PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION OF A-SI:H TO PROVIDE SURFACE PASSIVATION OF C-SI SURFACES AT LOW TEMPERATURE

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ABSTRACT: Excellent surface passivation has been obtained by post-deposition annealing of PECVD deposited a-Si:H thin film layers, which otherwise had low as-deposited passivation properties. Annealing near the deposition temperature was sufficient to improve the surface passivation for both n- and p-type silicon substrates, as demonstrated by effective carrier lifetimes increasing from initial values below 100µs to above 1ms on average. FTIR analysis of total hydrogen content and of mono- and dihydrides indicates that the presence of the latter bonds are a condition (but do not guarantee) for potential passivation. Neither total hydrogen content nor hydride concentration changes significantly with annealing. The surface passivation mechanism was studied by sequentially measuring the effective lifetime as a function of annealing time and temperature. The activation energy obtained in this way suggests that it is not the diffusion of hydrogen from within the a-Si:H film, but instead a re-arrangement of H already near the interface, that causes the improved passivation.
Keywords: a-Si:H, passivation, interface

1 INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) provides an excellent alternative to the problems of high-temperature junction formation [1,2]. The performance of this heterojunction is highly dependent on the recombination at the a-Si:H/c-Si interface. The interaction of hydrogen, provided by the a-Si:H layer, with the c-Si surface is of particular importance to improving surface passivation and overall cell performance.

It is known that the deep trapping sites (i.e. dangling bonds) at the c-Si surface act as recombination centers for photogenerated carriers from the base wafer. Hydrogen has been shown to passivate these bonds effectively using hydrogenated materials including a-Si:H [3] and a-SiN:H [4]. In the past, hydrogen has been assumed to diffuse from within the thin-film layer bulk towards the c-Si surface whereby passivation occurs [3,5,6,7]. However, bonded hydrogen requires 3.5eV [7,8] for release, leading to the conclusion that hydrogen must already be in a free or quasi-free state. The high dangling bond density eliminates the first assumption, leading Pantelides [9] to conclude the latter case, in the form of loosely-bonded hydrogen which can diffuse by 'bond interconversion' with an energy of 1.5eV. This represents the most-likely diffusion mechanism for hydrogen from the thin-film bulk. The defect density within a-Si:H is typically 10^{15}-10^{17} [10] which would significantly inhibit this diffusion process and reduce the passivation response to thermal annealing.

In this paper, we report our work on the study of intrinsic a-Si:H layers ability to reduce interface recombination at the c-Si surface. Understanding and optimising this layer is the first step in fabrication of a-Si:H/c-Si heterojunctions, and at the same time providing insight into the method of surface passivation. In particular, we have concentrated on the activation energy for the thermal surface passivation, gaining insight into the process itself, and an alternative method by which surface passivation can occur without relying on thin-film bulk-diffusion processes.

2 EXPERIMENTAL

1.4Ωcm c-Si(n) FZ, 0.7Ωcm and 2.5Ωcm c-Si(p) FZ were HNO_3/HF shiny-etched, RCA cleaned and received a HF dip immediately prior to deposition. The removal of the native oxide has been previously shown to influence the effectiveness of the a-Si:H layer to passivate the dangling bonds at the c-Si surface [11]. Intrinsic a-Si:H layers were deposited using a 5 Watt, 13.56MHz PECVD parallel-plate reactor, where the growth surface is inverted to the plasma allowing undesirable plasma components to be removed before reaching the surface. Wafers were heated to 225°C for deposition. Previously, relatively thick a-Si:H layers deposited have shown that annealing above the deposition temperature can improve the surface passivation significantly [11]. In this work, relatively thin layers (5nm, 10nm, 30nm, and 50nm) were deposited by plasma-enhanced chemical vapour, and the effective carrier lifetimes at mid-injection (1.0 x $10^{15}cm^{-3}$) measured by QSSPC and PCD [12].

3 RESULTS

3.1 Surface Passivation

The as-deposited carrier lifetime of these samples are shown in Figure 1 and are all below 100µs, indicating that any surface passivation present directly from deposition was not sufficient to dramatically reduce the overall surface passivation. Also shown are the effective carrier lifetimes following post-deposition annealing at 185⁰C, 215°C, 245°C and 275°C. This demonstrates that a significant overall improvement in surface passivation can be achieved, with lifetimes greater than 1ms on average at temperatures above and below the deposition temperature of 225°C. De Wolf shows similar improvements from post-deposition annealing, however, only for 50nm a-Si:H films deposited below 205°C [13,14].

