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Using an inductively coupled plasma, hydrogenated amorphous silicon (a-Si:H) films have been prepared at very low temperatures (<50 °C) to provide crystalline silicon (c-Si) surface passivation. Despite the limited nanostructural quality of the a-Si:H bulk, a surprisingly high minority carrier lifetime of ~4 ms is demonstrated after a rapid thermal annealing treatment. Besides the excellent level of surface passivation, the main advantage of the low-temperature approach is the facile suppression of undesired epitaxial growth. The correlation between the a-Si:H nanostructure and the activation of a-Si:H/c-Si interface passivation, upon annealing, has been studied in detail. This yields a structural model that qualitatively describes the different processes that take place in the a-Si:H films during annealing. The presented experimental findings and insights can prove to be useful in the further development of very thin a-Si:H passivation layers for use in silicon heterojunction solar cells. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4994795]

INTRODUCTION

The excellent surface passivation of the crystalline silicon (c-Si) surface that is attainable by thin films of hydrogenated amorphous silicon (a-Si:H) lies at the basis of the extremely high open-circuit voltages ($V_{oc}$) of silicon heterojunction solar cells.1,2 These have enabled the world record efficiencies of 25.6% (Ref. 3) and 26.6% (Ref. 44) for c-Si photovoltaics in 2014 and 2016, respectively. The typically 5–10 nm thick intrinsic a-Si:H layers in such solar cells are usually prepared by chemical vapour deposition (CVD), either by plasma-enhanced CVD (PECVD) or by hot-wire CVD (HWCVD).4,5

The bulk properties of a-Si:H, its passivating properties, and the correlation between them have been studied in detail. Studies on a-Si:H were originally mostly motivated by the application of a-Si:H in thin-film solar cells and thin-film transistors,6 whereas surface passivation became a crucial topic for silicon heterojunction solar cells.7 With respect to the a-Si:H bulk properties, the highest quality a-Si:H (i.e., material with the lowest defect density) is typically found in single-crystalline silicon (c-Si) and the correlation between the a-Si:H bulk properties and the c-Si surface is desired.7 This is most often achieved during the deposition of the a-Si:H layers, which is typically done by PECVD and usually at low pressures,8 although it has been shown that high pressures can yield good passivation as well.9,10 Additionally, post-deposition annealing is frequently employed as a tool to further relax the a-Si:H nanostructure and accommodate migration of atomic

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H from the bulk of the a-Si:H towards the a-Si:H/c-Si interface. Therefore, a sufficiently high hydrogen content in the film is generally preferred. Secondly, the lowest defect density and best surface passivation is typically obtained by preparing dense a-Si:H films close to the amorphous-to-crystalline transition, while making sure that the film maintains fully amorphous. Nonetheless, it has recently been demonstrated that highly porous a-Si:H layers prepared at 200 °C can significantly enhance the performance of silicon heterojunction (SHJ) solar cells by increasing the c-Si surface passivation quality. Such porous a-Si:H layers especially yield a superior passivation quality with ultrathin ~5 nm thick layers, which is in stark contrast to dense a-Si:H for which it is commonly observed that thicker films yield a better passivation quality. Thirdly, an atomically smooth a-Si:H/c-Si interface is desired, i.e., epitaxial growth should be avoided. The presence of epitaxial results in reduced levels of interface passivation, especially upon post-deposition annealing. Unfortunately, films prepared near the amorphous-to-crystalline transition are especially prone to epitaxy, generally limiting the experimental window for obtaining high levels of passivation in the as-deposited state. Epitaxial growth is typically avoided by tuning the plasma parameters, although “pulsed” material deposition with interleaved H2 plasma treatments has been shown to be effective as well.

In this work, we show that a different approach can be employed to produce highly passivated a-Si:H/c-Si interfaces that are free of local epitaxy. Using an inductively coupled plasma (ICP), highly porous 10 nm thick a-Si:H thin films have been prepared at very low deposition temperatures of 10–50 °C. Although such highly porous films provide virtually no passivation in their as-deposited state, a high level of surface passivation can be obtained by a very brief post-deposition annealing treatment of 30 s at 300 °C, as evidenced by minority carrier lifetime values in the range of ~1–4 ms. One of the key benefits of the low-temperature deposition is the facile suppression of epitaxial growth. Also, heavy ion bombardment during film growth is absent in this approach due to the remote plasma used in ICP, thereby avoiding the potential risk of damage to the c-Si substrate.

