy diagram illustrating the presence of ion traps at each interface and the effect of an external electric field.

Snow and Hofstein's studies of the MOS structure first revealed that ionic charge transport was primarily limited by ion release from traps at the interfaces, rather than by the diffusion behaviour of the ionic species in the bulk SiO₂. Hickmott [39,43], and Boudry and Stagg [41,44] later studied trap-mediated ion dynamics in the Si-SiO₂ system using Thermally Stimulated Ionic Conductivity (TSIC) and concluded that the ionic species would concentrate at the interface traps with a range of energies rather than a single energy. The accumulation of sodium at interfacial traps has also been recently confirmed by Krivec *et al.* [45] using TSIC and time-of-flight-secondary ion mass spectrometry (ToF-SIMS). First order kinetics has been shown to accurately predict the trapping-detrapping ion dynamics. However, the initial distribution of energy of the trapped ions at an interface should be known [39]. Approximations to this distribution have been used by assuming a single activation energy [39], a Gaussian distribution of traps as a function energy [8,46], or even a convolution of Dirac functions and the measured current density [47]. Choquet and Balland [48] published an elegant algorithm to calculate the initial ion distribution yet some discrepancies were found in their calculation, thus there still exists uncertainty in determining the initial concentration and energy distribution of trapped ions.

Using first-order kinetics, the concentration of trapped ions at the air-oxide interface $C_{AO}(E, t)$ is given by [11,46]:

$$\frac{dC_{AO}(E,t)}{dt} = C_b \times (N_{AO}(E,t)R_{trapAO}(E)) - C_{AO}(E,t) \times s \exp\left(-\frac{E_{a1}}{kT}\right), (2)$$

where E is the trap of energy, while C_b is the concentration of ions outside the traps and free to flow in the bulk, Figure 1.b. C_{AO} increases in time if ions from the bulk C_b are trapped with probability $N_{AO}(E)R_{trap}$, where N_{AO} is the number of empty traps at an energy E_{a1} , and R_{trap} is the trapping rate for such energy. C_{AO} also decreases in time when ions are thermally ejected from their traps, as given by the second term on the right hand side of equation (2). Here s is a pre-exponential factor that includes the attempt frequency at which ions try to enter the dielectric and is taken as 10^{10} s^{-1} as reported in [44], and $T(t)$ is the temperature which can be dependent on time. It is noted that trapping at the air-oxide interface can also be understood as injection of ions from the surface and into the bulk of the oxide film. However, the nomenclature of trapping has been kept here as it was established by the works of Hickmott, and Boudry and Stagg.

To simplify the simulation in this section the initial distribution of trapped ions will be assumed as a concentration C_{AO_0} at a single trap energy E_{a1} , which is thus the activation energy for injection into the dielectric.

$$C_{AO}(E_{a1}, 0) = C_{AO_0}, (3)$$

If all traps are filled at time zero, $N_{OS}(0) = C_{AO_0} - C_{AO}(0) = 0$.

The oxide-silicon interface can be treated similarly to the air-oxide interface. Trapping and de-trapping will take place as determined by:

$$\frac{dC_{OS}(t)}{dt} = C_b \times (N_{OS}(t)R_{trapOS}) - C_{OS}(t) \times s \exp\left(-\frac{E_{aS}}{kT}\right), (4)$$

The initial concentration of trapped ions at this interface is assumed zero $C_{OS}(0) = 0$, such that $N_{OS}(E, 0)$ is equal to the maximum concentration that can be stored at the interface $N_{OS}(0) = C_{OS_0} - C_{OS}(0) = C_{OS_0}$. Equations (2) and (4) have been solved using an ordinary differential equation system solver in Matlab. Figure 2 illustrates an example solution of Equations (2) and (4) to determine the concentration of ions at either interface and in the bulk of the dielectric as a function

of time. Common and physically possible values were chosen for the model parameters: activation energies of 2 eV and 1.5 eV were used for the de-trapping of ions at the surface and interface respectively. Capture rates R_{trap} of $10^{-14} \text{ s}^{-1} \text{ cm}^{-2}$ and $10^{-13} \text{ s}^{-1} \text{ cm}^{-2}$ were chosen for trapping of ions at the surface and the interface, respectively. The initial trap density at both interfaces was assumed as $C_{OS_0} = C_{AO_0} = 10^{13} \text{ cm}^{-2}$.

From Figure 2 it is clear that the de- and trapping processes require periods of time in the order of thousands of seconds for substantial migration to occur. This, once again, agrees with previous reports indicating that trapping of ions is the rate limiting step in their migration into and across oxide thin film. At 400 °C over 2 hours are required before the concentration of ions at the oxide-silicon interface exceeds $10^{12} \text{ atoms/cm}^2$, while 20 seconds are required at 500 °C. This is two orders of magnitude longer than the time constant for a pure diffusion limited process as calculated before. It can also be noted that, for these trapping/de-trapping parameters, the large majority of the available ions at the oxide surface remain there, with only a tenth migrating and being trapped at the interface. Additionally, substantial de-trapping from the oxide-silicon interface is observed at 500 °C such that the bulk concentration of species is higher than at the oxide-silicon interface. This is an important effect not previously considered and will be shown to be significant when explaining the observed behaviour of K migration into and across oxide films.

Although first-order kinetics has been commonly employed to model ion transport in dielectric matrices, it is important to highlight a number of assumptions and shortfalls in this model. Firstly, the effect of an externally applied electric field is not considered in the simulation in Figure 2. No experimental data has been yet reported where such a field is applied in absence of a metal gate and thus this problem is not one that has been yet treated. As proposed by Piprek [46] and Krivec [45], the effect of an external electric field can be to reduce the activation energy for injection of ions from the surface in $\alpha_1 \Delta E$. The exact values that α and ΔE take are still under debate in MOS structures since it can be influenced by the metal deposition and surface conditions. In absence of the metal, as it is the case in this work, the electric field can be difficult to control and could not be investigated. It is only stated that it can reduce the activation energy for ion injection into the oxide.