Layers 50nm and thicker, are on average have lower τ_{eff} than thinner layers. Very thin layers (≤5nm), which are the preferred choice for surface passivation at the device level, were difficult to obtain with the single-chamber; simple PECVD reactor used in this study,

however, very good passivation was still possible. The quality of this passivation from such layers strongly relies on a high quality, carefully pre-conditioned surface and a high level of control over the initial stages of the deposition, which was not easily obtainable during this work.

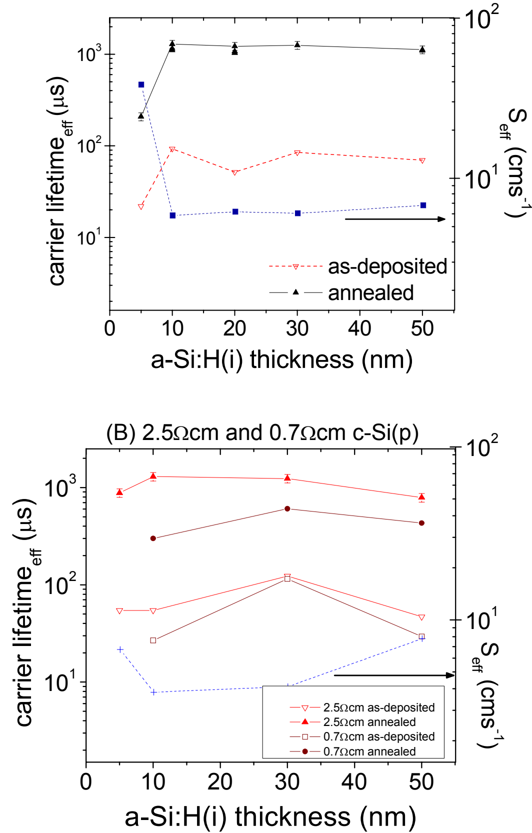

Figure 1: Effective carrier lifetime for a). n and b). p-type FZ c-Si with a deposited layers of a-Si:H(i) of varying thickness and the effect of post-deposition annealing. S_{eff} is shown (dashed line) for 1.4Ωcm c-Si(N) and 2.5Ωcm c-Si(P). All lines are guides.

3.2 Chemical bonding composition of layers

The total bonded hydrogen content, and the ratio of monohydrides (SiH)/dihydrides (SiH_2), all of which are potentially important to surface passivation, were measured by Fourier transform infrared spectroscopy (FTIR). No dynamic relationship is apparent between the effectiveness of the a-Si:H layers to passivate and the total bonded hydrogen within the bulk of the layer and at the interface. No noticeable change in the total bonded hydrogen was observed, irrespective of whether the measured effective carrier lifetime remained small or significantly increased. Furthermore, the mono- and dihydride bonds [15] showed little change despite the improvements from post-deposition thermal annealing (Fig. 2). No significant relationship is apparent for these bond concentrations relative to thin film layer thickness, and the total bonded hydrogen remains equivalent across all thicknesses indicating comparative similarity in hydrogen distribution within the a-Si:H as–deposited and after annealing.

An important feature integral to surface passivation is the concentration of the mono- and dihydride bonds. Whilst poor (as-deposited) and excellent (post-deposition anneal) surface passivation can be obtained when these bonds are present in significant quantities. When the as-deposited thin film layer is deficient in both these types of bonds no passivation occurs, even after significant thermal annealing. This also indicates that annealing does not form significant numbers of new hydride bonds which would occur if new hydrogen was made available.