Thermal annealing of the films is employed as a well-controlled tool to both activate the surface passivation and relax the a-Si:H structure. The evolution of both the interface passivation quality and the optical and nanostuctural properties of the a-Si:H films is studied on very short (~30 s) and very long (~10^3 min) timescales. This study reveals insights into the physical mechanism behind the observed rapid passivation of the c-Si surface on short timescales (30 s) and subsequent depassivation on longer timescales (~10^1–10^3 min). These findings are explained in a model describing the relaxation of the system in terms of an anisotropic disordered a-Si:H network with mobile open volume deficiencies and hydrogen.

**EXPERIMENTAL SECTION**

**Sample preparation**

Si (100) wafers were used as substrates. Prior to deposition, the wafers were dipped in 1%-dilute hydrofluoric acid (HF) for 1 min in order to remove the native oxide. The 10 nm thick a-Si:H films were deposited using an inductively coupled plasma tool (PlasmaLab 100 ICP) from Oxford Instruments. The substrate temperature was varied between 10 and 100 °C, where active cooling through a chiller was used to enable depositions below room temperature. Helium backflow to the sample was applied to ensure a good thermal contact between the sample holder and the substrate. Argon and silane were both injected with a flow of 20 sccm and a plasma power of 400 W was applied. The pressure was actively controlled by an automated pressure controller (APC) to 10 mTorr. Annealing was performed in a Jipelec rapid thermal anneal (RTA) furnace under N2 ambient.

**Film analysis**

The passivation quality of the a-Si:H layers was evaluated using a commercial quasi steady state photoconductance setup (Sinton WCT-120TS) and quantified by the minority carrier lifetime τ_eff at an injection level of 10^15 cm^-3. Spectroscopic ellipsometry (SE) was performed using a Woollam M-2000 U rotating compensator ellipsometer, which provides (Ψ, Δ) data over a photon energy range of 1.24–6.50 eV. Ellipsometric spectra were collected at 60°, 70°, and 80° angles of incidence using a variable-angle sample stage. An optical-structural model for analysis of ellipsometric spectra consisted of a finite thickness a-Si:H film with optical response generated using a Tauc–Lorentz oscillator model on a semi-infinite c-Si substrate. The fit parameters obtained from this model include the a-Si:H film thickness, high-frequency dielectric constant ε∞, Tauc–Lorentz bandgap E_g, peak broadening B, oscillator strength A, and the peak central energy E_D. Raman spectra were recorded using a Renishaw inVia system, employing an excitation wavelength of 514 nm. The Raman spectra were fitted with two Gaussian functions that represent the low and high stretching modes LSM and HSM located at ~2000 cm^-1 and 2100 cm^-1, respectively. The LSM corresponds to hydrogen bonded in small open volume deficiencies like divacancies, whereas the HSM is indicative of hydrogen bonded at the surface of nanosized voids. The integrated absorption strengths of the LSM and HSM are used to evaluate the value of R^*. Since the R^* value represents the relative contribution of the hydrogen residing on the surface of nanosized voids to the total amount of Si-bonded hydrogen, it is a measure of the porosity of the film. Transmission electron microscopy (TEM) analysis (JEOL ARM 200 probe corrected TEM, operated at 200 kV) was used to study the cross-sections of films using focused ion beam (FIB) made lamellas.

**RESULTS AND DISCUSSION**

In order to obtain a range of a-Si:H nanostructures, the deposition temperature has been varied in the range of 10 °C to 100 °C. At low deposition temperatures, the films are expected to feature a high degree of porosity (as characterized by a high R^* value) and a high atomic hydrogen content due to a reduced surface diffusivity of radicals, which results in a limited restructuring of hydrogen and yields less thermal hydrogen desorption during growth. In order to investigate the nanostructure in the as-deposited state, the stretching
modes of the Si-H bonding have been investigated by Raman spectroscopy, as shown in Fig. 1. The sample prepared at 10°C shows a strong contribution of the HSM, indicating that it is a highly porous film. As expected, the relative contribution of the HSM reduces when increasing the deposition temperature to 50°C, indicating a reduced porosity. Interestingly, at higher temperatures of 75 and 100°C, additional stretching modes appear besides the LSM and HSM, which we attribute to the significant occurrence of epitaxy and/or nanocrystalline growth. This is corroborated by the fact that the SE spectra of such films could not be fitted with an a-Si:H-based model, as will be discussed later. Note that when deposited on a c-Si wafer with a native oxide, no epitaxial growth is observed and the relative contribution of the HSM decreases monotonically up to 100°C, as expected (not shown).