Secondly, the effect of the Columbic attraction between charged ions and mirror charge in the Si is not considered. This effect has been largely ignored in the literature yet it is of importance to fully account for ion transport and stable interface concentrations. This was recently highlighted in a study of potassium in a MOS system where the driving mechanism was the electric field provided by the contact potential between metals and silicon [49]. Both the electric field established by the migrating charged particles, and that given by an external source, can contribute to forcing charged ions to or from the oxide-silicon interface. This can therefore change the probability for ion capture at that interface in $\alpha_2 R_{trap}$. The values for these constants are not investigated in the present work since at present the experimental data is insufficient to make accurate estimations. Here it is only assumed that the trap capture rate estimated contains an element related to the ions self-electric field.

Lastly it is noted that the activation energy for ion injection or de-trapping at the oxide surface relates, at least partly, to the binding energy of the anion to the cation. When ion precursor species are purposely deposited on the surface of the oxide, it is believed that only a small portion of ions are in an unbound state.

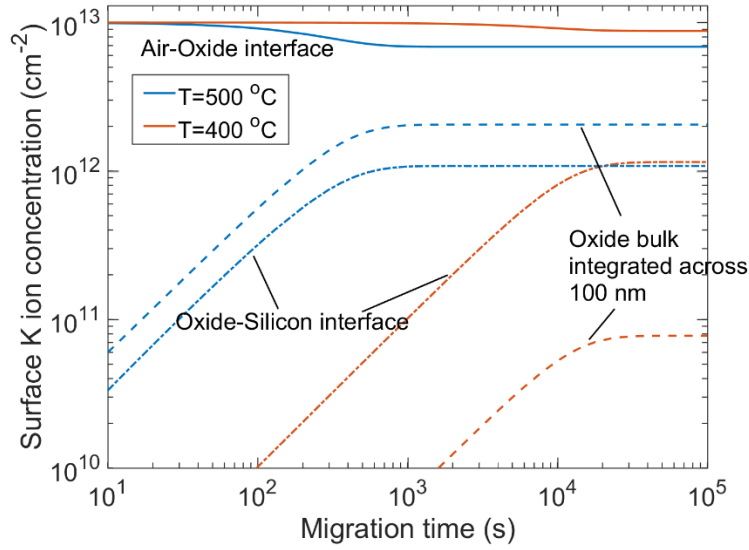


Figure 2. Migration of K ions via de-trapping and trapping at the oxide-silicon interfaces as a function of time, at 400 °C and 500 °C. The available K ion traps at both interfaces were $C_{OS_0} = C_{AO_0} = 10^{13} \text{ cm}^{-2}$, with all traps initially filled at the air-oxide, and empty at the oxide-silicon interfaces. Activation energies for the de-trapping of ions at the surface and interface were 2 eV and 1.5 eV, and capture rates $10^{-14} \text{ s}^{-1} \text{ cm}^{-2}$ and $10^{-13} \text{ s}^{-1} \text{ cm}^{-2}$.

3 Methods and characterisation

The migration of potassium ions in SiO_2 thin films has been studied using capacitance-voltage (CV) measurements in metal-oxide-semiconductor (MOS) structures. SiO_2 films were produced by thermally oxidizing 1 Ωcm , n-type, float zone (FZ) silicon wafers, 200 μm thick. Oxidation was preceded by RCA cleaning and took place in a dry oxygen/dichloroethylene environment at 1050 °C, at Fraunhofer ISE. The final film thickness was $100 \pm 2 \text{ nm}$ as corroborated by ellipsometry using a Film Sense FS1. A subset of wafers then underwent a forming gas anneal (FGA) in 5% H_2 at 425 °C for 30 min. A temporary top metal contact was achieved using a mercury probe (Hg-p) as described in [35]. A controlled concentration of KCl molecules were deposited on the oxide surfaces as a precursor for migration of K^+ ions. This was done using thermal evaporation following the technique described in [24]. A nominal surface concentration after deposition was calculated to be 10^{14} cm^{-2} . This was corroborated by integrating the current profile in a thermally stimulated ionic conductivity (TSIC) experiment as described in [39,49]. TSIC was performed in a MOS capacitor with a permanent top metal contact fabricated by evaporating 100 nm of aluminum through a shadow contact mask to form a $\sim 0.5 \text{ mm}$ radius front dot. Rear contact to the silicon was formed by removing the back surface oxide and evaporating of a full area Al contact, or smearing on a gallium-indium eutectic. It is noted here that a substantial proportion of the ion species at the surface (KCl) are thought to be free ions since the concentration is much less than a monolayer. This is a key parameter since when excessive KCl is deposited and a crystal is created on the oxide surface, the energy for ion injection into the oxide increases substantially. This is concluded since it was qualitatively observed that very few ions migrate into the oxide when the precursor species concentration exceeds that of a monolayer.

Transport of K ions in SiO_2 took place by submitting samples to a high temperature anneal. Diffusion at high temperature was performed in a box furnace under standard laboratory conditions. Electric field assisted migration was applied by submitting samples to corona discharge using an apparatus as

described in [37,50]. The charge concentration at the surface of the oxides was measured using Kelvin Probe (KP) surface potential [51].

CV was conducted using a Keysight E4980A LCR meter for the frequency regime 20 Hz-2 MHz. The flat-band voltage V_{fb} was found by correcting the measured gate voltage V_g to account for the stretching produced by interface states D_{it} thus producing a V_{g0} . The measured high frequency capacitance C_{HF} vs V_{g0} curve was translated in the voltage axis to find the V_{fb} that produced the best fit between the measured and the theoretical relations. V_{fb} was used to calculate the dielectric fixed charge Q_f as explained in [52,53]. The insulator capacitance C_i was determined in the accumulation regime using the McNutt-Sah method [54] with the extension in [55], and used to calculate the contact area from the known oxide thickness d as: $Area = C_i d / \epsilon_0 K_{SiO_2}$. An expansion of these methods is found in [14].