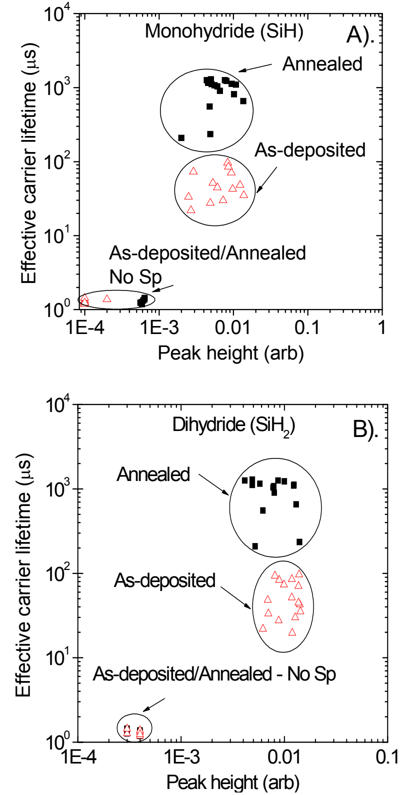

Figure 2: FTIR for a). monohydride (Si-H) and b). dihydride (SiH2) bond content for different a-Si:H layers. The lack of surface passivation even with annealing when mono or dihydrides are not present is shown.

3.3 Thermal activation energy of surface passivation

The method by which hydrogen passivates the c-Si surface has had limited debate. The complexity in studying the surface itself in combination with a narrow degree of indirect observation has led to the conclusion that hydrogen diffuses from the thin-film bulk towards the surface. Whilst hydrogen diffusion can of course occur, our results suggest that an alternative reaction-based mechanism involving hydrogen already very close to the interface may provide a valid alternative explanation.

The quality of the surface passivation provided by a-Si:H has been shown to improve drastically following post-deposition annealing from an otherwise poorly-passivated surface. Arrhenius calculations for the thermal activation energy for the surface passivation at the interface between a-Si:H and c-Si were performed from effective lifetime measurements taken as a function of time and temperature. The reaction rate of this improved surface passivation was determined by sigmoidal fit (Fig 3) to the measured effective carrier lifetimes using Eq1:

$$\tau_{reac} = 1 \Big/ \left[\frac{1}{\tau_B} + A \exp\left(\frac{1}{\tau_{reac}} \right) \right]$$

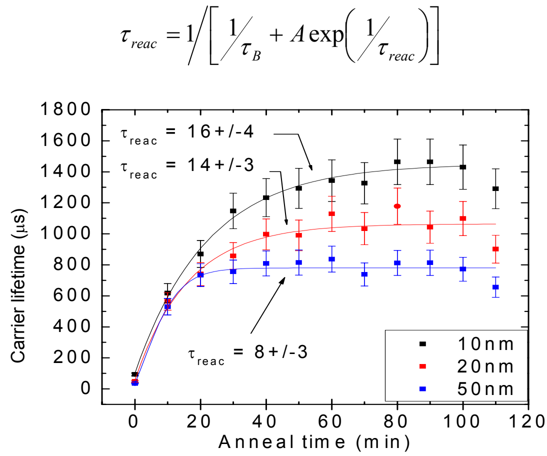

Figure 3: Improvements in the carrier lifetime from the as-deposited state, showing the result of the annealing process at 225°C upon differing thicknesses of a-Si:H(i). Sigmoidal fits are shown for each thickness.

It can be seen in Figure 4 that the annealing temperature determines the rate of surface passivation reaction. The lower 185°C requires extended anneal times.

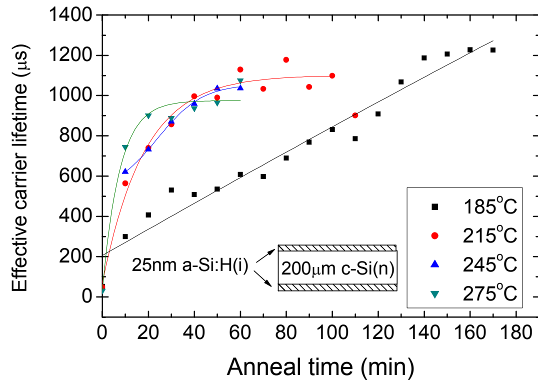

Figure 4: Annealing temperature dependence for 25nm a-Si:H indicating an increasing reaction rate for surface passivation with higher annealing temperatures. Fitted lines are shown

Anneal temperature near or higher than that used during deposition accelerate this reaction, and the saturation point for surface passivation occurs earlier.

