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Shielded hydrogen passivation – a novel method for introducing hydrogen into silicon

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Abstract

This paper reports a new approach for exposing materials, including solar cell structures, to atomic hydrogen. This method is dubbed Shielded Hydrogen Passivation (SHP) and has a number of unique features offering high levels of atomic hydrogen at low temperature whilst inducing no damage. SHP uses a thin metallic layer, in this work palladium, between a hydrogen generating plasma and the sample, which shields the silicon sample from damaging UV and energetic ions while releasing low energy, neutral, atomic hydrogen onto the sample. In this paper, the importance of the preparation of the metallic shield, either to remove a native oxide or to contaminate intentionally the surface, are shown to be potential methods for increasing the amount of atomic hydrogen released. Excellent, damage free, surface passivation of thin oxides is observed by combining SHP and corona discharge, obtaining minority carrier lifetimes of 2.2 ms and J_0 values below 5.47 fA/cm^2. This opens up a number of exciting opportunities for the passivation of advanced cell architectures such as passivated contacts and heterojunctions.

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1. Introduction

The use of atomic hydrogen to passivate impurities and defects in silicon has been widely reported in the literature with the broad consensus being that the effectiveness of this process is heavily reliant upon the quantity of

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hydrogen introduced into the silicon [1], [2]. In particular, recent work on thin oxides for passivated contacts has shown significant reductions in recombination at silicon interfaces after exposure to hydrogen [3], [4].

Whilst hydrogen containing dielectrics, such as silicon nitride or aluminium oxide, have proven to be excellent sources of atomic hydrogen under annealing at temperatures ranging from 400-900 ^{o}C [1], [5], [6], not all cell structures incorporate such dielectrics or high temperature processing. For these devices it would be preferable to have a direct source of atomic hydrogen. In the absence of a dielectric source typical sources include forming gas anneals or hydrogen plasma exposure.

Forming gas annealing causes no damage to silicon surfaces, and has been demonstrated to be capable of significantly improving surface passivation of Si/SiO2 interfaces [7], [8], however because the hydrogen is in the molecular form it is less effective in the absence of surface damage or a layer to split the hydrogen molecules [2]. In contrast direct exposure to a hydrogen containing plasma introduces vastly greater concentrations of atomic hydrogen, unfortunately a consequence of the plasma exposure is significant damage to the silicon surface [2]. This damage can be greatly reduced through the use of a remote hydrogen plasma system [9], [10], where the plasma is confined such that there is no direct line of sight between the plasma and the samples. Such systems have been successfully used in high efficiency passivated contact cell architectures [11].

The primary sources of damage from plasmas are a) hard UV radiation, b) impingement of energetic particles and c) charge deposition on unearthed surfaces (e.g. on an existing dielectric layer). The effect of each of these will vary based on the structure of the sample being exposed and the temperature of exposure. In a recent letter the authors proposed Shielded Hydrogen Passivation (SHP) as an alternative approach to avoid such damage, whilst still exposing samples to atomic hydrogen [12]. This was achieved through the insertion of an appropriate “shield” between a hydrogen containing plasma and the samples. In order to be most effective this shield should possess the following properties:

1. It should not transmit UV radiation
2. It must be chemically stable such that it is not itself damaged through plasma exposure
3. It should be electrically conductive such that it can be grounded. This ensures that electrical charges will not penetrate and build up on the sample
4. It should be highly permeable to hydrogen

The materials most likely to fill all these requirements are metals, with the extensively studied interactions of palladium with hydrogen making this a logical starting point.

1.1. Behavior of hydrogen in palladium

The diffusion mechanisms of hydrogen through palladium are well known due to extensive research in the hydrogen purification sector [13]. Palladium is commonly used as a purification membrane due to its catalytic properties and the high concentration of hydrogen that can be dissolved in the bulk [8]. The diffusion of hydrogen through palladium occurs in distinctive steps, as described by Pick *et al* [14].

If the hydrogen source is in molecular form, the first step, upon reaching the surface of Pd, is its dissociation into atomic hydrogen adsorbed to the metal surface. Atomic hydrogen then diffuses into the bulk until it reaches the opposite surface (diffusion of molecular hydrogen through the bulk does not occur). The release mechanism of hydrogen from Pd is usually reported as a recombinative desorption process by which atomic hydrogen recombines into its molecular form on the surface and is only then released into the surroundings.

