

# A novel source of atomic hydrogen for passivation of defects in silicon

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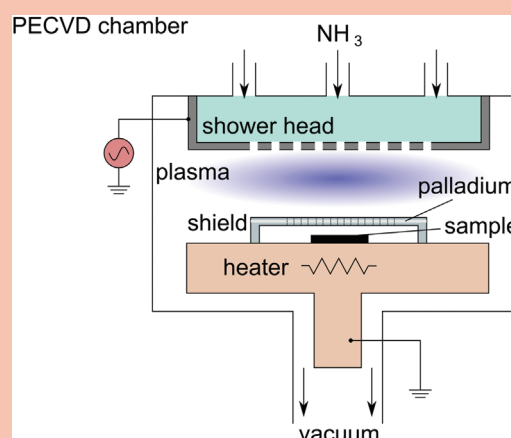
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Palladium membranes have been used for decades for the separation of hydrogen from other gasses. In this letter the use of thin palladium leaves to act as sources of atomic hydrogen for silicon samples is explored. It has been assumed in the past that although hydrogen diffuses through palladium in atomic form, the atoms recombine to form molecular hydrogen at the surface. In this letter it is shown that hydrogen supplied to one surface of a palladium leaf can result in atomic hydrogen being released from the opposite surface at low pressure. This is demonstrated through the use of a palladium leaf in a direct plasma system which allows for atomic hydrogen to be supplied to a sample while avoiding exposure to UV radiation from the plasma and high energy charged particles. This method is shown to provide significant atomic hydrogen to silicon samples and improve passivation of silicon surfaces.



Method of Shielded Hydrogen Passivation: Schematic of direct plasma chamber with a shield inserted between the plasma and the silicon sample.

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**1 Introduction** It is well established that hydrogen can be used to passivate surface and bulk defects in crystalline silicon. For traditional screen-printed solar cells, hydrogen has been incorporated into dielectrics such as  $\text{SiN}_x$  or  $\text{AlO}_x$  that are deposited on the surface and released through high temperature firing steps [1–3]. Increasingly, there are a number of solar cell architectures, including those based on passivated contacts or traditional heterojunctions [4–7], which seek to introduce hydrogen while avoiding further high temperature processing. Hydrogen passivation can still be a critical process for these architectures and has typically been introduced either via an anneal in an environment

containing molecular hydrogen, such as forming gas, or by exposure to an atomic hydrogen source, such as a remote plasma. In this letter, a novel source of atomic hydrogen is demonstrated which may be valuable for these devices.

**2 Method** This method is provisionally dubbed Shielded Hydrogen Passivation (SHP). This approach mitigates some of the common drawbacks of plasma exposure, while still acting as an effective source of atomic hydrogen. In this approach a 100 nm thick layer of 99% pure palladium, referred to as palladium leaf, is introduced between a hydrogen generating ammonia plasma and the

sample, as shown in Fig. 1. This palladium leaf is intended to absorb the UV photons and prevent them reaching the silicon surface, while allowing hydrogen to pass through. Palladium was chosen due to its high permeability to hydrogen, as evidenced by its use in hydrogen purification membranes [8, 9]. Furthermore, since the palladium leaf is electrically connected to ground, hydrogen passing through the leaf will be neutralized preventing ions or any energetic species striking the sample. While not attempted in this work it may also be possible to use this barrier layer to separate the sample from the plasma chamber entirely, allowing for rapid in-line hydrogen exposure. The system used in this work was an Oxford Instruments Plasmalab Plus 80, operated with a chamber pressure of 650 mTorr with a microwave power of 100 W.

Temperatures reported in this work are those of the system base-plate as measured by the internal thermocouple. While the samples are in intimate contact with the base-plate and are expected to be within a few degrees of the set temperature the leaf may be at a significantly higher temperature when exposed to the plasma.

Throughout the experimental process it became clear that the history of the palladium leaf played an important role in the results. It was observed that the amount of atomic hydrogen released appeared to increase when a single leaf was used multiple times. In order to investigate this, two types of leaf were used in these experiments. “New” refers to leaves that were placed into the holder with no prior processing before use. “Prepared” leaves, however, were loaded into the holder and exposed to ammonia plasma before being used for SHP. The preparation process took place with a base plate

temperature of 523 K and lasted 90 min, which had been empirically observed to lead to the greatest increase in atomic hydrogen release for temperatures between 373 and 573 K. The holder and leaf were then removed from the chamber and the chamber was cooled/heated to the processing temperature. The samples and the holder were then placed back into the chamber and SHP processing proceeded as normal.