The effect of charged potassium ions on the surface recombination at the oxide-silicon interface was evaluated using photo-conductance decay (PCD) lifetime measurements using a Sinton WCT120 instrument [56]. These were conducted on $3 \times 3 \text{ cm}^2$ samples where K ions had been deposited and driven in at high temperatures. Surface recombination velocity (SRV) and recombination current densities (J_{0s}) were calculated using a methodology adapted from Kane and Swanson's method [57] as described in [18]. Richter's parameterization [58] for Auger and radiative recombination was used to calculate the bulk lifetime component.

4 The transport of K ions in SiO_2

The dynamic behaviour of K ions in a SiO_2 -Si system was studied by depositing a concentration of ionic species on oxidised Si specimens and migrating them at high temperature. KCl was used as precursor for K ions. After deposition of ionic species, samples were submitted to two different processes in order for migration of ions to occur. These are depicted in Figure 3. In the first case, the dielectric film is subjected to high temperature without any metallic contact on top of the dielectric, as it is the case in MOS structures. In this case ion de-trapping or injection from the oxide surface is purely temperature activated. Secondly, a concentration of corona charge is deposited on the surface of the film prior to high temperature annealing. The de-trapping ionic species from the oxide surface and subsequent motion is thus assisted by the corona electric field during the high temperature migration. Measurements of KP surface potential and CV flat-band voltages were used to characterise the migration of K charged ions from the air-oxide to the oxide-silicon interface. CV measurements were performed in MOS structures with a temporary Hg-probe contact after submitting ion-deposited specimens to subsequent high temperature steps.

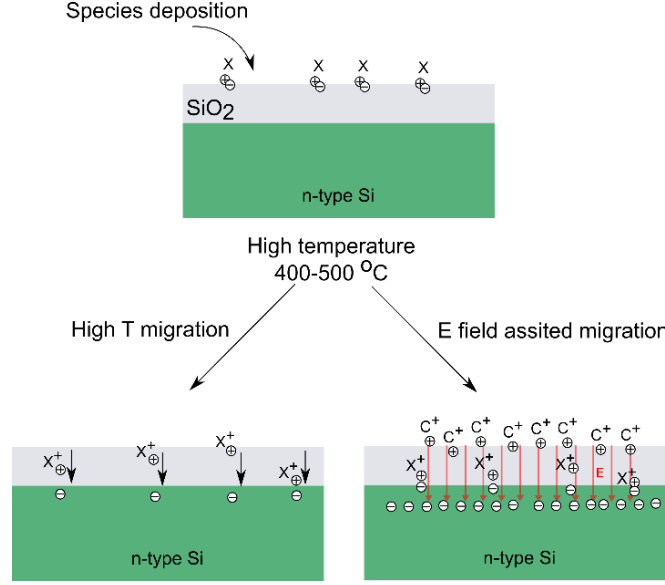


Figure 3. Mechanisms for ionic charge migration into silicon dioxide. X indicates an ionic species while C indicates a corona ion.

4.1 High temperature migration

Figure 4.a illustrates the flat-band voltage change due to ions that migrated to the oxide-silicon interface after a high temperature anneal step, for various temperatures. Flat-band voltage relates to the bulk concentration of charged K ions $\rho(x)$ as [35,52,53]:

$$V_{fb} = \frac{\Phi_{ms}}{e} - \frac{Q_{itd}}{\epsilon_i} - \frac{1}{\epsilon_i} \int_0^d x \rho(x) dx, \quad (5)$$

Where Q_{it} is the interface charge at the silicon surface in flat-band conditions, commonly disregarded since it is of the order $\sim 10^{10}$ e/cm² [59]. Φ_{ms}/e is 0.178 V for a mercury contact to 1 Ω cm n-type silicon. Here it is clear that a substantial concentration of positively charge K ions is building up at the oxide-silicon interface. The highest concentration was observed for a migration at 475 °C leading to $\sim 5 \times 10^{12}$ ions/cm² at the interface. Control samples in which no concentration of KCl was intentionally deposited showed negligible (< 2 V) flat-band voltage change and thus charge.

The modelling formalism established in Section 2 was used to find the energy trapping parameters that best described the transport of K ions from the oxide surface into the film, and towards the oxide-silicon interface. The solid lines in Figure 4.a show the best fitted V_{fb} using equation (5), with bulk charge concentration ρ calculated from the modelling results. The parameters were varied empirically to find the best model of ion migration and are shown in Table 1. The values of activation energy found for potassium de-trapping at the air-oxide interface compare well to those found in ref [24] for 100, 70 and 45 nm oxides subjected to 500 °C anneals. This corroborates that bulk diffusion of ionic species occurs much faster than trapping and de-trapping at the interfaces and is thus less influential to the total migration dynamics of K ions in SiO₂. A comparison to the activation energy for injection of ions in a MOS structure is also included in Table 1. In the presence of a metal contact, and an applied bias, de-trapping of ions from the oxide surface has an activation energy significantly smaller than in absence of a metal. This indicates that in a oxide-silicon system alone the migration is slower than that of a metal-oxide-silicon system, as previously suggested in [24].

It is also noted that the modelling formalism used here includes de-trapping at the oxide-silicon interface, which had not been considered in previous studies of the SiO₂-Si system. When these are included it is clear that a better fitting model can be constructed thus indicating that de-trapping

contributes largely to the dynamic behaviour of ions. This is especially evident in the higher maximum concentration of migrated ions observed for higher temperatures after steady state, Figure 4.a, and in the larger concentration of ions being injected back into the bulk at higher temperatures, Figure 4.b.