The situation in the present work is different to most reported conditions in that the Pd is exposed to atomic hydrogen from the plasma. This condition means that the catalytic action of dissociating molecular hydrogen into its atomic form before transport is no longer required. In the experiments presented in this paper, there is still fast transport of atomic hydrogen through bulk Pd, but the recombinative desorption step is counterproductive as it would release molecular hydrogen from below the shield, which is not useful in passivating defects in silicon [15].

Since results presented here have shown successful introduction of atomic hydrogen into silicon samples using SHP, it is inferred that atomic hydrogen is released from the surface of the Pd shield. The authors do not believe that exposing Pd to an atomic hydrogen source has stopped the release of molecular hydrogen, but that it leads to

substantial release of atomic hydrogen via a parallel process. Release of atomic hydrogen from Pd has recently been reported by Tyurin *et al.* [16] although the experimental situation was rather different.

The experiments presented here aim to determine the amount of atomic hydrogen released under different conditions (such as temperature), and if this quantity can be increased by stopping the catalytic behavior of Pd in order to reduce the amount of molecular hydrogen released. Additionally, successful passivation of silicon-silicon oxide interfaces were demonstrated. This demonstrates SHP has the potential not only for use in a research environment but also to become an industrially relevant technique to be used for the passivation of complex cell architectures which require hydrogenation without the use of dielectrics, such as heterojunctions and passivated contacts.

2. Method

2.1. Shielded hydrogen passivation

A 100 nm layer of palladium, hereafter referred to as palladium leaf, is held in place by an aluminium holder and positioned between the atomic hydrogen generating plasma, which in this work was ammonia, and the sample to be passivated, as shown in Figure 1. For this work, palladium was used based on its high permeability for hydrogen [6], [7].

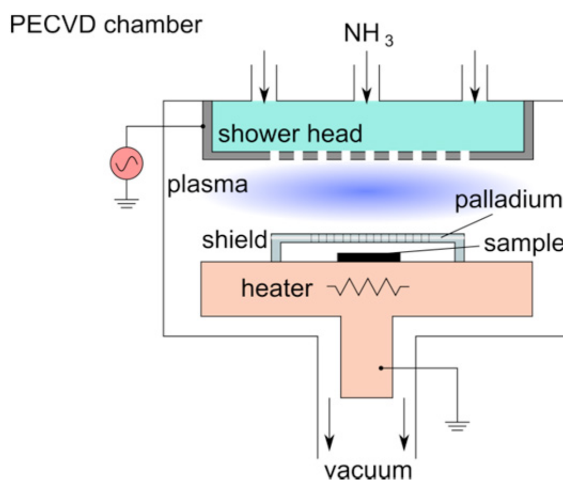

Fig. 1. Schematic of SHP apparatus used in this work. 100 nm Pd leaf held in place by two aluminium grids, 10 cm by 10 cm with 5 mm lattice and 2 mm thickness.

The PECVD parameters used for SHP on Si substrates are as follows: 100W RF power, 650 mTorr chamber pressure, 100 sccm ammonia gas. Temperature and time is varied depending on experimental purpose. Palladium leaf is readily available at low cost from decorative gold leaf suppliers in the form of 99% pure, 100 nm thick, 10 cm x 10 cm leaves.

2.2. Measuring hydrogen concentrations

The concentration of atomic hydrogen incorporated into silicon wafers was observed through the electrical deactivation of boron in 0.175 Ω.cm p-type silicon. The reduced active dopant concentration in the deactivated region is then measured using capacitance-voltage techniques (Wafer Profiler CVP21 from WEP) which provide a

lower limit for the total amount of hydrogen present [17], [18]. When atomic hydrogen is introduced into the samples it can either be trapped by boron atoms, by defects or pass straight through. As such, the level of boron concentration deactivated represents a lower limit for the concentration of atomic hydrogen introduced.

3. Results

3.1. Surface preparation

A critical parameter for the amount of hydrogen released from the leaf is the preparation of the Pd surface as discussed in a recent letter [12]. Figure 2 presents averaged active boron concentrations in the first 3-7 nm of the silicon wafer with a range of different surface preparations, clearly demonstrating significant de-activation of the boron acceptor. The background boron concentration level for all samples is 1.17 x 10^{17}/cm^3.