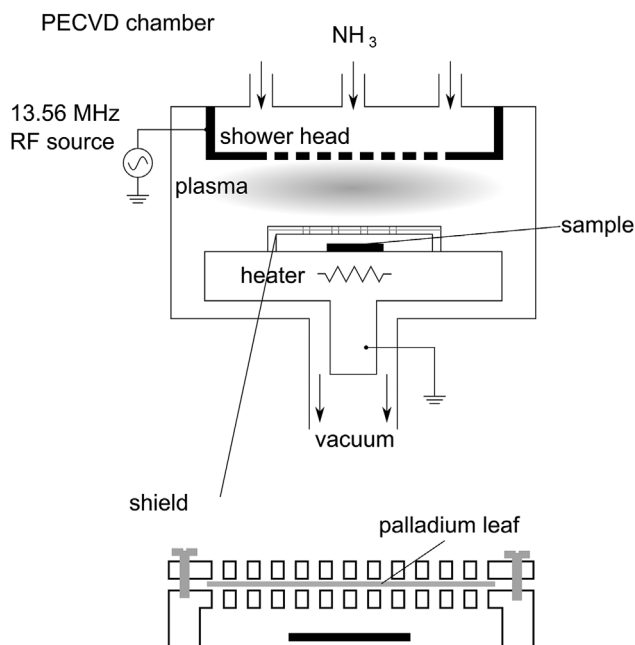
### 3 Atomic hydrogen release

**3.1 Experimental** The incorporation of hydrogen into silicon samples was observed via the passivation of boron in 0.175  $\Omega$  cm silicon. Atomic hydrogen entering the silicon rapidly becomes positively charged and subsequently bonds to substitutional boron [10], electrically de-activating it. This can be exploited via the use of the electrochemical capacitance–voltage (eCV) technique [11] to determine the hole concentration as a function of depth. This characterization technique has been demonstrated to be very sensitive to introduced hydrogen at temperatures below 473 K [12]. It becomes less effective at higher temperatures due to increased dissociation of the hydrogen-boron pairs [13].

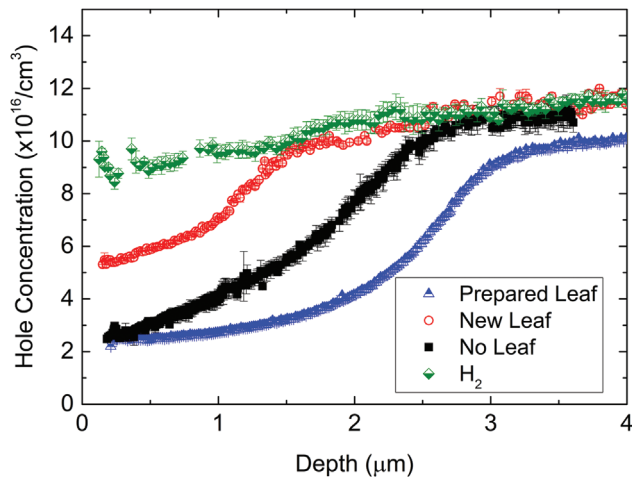
The first important question to be answered for this approach is whether sufficient atomic hydrogen reaches the surface of the sample through the palladium leaf. Samples were cleaned in a piranha etch, then any native oxide was removed using dilute HF. Samples were exposed with a new leaf, with a prepared leaf and with no leaf present (direct plasma exposure) for 20 min with a base plate temperature of 473 K. For comparison a sample was also exposed to molecular hydrogen in a quartz tube at 473 K at 1 atmosphere for 20 min. A WEP CVP21 eCV profiler was then used to determine the hole concentration near the surface.

**3.2 Results** Figure 2 presents the eCV profiles after each treatment. The reduced majority carrier concentration observed near the surface of samples treated in the plasma chamber demonstrated that significant deactivation of boron acceptors has taken place, presumably via atomic hydrogen de-activation. In contrast the sample exposed to molecular hydrogen showed no significant boron deactivation. The total density of boron de-activated in the sample with a prepared leaf was  $\sim 2 \times 10^{13}$  atoms/cm<sup>2</sup>, which provides a lower limit for the amount of hydrogen introduced.