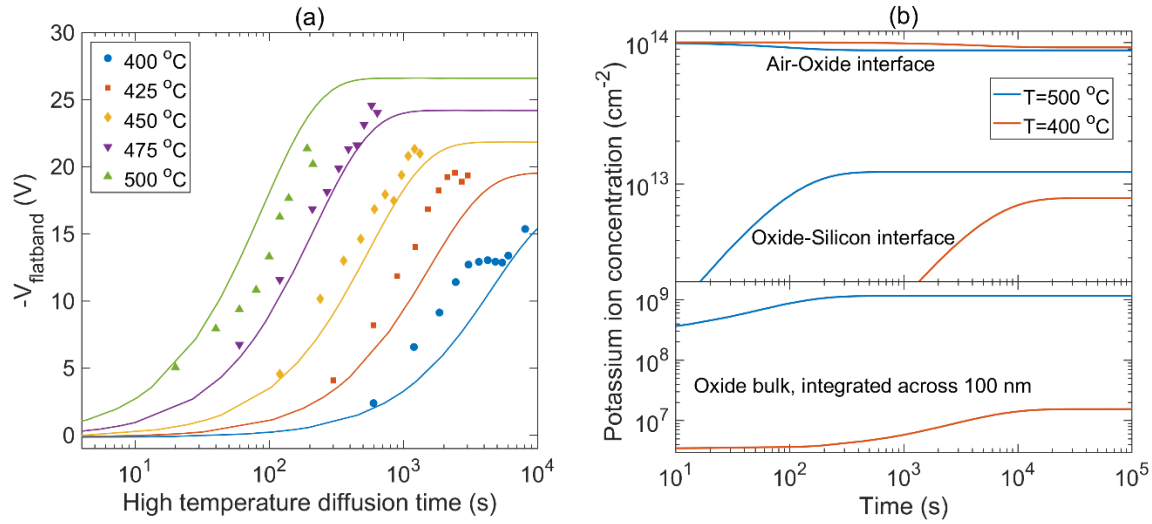


Figure 4. (a) Flat-band voltage as a function of annealing time and temperature in oxide-silicon specimens with a surface concentration of potassium ions, (b) Simulated depth profile of the K ions migrated to the oxide-silicon interface at the end of the annealing time.

System	Process	Migration model parameters
K in oxide-silicon	High temperature migration	$E_{a1}=1.96$ eV
		$E_{aS}=1.74$ eV
		$R_{trapAO}=0.32 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$
		$R_{trapOS}=10^{12} \text{ cm}^{-2} \text{ s}^{-1}$
		$C_{AO,0}=5 \times 10^{14} \text{ cm}^{-2}$
		$C_{OS,0}=5 \times 10^{14} \text{ cm}^{-2}$
K in MOS*	TSIC	$C_{AO}(t=0)=10^{14} \text{ cm}^{-2}$
K in MOS*	TSIC	$E_{a1} \sim 1.65$ eV
		$C_{AO,0} \sim 10^{13} \text{ cm}^{-2}$

Table 1. Summary of parameters used to model ion dynamics in MOS and oxide-silicon systems. * Data from reference [60].

4.2 Electric field assisted migration

When ion de-trapping and migration are purely driven by high temperature, time periods between 2-90 minutes are required. This timescale is unlikely to be commercial in, for example, the manufacture of silicon solar cells. These processes should be executed in seconds with easily scalable equipment.

In this section an additional mechanism of ion migration is suggested to address this drawback. By including the presence of an electric field, de-trapping and transport of K ions into and across SiO₂ films is assisted. The electric field was applied using corona charge deposited prior to the high temperature anneal, as shown in Figure 3. Kelvin Probe surface potential and CV flat-band voltage measurements were used to monitor the concentration and location of both, K charged ions and corona discharge ions, in the SiO₂ film.

Oxidised silicon specimens, with and without a FGA, were deposited with a concentration of 10¹⁴ KCl molecules/cm², then corona charged to a surface potential of ~10-14 V, ($Q_f \sim 3 \times 10^{12} \text{ e cm}^{-2}$), and submitted to a high temperature anneal at either 400 or 450 °C. Figure 5.a illustrates the KP surface potential for these specimens as the different processing steps take place. After deposition of K ionic species the surface potential is negligible in all samples. Corona discharge then increases surface potential as charge accumulates at the oxide surface. At high temperature the K ions are migrated into the oxide film using electric field assisted migration. In parallel to this process, thermally activated migration of corona charge also takes place leading to a rapid decay in the surface potential at high temperature [35,50]. This results in the presence of the added electric field being only temporary.

After high temperature migration, samples intentionally deposited with K ions show a reduction in surface potential to pre-corona values after 2 min. This indicates that the corona charge at the surface of the specimens has decayed entirely. On the other hand, unintentionally contaminated (control) samples show a significant surface potential indicating that some corona charge remains at the surface. In the samples processed at 400 °C the charge transport was continued for an additional 8 min, orange and yellow traces in Figure 5.a. This showed that a longer time was required for the surface potential to reach its initial value. When compared to samples purposely deposited with KCl ions, this could indicate that the decay dynamics of corona charge are modified, possibly by a component that accelerates the decay or neutralisation of corona charge. Here it is suggested that such a neutralising mechanism may be due to the Cl⁻¹ ions left at the surface as the K⁺¹ cations separate and migrate across the oxide. Charged K ions, on the other hand, migrate quickly across the oxide to the oxide-silicon interface, and no surface potential is thus observed in KP measurements after the migration.