Figure 2 presents results from samples subjected to SHP treatment under five different leaf conditions:

1. The leaf as received directly from the manufacturer without any treatment
2. "Prepared" leaf: one side of the leaf exposed to hydrogen plasma for 90 minutes prior usage at 250 ˚C
3. Re-oxidised leaf: after "preparation" the leaf is subjected to 5 mins of oxygen ashing on both sides in a Reactive Ion Etcher (RIE), to form a thin PdOx layer on both surfaces. (PlasmaLabs 80+, 100 sccm O_2, 200 W, 30 mTorr at room temperature)
4. Poisoned leaf: surface of the leaf is contaminated with sulphur by exposure to very small concentrations of H_2S gas
5. No leaf: sample is directly exposed to the plasma

It can be seen in Figure 2, that when the leaf is used without any preparation treatment, low quantities of boron are deactivated in the sample, and thus little to no atomic hydrogen is inferred to have diffused through the leaf. When the leaf is prepared, the concentration of active boron atoms decreases from 1.1 x 10^{17} /cm^3 to 3.4 x 10^{16} /cm^3. When this same leaf is then re-oxidized and used in the SHP process, less boron is deactivated than with a prepared leaf. When a prepared leaf is contaminated with H_2S, levels of boron deactivated are similar if not slightly more than with a prepared leaf. Lastly, when no leaf is used and the sample is directly exposed to the plasma, a concentration of 6.1 x 10^{16} /cm^3 boron atoms is recorded.

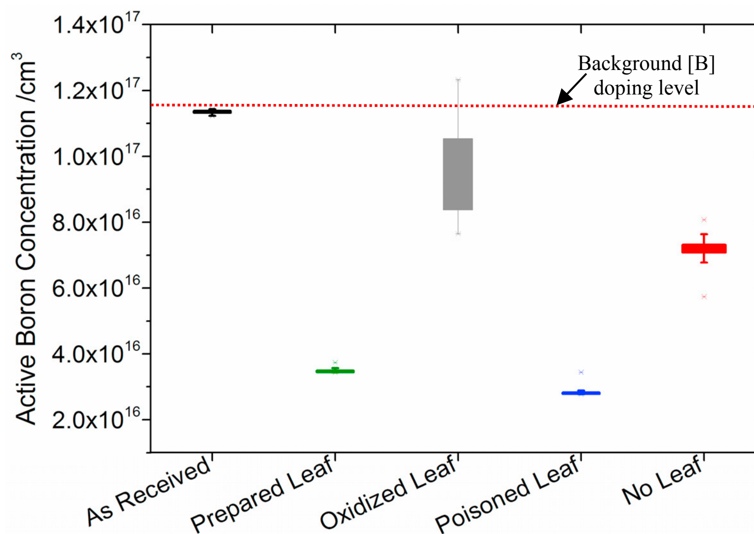

Fig. 2. Measured average active boron concentration in the first 3-7 nm of silicon samples with a uniform doping concentration of 1.17×10^{17} boron/cm^3 after exposure to an ammonia plasma for 20 minutes at 200 °C. Smaller values of active boron indicate a larger concentration of atomic hydrogen has been absorbed by the Si. Samples were exposed under the following Pd leaf conditions: as received, prepared, re-oxidised, poisoned and directly under direct plasma without a leaf.

The lower quantity of atomic hydrogen released by the as-received leaf is attributed to the presence of a surface oxide that acts as an effective barrier to atomic hydrogen. Literature suggests that the native oxide on palladium acts as an initial barrier for hydrogen diffusion [13] but that prolonged exposure to atomic hydrogen would cause its reduction so leaving the surface of the Pd bare [19]. Therefore, a leaf preparation step was used so as to remove the potential PdOx layers and facilitate the diffusion of hydrogen through palladium. Such treatment greatly increased the release of atomic hydrogen as shown in Figure 2.

Further evidence of PdOx being the cause of unprepared leaves opposing the diffusion of atomic hydrogen was obtained when a layer of oxide was intentionally grown on a prepared leaf by exposure to an oxygen plasma – an "ashing" treatment. When this re-oxidized leaf was used, little to no boron deactivation was recorded, suggesting that very little atomic hydrogen penetrated the leaf.

Another type of preparation thought to potentially impact the level of hydrogen introduced in samples is the contamination of Pd with sulphur. This poisoning has been shown to suppress the catalytic properties of Pd for splitting and re-forming hydrogen molecules [20]. By drastically reducing the rate at which molecular hydrogen is formed on the surface of Pd, it is hypothesized that relatively more atomic hydrogen will be released, resulting in higher levels of atomic hydrogen present in Si samples. It can be seen in Figure 2 that the samples exposed to plasma under a poisoned leaf appear to have slightly fewer active boron atoms, and thus slightly more atomic hydrogen present.