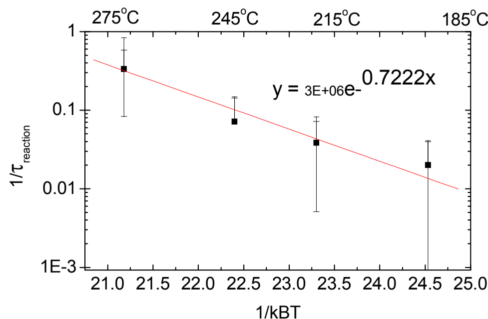

Figure 5: Arrhenius plot of inverse reaction rate showing the fit for determining the activation energy of this process. A-Si:H(i) layer is 25nm upon 200µm 1.4Ωcm c-Si(N). Fitted line according to Eq 2 is shown.

The reaction rates (τ_{reac}) were then plotted against inverse temperature (Fig. 5), where the activation energy for the greatly improved surface passivation from thermal annealing was calculated from the slope, according to Eq.2:

$$\tau_{reac} = A \exp\left[- E_A \big/ k_B T \right]$$

A value of 0.7 ± 0.1eV for the activation energy was calculated for shiny-etched (mirror-like), 1.4Ωcm n-type c-Si FZ wafers with varying intrinsic a-Si:H layer thicknesses for a range of temperatures (Fig 6). De Wolf reports a similar value for E_A of 0.6eV for a-Si:H films deposited at lower temperatures [14] than those used in this work. Biegelson [15] has previously reported an E_A of 0.5eV from electron-spin resonance measurements with thermal annealing up to 250°C and the concurrent reduction in Si dangling bond density. The lower E_A determined in this work would indicate surface passivation dependent upon surface states, rather than diffusion.

This value also differs from those reported for hydrogen diffusion processes in amorphous silicon (~1.5eV) [9,10], spontaneous hydrogen release (3.5eV) [7,8]. This would suggest that a different mechanism may be responsible for the surface passivation observed for a-Si:H deposited onto the crystalline surfaces in this work. One possible explanation is that this lower activation energy reflects the chemical re-arrangement of atomic hydrogen already present at the interface prior to deposition (HF-dip step), or else from hydrogen deposited during the initial stages of deposition.

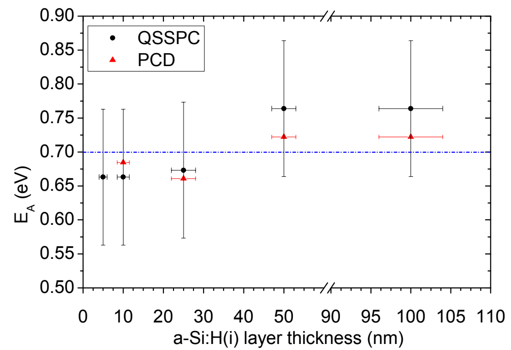

Figure 6: Calculated activation energies for a-Si:H(i) layers to passivate the c-Si surface.

4 CONCLUSION

In this work we have performed a comprehensive experimental study of the surface passivation that can be provided by PECVD intrinsic a-Si:H on n- and p-type c-Si. We have demonstrated that excellent surface passivation is achievable with an inverted growth surface at a very low deposition power which is seen following post deposition annealing on both n- and p-type substrates. The a-Si:H layers, from 5nm up to 50nm, in this work are shown to be thermally stable once the interface dangling bonds reach a hydrogen saturation/stable surface configuration point.

A principal finding of this work is the activation

energy for thermal surface passivation 0.7 ± 0.1eV, below the energies reported for hydrogen diffusion processes. Whilst H-diffusion may still occur for the purposes of providing interface surface passivation, our results indicate that hydrogen is already present at the c-Si surface in a state that does not passivate the surface fully. Additional hydrogen is provided by a a-Si:H during the initial stages of deposition. The activation energy determined in this work is associated with a reconfiguration of this near-surface hydrogen that results in stable hydrogen-bonds forming where recombination centers were previously present.

Of importance is the significance of the H-bond concentrations. Whilst the concentration of mono- and dihydrides appears to be standard in the bulk and at the a-Si:H/c-Si interface, there appears to be no noticeable change between the as-deposited and post-annealed samples despite the concurrent increases in carrier lifetime. Of particular note, is the near total deficiency of surface passivation when these bond types are not present, which identifies an additional method for in situ process measurements. In addition to the improved understanding for the surface passivation process, obtained from the new activation energy obtained in this work, further development in tailoring deposition conditions is possible for improving the performance of the a-Si:H /c-Si heterojunctions.

5 ACKNOWLEDGEMENTS

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