A disadvantage of this process is that some of the driving force given by the electric field is eliminated at the same time as the K ions are transported through the dielectric. If the leakage of corona charge is faster than the migration of K ions, a concentration of the latter may remain at the surface after the high temperature step. Those ions which remain at the surface are like to be bound to the precursor anion thus forming neutral complexes. Those which split off become positively charged (cations) and diffuse rapidly to the oxide-silicon interface. Once there it is not possible to assess their concentration using KP measurements, since KP is only sensitive to charge at the surface of the oxide, and thus provides incomplete information regarding the behaviour of ionic species [35,61]. To better understand the latter, the CV flat-band voltage was recorded in a subset of samples as illustrated in Figure 5.b. Here it is evident that in samples intentionally deposited with K ions the flat-band voltage increases to ~-12 V ($Q \sim +2.5 \times 10^{12} \text{ e/cm}^2$), while for specimens without K ions the flat-band only increases to ~-3 V ($Q \sim +0.7 \times 10^{12} \text{ e/cm}^2$). A substantial concentration of charge is thus built into the dielectric coating after K ions are migrated, while a small yet non-negligible concentration is seen on specimens lacking intentional K ions. This confirms that the K⁺¹ ions are migrated into the oxide film and sit very near the oxide-silicon interface, upon annealing at 400-450 °C. The concentration of charge observed in control specimens is believed to be due to unintentional contamination of KCl and NaCl ions largely present in laboratory conditions. Corona charge is only believed to be present at the surface of the dielectric and thus to fully decay after sufficient high temperature processing.

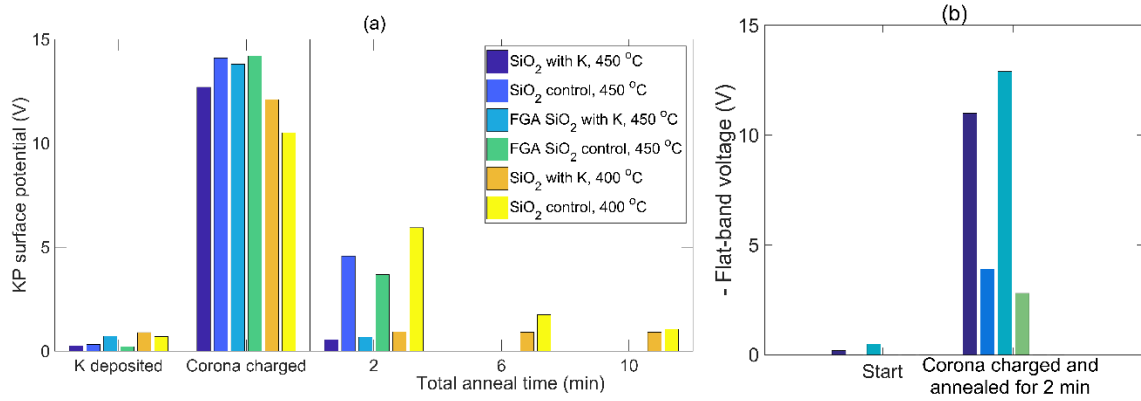


Figure 5. a. Kelvin Probe surface potential for oxidised n-type FZ Si when K ionic charge is migrated using electric field assisted migration for different times and temperatures, b. Subset of samples which underwent CV measurements of flat-band voltage prior to corona deposition and after high temperature anneal.

5 Surface passivation from K ion charged SiO₂

The effect of K ions on surface recombination was evaluated by submitting 3 x 3 cm² oxidised FZ n-Si samples, previously deposited with a known concentration of species, to a high temperature anneal in the presence of an electric field given by corona charge. Previous work has shown that the effective lifetime increases substantially when K ions are diffused into an oxide film in absence of an electric field [24,25]. In this manuscript the focus lies on the surface passivation achieved from K ions transported using electric field assisted migration.

The migration of K ions was conducted at different temperatures and time periods after a corona charge concentration of $\sim 3 \times 10^{12}$ q/cm² was deposited on the dielectric. Figure 6 illustrates the effective lifetime after the different processing steps are carried out. Figure 6.a shows the dependence of lifetime with carrier injection. After corona charge deposition, the effective lifetime at $\Delta n = 10^{15}$ cm⁻³ increases from 0.08 (0.1) ms to ~ 3.2 (3.5) ms for non-FGA (FGA) specimens. Both purposely K-deposited and control samples behave similarly and thus no difference has been drawn on Figure 6.a. Such high lifetimes are equivalent to a $S_{eff} < 1.5$ cm/s and $J_0 < 3$ fA/cm², for these 1Ωcm n-Si samples. Figure 6.b shows that after high temperature migration the effective lifetime decreases to ~ 1 -2 ms for all samples, indicating that a small portion of the charge was neutralised or compensated, or that surface states have been generated at the oxide-silicon interface. If the lifetime lowering was only due to neutralised charge, this is estimated to be $\sim 2 \times 10^{12}$ q/cm², according to the analysis presented in [62]. The surface potential of samples deposited with K ion precursors fell to near zero after the anneal, Figure 5.a. It is thus believed that all charge remaining in the film is located at or near the oxide-silicon interface which is in agreement with transport using only diffusion [24]. In control samples the KP surface potential only decayed to 3-5 V upon 2 minutes anneal, such that corona charge seems to still be providing FEP.

When migration of ions is further done by subsequent thermal anneals, the effective lifetime is seen to stabilise over the first 2-6 minutes, at 400 °C. Only a marginal change in lifetime is observed after annealing for 6 and 10 minutes, compared to that after 2 minutes, and no substantial difference in effective lifetimes is noticed between K and control samples. In these samples the KP surface potential (Figure 5.a.) continued to decrease and thus it appears FEP is provided by both corona discharge and unintentional contamination. As mentioned in Section 4, a disadvantage of this method is that part of

the electric field driving force is eliminated as corona charge also leaks away. Effective lifetime measurements directly after ion migration could not elucidate any further differences between the dynamics of ions or that of corona charge. Nevertheless it is possible to demonstrate that ionic charge can, at least partly, produce high quality surface passivation.