Lastly, the sample directly exposed to ammonia plasma without the protection of a Pd leaf showed a boron concentration of $7.1\text{x}10^{16}$ /cm^3 as shown in Figure 2. This suggests a lower concentration of atomic hydrogen than that observed with the use of a prepared leaf. It is possible that this lower level is not due to less atomic hydrogen being introduced but to less being trapped by boron atoms. Direct exposure to the plasma would be expected to create substantial surface damage, thus creating more traps for atomic hydrogen. Leaving less atomic hydrogen to deactivate boron atoms.

Through this experiment, methods of increasing levels of atomic hydrogen introduced in samples are investigated. It was found that preparation plays a critical role when using palladium leaves as shields as the native oxide, PdOx, may be detrimental to hydrogen diffusion. The effect of sulphur poisoning was also highlighted here as a potential way of increasing atomic hydrogen released from Pd surfaces.

3.2. Temperature dependence

One of the advantages of SHP over alternative processes is the ability to perform hydrogenation at low temperatures. In this experiment, the temperature dependence of levels of atomic hydrogen introduced was investigated. Fig. 3 presents the active boron concentration as a function of depth for wafers subjected to 20 minutes of SHP, performed with a prepared leaf, at temperatures between 150 °C and 250 °C. It is observed that at 150 °C boron acceptors trap large quantities of atomic hydrogen but at a very shallow depth. As the temperature is increased the surface hydrogen concentration is reduced but the depth over which atomic hydrogen is trapped increases so that the overall quantity of hydrogen present increases. This is in agreement with previous results [21].

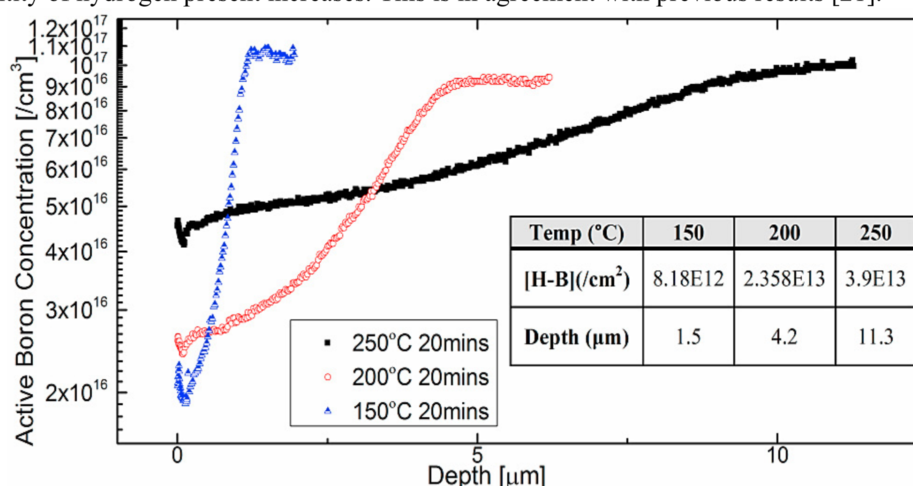

Fig. 3. Depth profile of active boron concentration as measured using ECV after exposure to SHP at temperatures between 150 °C and 250 °C. Inset: table with integrated [H-B] and corresponding penetration depth.

The shape of the curves seen in Figure 3 could be due to the bond between hydrogen and boron acceptors becoming weaker with increased temperature, thus causing de-trapping and re-trapping processes. More interestingly, Figure 3 shows that the total amount of hydrogen bonded to boron is increasing strongly with temperature in this range. It is unlikely that this increase could be caused by faster transport of atomic hydrogen through the Pd leaf, as this process is extremely fast and is not expected to be rate limiting in this temperature range. Instead, it is hypothesised that as temperature increases, the rate at which atomic hydrogen is released from the surface of Pd increases, which in turn would cause a relative increase of atomic hydrogen diffusing into samples.