The most striking feature of these results is that more boron appears to have been deactivated when a prepared leaf was present than when the samples were exposed to the plasma directly. It is considered unlikely that this represents an increase in the flux of hydrogen incident on the sample. The most plausible explanations are that this difference is due to either etching of the silicon or the creation of significant quantities of defects near the silicon surface through the plasma exposure [14, 15]. The defects can effectively trap hydrogen, and thus reduce the amount of hydrogen available to deactivate boron or diffuse further into the wafer, while hydrogen located at the defects cannot be detected using the eCV method. This would indicate that such damage was not introduced when the palladium leaf is



**Figure 1** Schematic representation of SHP apparatus used in this work. The palladium leaf is held in place between aluminium grids with 5 mm diameter openings.



**Figure 2** Hole concentration as a function of depth as measured using eCV for samples exposed to an ammonia plasma for 20 min at 473 K with a plasma power of 100 W. Samples were exposed directly to the plasma (black squares), with an as-received 100 nm palladium leaf inserted between the plasma and the sample (red circles), with this leaf prepared via a prior 90 min exposure to the plasma (blue triangles) and with exposure to molecular hydrogen (no plasma) at 1 atmosphere (green diamonds).

present. Despite these qualifications, it is plausible to suggest that the flux of atomic hydrogen on the sample surface for SHP was a non-negligible fraction of that for direct exposure to the same plasma.

The other important result is the critical importance of prior exposure of the leaf to the plasma. The rate of hydrogen desorption from Pd is such that almost no hydrogen is expected to remain in the leaf after short exposures to air at temperatures above 300 K [8]. As more than 300 s was required to vent the chamber and load a sample between preparation and subsequent hydrogen exposure significant storage of hydrogen in the film is unlikely. Rather it is proposed that this difference is a result of the removal of a surface layer such as an oxide or contamination on the palladium leaves, which initially acts as a barrier for atomic hydrogen.

## 4 Surface passivation

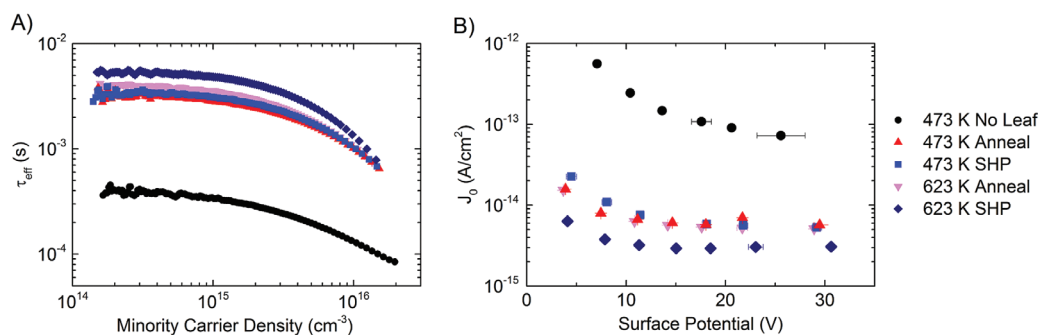
**4.1 Experimental** In addition to the ability to supply sufficient atomic hydrogen to the sample surface the other significant aspect of SHP to be confirmed was that it effectively blocked UV radiation and charged particles. In this experiment lifetime samples consisting of 200 μm thick 1 Ω · cm n-type float zone silicon with a 100 nm thermal oxide on both surfaces was used. The samples were exposed for 40 min per side with a base plate temperature of 473 and 623 K. Hydrogen passivation at the oxide interface was expected to be largely ineffective at 473 K and hence have no impact on the passivation, while at 623 K some passivation may occur [16]. Controls were provided by performing the identical process with no leaf present to observe the effects of unshielded plasma exposure and by switching the plasma off to determine the effect of the thermal process.

In order to characterize the quality of the interface, effective lifetimes were recorded as the surface charge was modified using corona charging in a point-to-plane set-up with a 30 kV bias and 10 s intervals [17, 18]. The resulting surface potentials were measured using Kelvin Probe. Effective minority carrier lifetime measurements were carried out with a Sinton Instruments WCT120, with intrinsic recombination calculated using the Richter model [19]. From these measurements the  $J_0$  term was extracted through fitting the corrected inverse lifetime for minority carrier densities above  $3 \times 10^{15} \text{ cm}^{-3}$  using:

$$\frac{1}{\tau_{\text{corr}}} = \frac{2J_0(n_0 + \Delta n)}{qwn_i^2} \quad (1)$$

The implied assumption is that the material is free of any defects, which may not always be the case [20]. This assumption was nonetheless deemed preferable to the use of an arbitrary or variable bulk lifetime for comparison of surface passivation.