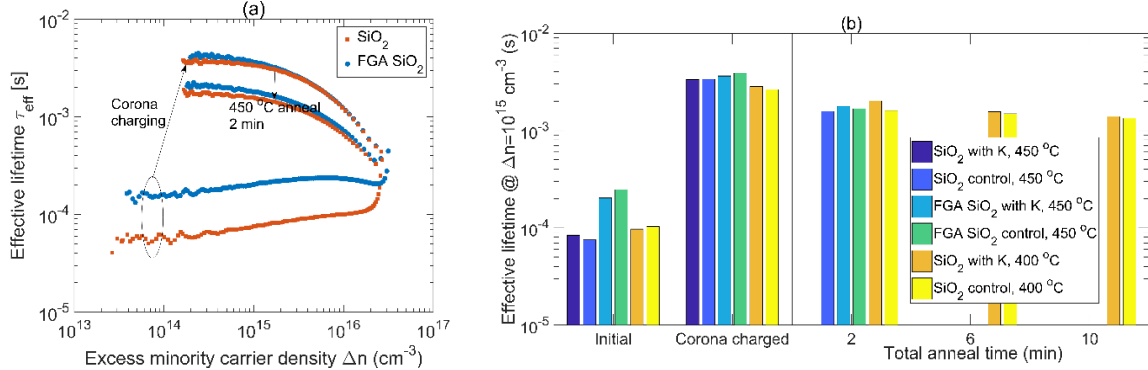


Figure 6. (a) Effective lifetime as a function of injection level, and (b) Effective lifetime for $\Delta n = 10^{15} \text{ cm}^{-3}$, for oxidised n-type FZ Si when K ionic charge is migrated using electric field assisted migration. Samples were annealed at either 400 or 450 °C. Samples annealed at 400 °C received subsequent anneals for 2, 4 and 4 minute periods.

6 The stability of K ion passivation in SiO_2 -Si

While it is clear that silicon surfaces can be passivated by ion-charged dielectric films, the challenge that remains is to demonstrate the stability of such passivation. This section presents an evaluation of the stability of extrinsic FEP achieved using K ion migration into oxide films. This is studied for both high temperature diffusion and electric field assisted migration.

After high temperature diffusion, samples were kept in plastic bags and measured sporadically over a period of 1500 days. Figure 7 illustrates the time evolution of τ_{eff} at $\Delta n = 10^{15} \text{ cm}^{-3}$ for specimens with potassium in-diffused at different temperatures. Here, an initial lowering of effective lifetime is observed over the first 50 days, for all temperatures. Disregarding any chemical change of the silicon-oxide interface, this initial lifetime decrease likely indicates that some of the cations at the oxide-silicon interface are either neutralised or de-trapped from the interface. After this initial period, the remaining ions are highly stable, as observed by the small decay in effective lifetime over 4 years. This is a significant finding in particular considering that samples in Figure 7 did not undergo chemical HDMS treatment which has been widely reported as a requirement for corona charge stability[21,50,63]. Water has been previously found to be a major contributor to leakage and/or neutralisation of charge in corona charged oxides. The effect of water was tested on K ion charged SiO_2 by chemically treating the film using HMDS. The blue void symbols in Figure 7 illustrate the effective lifetime for a specimen with K diffused at 400 °C and HMDS chemically treated. The initial lowering of effective lifetime in this specimen was observed to a lesser extent. Instead, a long slow decay over the whole measurement period was observed.

The decay time constant (TC) is used here as a figure of merit for stability of passivation. It is calculated by fitting the function $f(TC) = (\tau_{eff,max} - \tau_{eff,min})\exp(-t/TC) + \tau_{eff,min}$ to the measured lifetime using a non-linear least squares method. The fitting was done in the 100 to 1500 days period. In the best case, K ions migrated at 550 °C showed a decay time constant as long as $\sim 14,000$ days $\pm 40\%$. Time constants of $\sim 3,800$ days $\pm 20\%$ were estimated for the lifetime decay in samples both with and without HMDS treated samples diffused with K at 400 °C. K ions diffused at 450 and 550 °C

showed the most effective passivation with $\tau_{eff} > 0.7$ ms, $S_{eff} < 13$ cm/s for the whole measurement period.

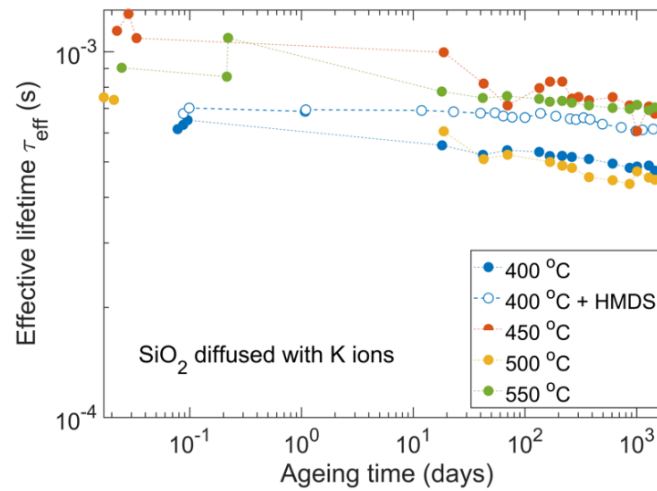


Figure 7. Long term measurement of effective lifetime for oxidised n-type FZ Si when K^+ ions are diffused into the oxide at 400, 450, 500 and 550 °C.

Samples with K ions transported using electric field assisted migration were monitored over a period of 500 or 1500 days. Once embedded in the dielectric, samples with K ions were also stable for a period of up to 4 years, while samples lacking ionic species were seen to decay quickly as illustrated in Figure 8.a. The oxide with embedded K ions at 400 °C showed a decrease in effective lifetime of $< 10\%$ over the first 10 days, after which a decay time constant of $\sim 17,000 \pm 22\%$ days was estimated. Four years later this specimen still showed a $S_{eff} < 7.2$ cm/s well within the range of the best passivation schemes [50]. The effective lifetime of control specimens, on the other hand, showed a fast decay period that extended for 200 days, reducing the effective lifetime to less than 50% of its original value. After this, charge in the dielectric was seen to decay with a time constant of $\sim 3,000 \pm 75\%$ days. This is substantially faster than for samples bearing K ions. This indicates that the nature of the charge in this SiO_2 films is different than that of corona charge alone. Here, once again, it is noted that samples did not undergo a chemical treatment with HMDS to prevent water absorption. Monitoring of the surface potential, Figure 8.b, showed it to be negligible over the entire measurement period for K bearing samples, while in control samples it was $\sim 5V$ after high temperature annealing, yet it decayed fully over the first 50 days.