The results in Fig. 1 show that a low deposition temperature is an effective way to suppress epitaxial growth. This is confirmed by cross-sectional TEM images, as illustrated in Fig. 2. The image shows a sample prepared at 50°C which was capped with molybdenum oxide (MoOx) and hydrogen-doped indium oxide (In2O3:H), both prepared by atomic layer deposition (ALD). Although the surface was not fully atomically flat, no or a very minor epitaxial growth can be observed. The occurrence of this minor epitaxy at a deposition temperature of 50°C can be understood by considering that (nano)crystalline growth is observed at a slightly higher temperature of 75°C, as is illustrated by the Raman spectra shown in Fig. 1.

As Fig. 3(a) shows, the interface passivation quality of our low-temperature films can be rapidly activated by an anneal of 30 s at 300°C, as evidenced by the minority carrier lifetime τ values in the range of a few milliseconds. Apparently, the sample prepared at 50°C can yield excellent surface passivation, even despite the fact that the interface is not fully atomically flat. For the samples prepared at 75 and 100°C, no passivation was observed neither in the as-deposited state nor after annealing, which is attributed to the aforementioned prominent occurrence of epitaxial growth.

![FIG. 1. Raman spectra of a-Si:H films prepared at various substrate temperatures on HF-dipped c-Si wafers. The spectra of films showing epitaxy are displayed as dashed lines.](image)

![FIG. 2. High resolution cross-sectional TEM image showing the passivating a-Si:H layer on c-Si, prepared at 50°C. This sample was capped with ALD MoOx and In2O3:H.](image)

![FIG. 3. (a) Temporal evolution during annealing of the minority carrier lifetime for a-Si:H layers deposited at 10, 25, and 50°C. The corresponding changes in the Tauc–Lorentz bandgap, E_g, and broadening parameter, B_r, of the Tauc–Lorentz oscillator that were used to fit the SE measurement data are shown in (b) and (c), respectively.](image)
For the sample prepared at 50 °C and annealed at 300 °C for 2 min, the light soaking stability of its passivation performance under 1 sun illumination (AM1.5 G) at 25 °C has been investigated. The passivation quality proved to be stable after 120 h of light soaking, as the lifetime of the light-soaked sample and a reference sample (not light-soaked) only showed changes within the measurement error.

In addition, it should be noted that the passivation of films prepared at 50 °C can also be activated at temperatures below the relatively high annealing temperature of 300 °C employed in this study, and similar values have been obtained after annealing at 200 °C for 10 min.41 Nevertheless we chose to anneal the samples at 300 °C in this work, since this annealing temperature has previously been demonstrated to result in a large temporary increase in the refractive index of the film.10 This increase is attributed to an agglomeration of hydrogen in open volume deficiencies. The corresponding enhanced migration of both open volume deficiencies and hydrogen during annealing can prove to be beneficial when trying to increase the c-Si surface passivation quality.42

In order to unravel the mechanism behind the rapid passivation and its relation to the a-Si:H nanostructure, the evolution of the minority carrier lifetime, optical properties, and H bonding configuration has been studied for annealing times ranging from 30 s to 10^4 min. As can be seen in Fig. 3(a), for all three deposition temperatures the interface passivation is activated after the first annealing step of 30 s, with the highest lifetime of ~4 ms obtained for the sample deposited at 50 °C. Interestingly, all three lifetime trends show an approximate plateau, the temporal duration of which increases with deposition temperature, i.e., ~10 min for the sample prepared at 10 °C and ~500 min for the sample prepared at 50 °C. Note that the time period corresponding to this plateau increases with deposition temperature while the HSM integrated absorption strength (shown in Fig. 1) decreases. This could indicate that the migration of hydrogen away from the c-Si surface, which corresponds to an undesired depassivation of the c-Si surface, takes place more efficiently during annealing in more porous materials. Interestingly, this is in line with the findings in an annealing study of various a-Si:H bulk materials where it was found that the migration of open volume deficiencies evolves more efficiently in less dense materials.42

Note that on long timescales, all the samples indeed show a decrease in lifetime, hinting at depassivation of the a-Si:H/c-Si interface caused by the breaking of Si-H bonds at the c-Si surface. The samples prepared at 75 and 100 °C did not show any passivation both in the as-deposited state and after annealing due to the occurrence of epitaxy, and have therefore not been investigated further.