**4.2 Results** Figure 3 presents the maximum injection level dependent lifetimes observed for each sample, as well



**Figure 3** (A) Maximum effective lifetime after corona charging as a function of minority carrier density for wafers processed for 40 min on each side, with direct plasma exposure (No leaf), SHP and thermal annealing (leaf in place, no plasma) at temperatures of 473 and 623 K. (B) Extracted  $J_0$  as a function of surface potential for each set of conditions.

as the extracted  $J_0$  as a function of surface potential. It is clear that when no leaf is present the interface between the silicon and the thermal oxide is significantly degraded, due to a combination of UV radiation and exposure to electric potentials that could cause breakdown of the dielectric. In contrast the sample which was processed underneath the prepared leaf at 473 K has a comparable effective lifetime and  $J_0$  to a wafer which has received the same thermal treatment without hydrogen present, indicating that there has been no significant degradation of the Si/SiO<sub>2</sub> interface.

At 623 K the  $J_0$  of the sample subjected to SHP reached a minimum of 2.9 fA, compared to 4.7 fA for the sample exposed to the thermal treatment alone. This corresponded to effective lifetimes of 4.8 and 3.6 ms respectively at a minority carrier density of  $1 \times 10^{15} \text{ cm}^{-3}$ . This result suggests that at 623 K hydrogen passivation at the silicon/oxide interface reduces the number of active interface traps, while still avoiding the introduction of any damage. Further evidence for a reduction in active interface trap density was provided by the observation that the sample subjected to SHP reaching its minimum  $J_0$  value at less than 20 V surface potential, while all other samples continued decreasing with surface potential up to 30 V.

**5 Discussion** It is important to note that these results are in apparent contradiction with the accepted literature on hydrogen permeation in palladium membranes as used in hydrogen purification. The accepted understanding of the permeation of hydrogen through a palladium membrane is that it consists of four steps [8]. The first is adsorption of molecular hydrogen onto the palladium surface. These molecules are split on the palladium surface, before diffusing through the palladium as atomic hydrogen. On the opposite surface it is widely reported [8, 9] that hydrogen undergoes recombinative desorption and is released once more as molecular hydrogen. Contrary to this expectation Fig. 2 clearly demonstrates that a substantial quantity of atomic hydrogen either passed directly through the leaf or was released from the palladium surface facing the sample.

The only previous reports of significant atomic hydrogen release from a palladium film are either during a phase transition [21] or under bombardment by electrons with energies in excess of 2 keV [22]. In comparison leaves in this work were exposed to ions with lower energies of up to several hundred eV [22, 23]. However the exposure to energetic ions and UV radiation may act to increase the energy of the hydrogen plasma within the leaf [22, 24]. This in turn may stimulate release of both atomic and molecular hydrogen.

The obvious difference between this work and most previous investigations on hydrogen permeation was the supply of atomic, rather than molecular, hydrogen to the palladium surface opposite the sample. Previous investigations with similar systems [25] have observed anomalously high permeations of hydrogen through a 20  $\mu\text{m}$  thick membrane, though with no distinction as to whether

hydrogen released from the membrane was in molecular or atomic form. While the mechanisms involved are still under investigation, it appears possible that there exist parallel processes for the release of atomic and molecular hydrogen from palladium. Under most hydrogen purification conditions described in the literature, the fraction released and detected as atomic hydrogen is insignificant [26], however, when hydrogen is supplied to a leaf in atomic form and released at pressures of around 1 torr this fraction becomes important.

An alternative explanation is that atomic hydrogen is passing through pinholes in the palladium leaf. Visual inspection against a bright light source detected some pinholes on particular runs, however no correlation was observed with the amount of atomic hydrogen detected. Furthermore, the total pinhole area was less than 0.1% of the total area of the leaf, making it unlikely that any hydrogen passing directly through these holes contributed significantly to the results.

**6 Conclusions** This paper has introduced the technique of shielded hydrogen passivation. It has been demonstrated that this method is capable of exposing silicon samples to significant quantities of atomic hydrogen, approaching those introduced by direct exposure to ammonia plasma at temperatures down to 473 K. This approach has also been shown to avoid any deleterious effects of exposure to UV photons and charged particles. The mechanisms involved in this process, as well as the importance of processing parameters on SHP effectiveness will be explored in future studies.

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