For oxides where K transport occurred at 450 °C the measurement period was 500 days. In this case the CV flat-band voltage was monitored as well, Figure 8.c. Here it is clear that samples purposely deposited with K ions show a much higher concentration of interface charge, and this charge is seen to remain stable after 1.5 years. In K-migrated specimens a concentration of charge of $\sim 3 \times 10^{12}$ e/cm² is estimated, while control samples only show 6×10^{11} e/cm². Here it is hypothesised that despite the lack of intentional K ions, the dielectric charge in control samples is due to an unwanted concentration of ionic contamination, most likely sodium and/or potassium, rather than due to the corona charge.

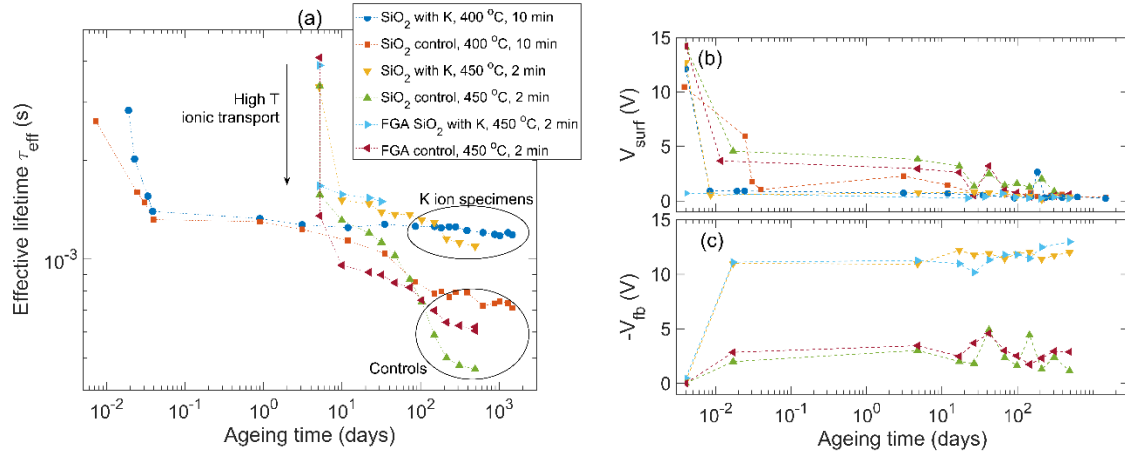


Figure 8. (a) Effective lifetime, (b) Kelvin Probe surface potential, and (c) CV flat-band voltage for oxidised n-type FZ Si when K ionic charge is migrated into the oxide using electric field assisted migration at high temperature.

7 Discussion

In this work, stable field effect passivation of silicon surfaces using K^+ ions has been demonstrated for the first time. A model for ion migration was suggested where trapping and de-trapping are possible and accurately predict the observed behaviour. The parameters deduced are in qualitative agreement with previously reported data. Higher de-trapping activation energies are found for ions located at a free surface compared to those for ions located at an oxide-metal interface. These results also indicate that other ionic species, not only K but also Cs, Rb, and perhaps some other metals, should have the potential to be fixed into a dielectric matrix and provide effective and durable FEP. This passivation technique provides an alternative method of passivation whereby chemical, field effect, and optical properties in a dielectric film can be exploited separately to produce improvements in the conversion efficiency of silicon solar cells.

The time constants for the decay in lifetime after passivation for different specimens is summarized in Figure 9. When only high temperature migration is used to drive ions into the film, good stability of passivation is observed with decay time constants exceeding 13,000 days. This high stability is observed for oxides with K ions diffused at 550 °C, which also showed the highest lifetime by the end of the 4 year measurement period, $\tau_{eff} \sim 0.7$ ms. The quality of passivation achieved using ions migrated at high temperature was not as high as that reported for corona discharge in [50]. SRV values of ~ 6 -12 cm/s were inferred thus indicating that either the chemical or the FEP components are not fully exploited. It appears that sufficient charge is present in the oxide yet these charged ions are mainly located at the oxide-silicon interface where they can damage the chemical properties of the interface. This level of passivation is acceptable for current commercial solar cells with efficiencies $\sim 18\%$. However, for high efficiency ($>20\%$) silicon cells this technique must be improved such that passivation is exploited to the maximum.

Previous reports showed that corona discharge passivation required sealing the oxide film's surface to prevent water absorption using a chemical treatment of hexamethyldisilazane (HMDS) vapour [63]. In Figure 7 it was shown that the stability of FEP in an HMDS treated specimen with K ions was similar yet it did not show the initial (~ 50 day) decay observed for un-treated samples. These results suggest that during the HMDS process, the moderate temperature provides energy to accelerate the fast decay such that it is not observed. Most importantly, these results indicate that the ionic FEP does not require application of HMDS or controlled humidity to deliver passivation stable over a period of years.

This is equally observed in the passivation achieved using electric field assisted migration of K ions, Figure 8.