3.3. Application to thin oxides

In order to demonstrate the application of SHP for the passivation of Si-SiO_2 interfaces, samples with 10 nm oxide layers were used. In this experiment, SHP was performed for 45 mins at 380 ˚C on both sides, using a prepared Pd leaf and 1 Ω.cm n-type FZ Si passivated with a 10nm thermal oxide, grown at 950 °C in a dry DCE environment. In order to obtain the optimal field effect passivation, the samples were corona charged post SHP as described in [22], [23]. Figure 4 illustrates the results obtained. It is observed that after SHP treatment, the surface passivation has been markedly improved as the minority carrier lifetime increased from 10 µs to 475 µs at 10^{15} cm^{-3} minority carrier injection level, shown as half-filled blue squares. Once extrinsic field effect passivation (FEP) was applied by means of surface charge using the corona discharge method, the lifetime improved to 2.2 ms at 10^{15} cm^{-3} injection level, shown as the empty red circles in figure 4. The sample that had not seen any SHP prior to corona, shown as the green triangles, only reached a lifetime of 1ms at 10^{15} cm^{-3} injection level. The J_0 values also confirm this improvement, as seen in Figure 4.

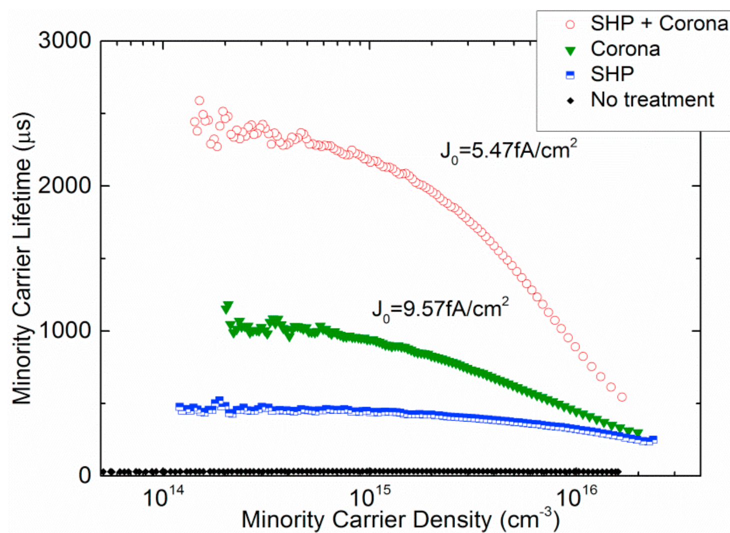

Fig. 4. Effective minority carrier lifetimes as a function of minority carrier density for a 1Ωcm 200µm n-type FZ Si sample with a 10 nm thermal oxide. The SHP exposure was performed at 380 °C for 45 minutes each side. The J_0 values were extracted using the Kane-Swanson method [24]

This is an important result as it demonstrates the potential of using SHP as a means of achieving excellent surface passivation at moderately low temperatures and on thin oxides. This also confirms that the potential damage caused by exposure to direct plasma was effectively avoided by the use of the leaf.

4. Conclusion

The somewhat unexpected observation of atomic hydrogen permeating and then being released from a Pd film opens up a number of exciting new possibilities. This novel technique is both an effective source of atomic hydrogen and is damage free. This paper has demonstrated the importance of leaf preparation and the effectiveness of SHP on thin silicon oxides, achieving minority carrier lifetimes lifetimes of 2.2 ms 10^{15} cm^{-3} injection level. The effect of temperature was also observed over a small range, where more atomic hydrogen is seen to deactivate boron acceptors as the temperature increases.

SHP has the potential to be an alternative to forming gas anneals and remote plasma exposures by performing efficient hydrogen passivation at low temperatures, with no damage and with minimal equipment needed. Furthermore, this technique could allow the samples to be located in a separate chamber from the plasma itself, opening up the possibility for in-line processing as depicted in Figure 5. In order to realize this shields will need to be demonstrated that are capable of withstanding pressure differences of up to 1 atm, while also maintaining sufficient atomic hydrogen fluxes at the sample surface.

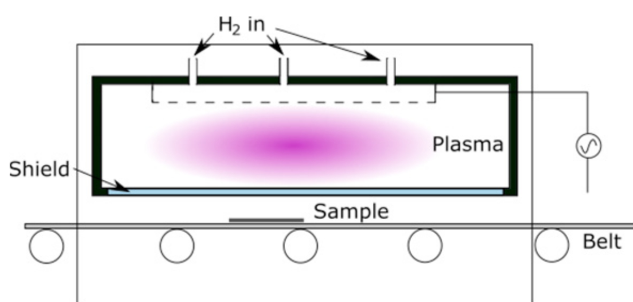

Fig. 5. Schematic of an in-line tool for SHP

For this reason, future work will focus on analyzing the effect of shield thickness or shield material on levels of hydrogen introduced. The effect of sulphur poisoning of the leaf and the potential application of SHP to a wide range of structures including passivated contacts will also be investigated.

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