In samples with K ions diffused at high temperature and no HMDS treatment, the initial decay in effective lifetime observed can be attributed to a reduction in either component of passivation. First, a reduction in chemical passivation may be taking place. In reference [24] we reported that charged ions migrating to the oxide-silicon interface produced a number of interface states during the migration process. The loss in chemical passivation in such case is likely due to the bond straining or breakage caused by the presence of ionic species at the oxide-silicon interface. Once the ions are there it is unlikely that they continue to produce loss in chemical passivation. In [50] we also reported that chemical de-passivation could take place due to hydrogen release or interface ‘bad spots’ with high electric field. If the long-term decay in ionic FEP was of chemical origin, it would likely be due to a similar mechanism yet it appears an unlikely scenario. The second component of passivation that could decay with time is field effect. This is a more likely scenario where some of the ions present in the film are neutralised, and thus the charge concentration decays. The concentration of charge first migrated into the film can be estimated using data in Figure 4. This estimation is shown in Table 2. It is clear that the ion diffusion process in these specimens could have produced a very high concentration of charge at the oxide-silicon interface. In this case effective lifetime is weakly dependent on charge [62,64], thus the decay in lifetime observed could not be used to estimate the rate at which ions are neutralised.

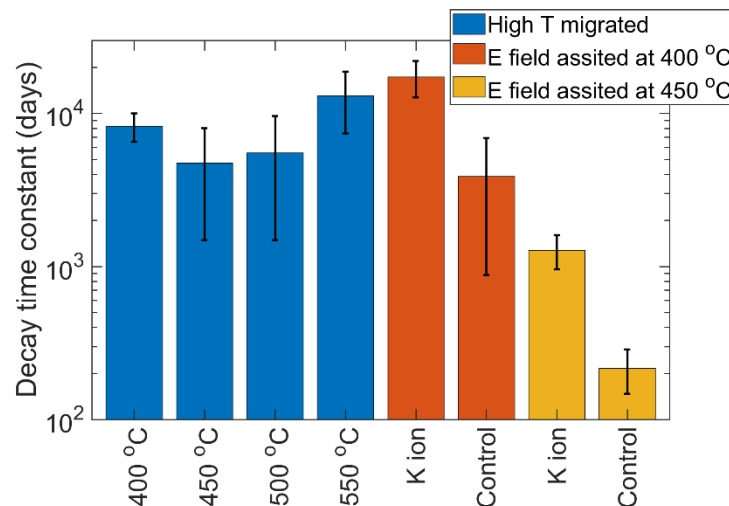


Figure 9. Summary of stability of passivation in oxides with potassium ionic charge migrated with and without electric field assistance. The decay time constant is estimated between day 10 and the end of the period. Error bars are the 95% confidence interval of the fit.

Process	Temperature [°C]	Total transport time [min]	Charged ion concentration [$10^{12} \text{ e cm}^{-2}$]
High temperature migration	400	100	$3 \pm 1^*$
	450	25	$5 \pm 1^*$
	500	12	$6 \pm 1^*$

Electric field assisted migration		550	4	$7 \pm 1^*$
		400	10	$1.5 \pm 0.5^*$
		450	2	$2.6 \pm 0.5^\dagger$

Table 2. Concentration of charged ions transported into oxide films at different temperatures and with different migration mechanisms. * Data estimated from data in Figure 4, while [†]data was calculated from CV flat-band voltage measurements.

In Section 4 it was postulated that injection and migration of ions in a dielectric film occurred faster thanks to the added driving component of an electric field given by corona charge. However, during the migration process, no difference in surface potential and effective lifetime was observed between specimens with and without ionic species. In Section 6 the decay of effective lifetime was seen to depend strongly on the presence of ions in the dielectric. This demonstrated that ions can be migrated using field assisted diffusion and are highly stable. Decay time constants exceeding 17,000 days have been measured, Figure 9. A comparison of stability of passivation for diffusion alone, versus electric field assisted migration, shows that when the electric field is present better levels of stability and effectiveness of passivation are achieved at lower temperatures. In Section 6 it was also noted that oxides that underwent FGA showed a better quality of passivation, as expected, but no improvement in stability. Overall, it is clear that regardless of FGA or HMDS treatments of the oxide films, K⁺ ions transported using field assisted migration provide effective (SRV<7.2 cm/s) and stable passivation. The slow decay observed over the 1.5 or 4 year measurement period has not been investigated in detail. Its origin can be the manipulation of the specimens, or a slow decaying change in chemical passivation as shown by Sperber in [65]. An extensive investigation of the decay mechanisms will be covered in a future publication.

Another important observation from Table 2 is the length of time required for the ion migration processes. The electric field effectively assists the migration reducing its length by about an order of magnitude. As noted in Section 2, the effect of such field is believed to be a modification of the barrier height for ion de-trapping at the oxide surface. Unfortunately, a study of different electric fields and temperatures is limited by the difficulty in maintaining a constant field in absence of a metal contact. Despite this, the results obtained here indicate that a much shorter process, potentially in the order of a few seconds, is possible by tuning the field, temperature and times. This process could produce an optimal concentration of charged ions in the dielectric, and thus provide adequate levels of surface passivation. This is an important remark as it points to the commercial viability of this method. In addition this method could be applied to different dielectric stacks beyond thermal oxides.

8 Conclusions

This paper has presented a comprehensive study of the release, migration and trapping of ionic charge in an oxide-silicon system, with direct application to the surface passivation of silicon. Ion dynamics in the air-oxide-silicon system were found to be comparable to that in a MOS system, indicating that ions are de-trapped from the surface of the dielectric, quickly migrate through the oxide before being re-trapped at the oxide-silicon interface. A new method was proposed by which an electric field assists the migration of ions using corona discharge prior to high temperature processing. This method was shown to produce rapid, effective and stable passivation of silicon surfaces. This is the first time such ionic charge has been used to produce *stable* passivation of silicon surfaces with values of SRV<7.2cm/s. It is shown that ionic charge is stable for over 1500 days with lifetime decay time constants of over 17,000 days. This indicates that passivation would degrade by less than 37% over a period of

45 years. This is a remarkable increase in the stability of any extrinsic field-effect passivation method. The short length of this process makes it an industrially viable method where fast and effective migration of ionic charge can be optimised by tailoring the corona charge concentration, ion type, ion concentration, and temperature and time of the drive-in step. Overall, ionic FEP is a potential technique to reduce surface recombination in a controlled and durable manner, and it is very promising for the industrial surface passivation in solar cells.

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