Figures 3(b) and 3(c) show the evolution of the band gap $E_g$ and broadening $B$ of the fitted Tauc–Lorentz oscillator. Interestingly, the band gap increases slightly after the first anneal step for all three samples, with the band gap value being the highest for the sample prepared at the lowest deposition temperature. This relatively large increase in band gap for the film deposited at the lowest temperature is in line with the earlier mentioned finding that the migration of open volume deficiencies takes place more efficiently in less dense materials. More specifically, when taking into consideration that the width of the band gap can be physically explained in terms of varying amounts of stress that open volume deficiencies exert on the surrounding matrix,43 it can be argued that the built-in stress is initially increasing during annealing, as evidenced by the increasing band gap. Upon subsequent annealing, the band gap values decrease monotonically and converge after ~10^5 min, indicating that the films have reached similar levels of stress. Interestingly, the band gaps decrease to values close to 1.4 eV, which appears to be the lowest band gap value that can practically be achieved for a-Si:H,43 corresponding to fully relaxed, defect-rich, hydrogen-poor a-Si:H. The broadening parameter shows a strong decrease after the first annealing step, indicating rapid rearrangement and thus a reduction of disorder in the a-Si:H network. Whereas the band gap values converge for the three deposition temperatures, the broadening of the oscillator does not, which shows that the final structure of the films is not equal, i.e., the amount of remaining stress in the films is likely comparable after prolonged annealing while the films can still exhibit different amounts of disorder.

The optical constants $n$ and $k$ of the films deposited at 10, 25, and 50 °C in both the as-deposited state and after 10^4 min of annealing at 300 °C are shown in Fig. 4 as a function of the photon energy. As can be seen, in the as-deposited state both $n$ and $k$ are higher for the samples prepared at higher substrate temperatures, indicating denser films, which is in line with the observed smaller HSM integrated absorption strength that appears for films grown at higher temperatures. After 10^4 min of annealing, the $n$ and $k$ values strongly increase, indicating film densification. This is also corroborated by an overall decrease in film thickness of approximately 6%, 5%, and 2% for the films prepared at 10, 25, and 50 °C, respectively, as indicated by SE measurements.

Using Raman spectroscopy, the hydrogen bonding configuration in the a-Si:H films has been tracked during isothermal annealing. Figures 5(a)–5(d) show the evolution of the nanostructure parameter $R^*$ as well as the LSM and HSM peak positions and widths. As expected, the $R^*$ value in the

![FIG. 4. Comparison of the optical constants $n$ and $k$ for films deposited at 10, 25, and 50 °C, both in the as-deposited state and after 10^4 min of annealing at 300 °C. The optical constants were determined from spectroscopic ellipsometry.](image-url)
as-deposited state decreases with deposition temperature, i.e., the relative contribution of hydrogen bonded at the surface of open volume deficiencies decreases. Interestingly, the temporal evolution of the \( R^* \) values upon annealing shows two regimes. At first, the \( R^* \) value is rather constant, but after a few hundred minutes of annealing a steady decrease starts. The peak positions of both the LSM and HSM contributions shift to lower frequencies upon annealing, with little difference observed for the various deposition temperatures. This shift is most likely related to film densification which is accompanied by a reduced screening of monohydrides that is typical for dense a-Si:H. The width of the LSM contribution is found to decrease monotonically upon annealing, pointing to a progressively more narrow distribution of the size of the small vacancies. Also here, no significant differences between the samples prepared at different deposition temperatures can be discerned. Interestingly, after \( 10^4 \) min of annealing there is a clear difference in the peak width of the HSM, with the sample prepared at the highest temperature having the highest peak width, i.e., this sample exhibits the broadest size distribution of various large vacancies and nanosized voids. This difference in size distribution can be the reason for the observed difference in the broadening parameter \( B_r \) in the Tauc–Lorentz analysis, i.e., the less disordered and more relaxed 50 °C sample allows for a wider size distribution of open volume deficiencies in the material. Furthermore, the size distribution difference after annealing is in line with the idea that agglomeration and effusion of open volume deficiencies take place less efficiently in denser materials, which—in this work—are the films deposited at higher temperatures. It can thus be argued that the final annealed state of the sample deposited at 10 °C is characterized by a narrower distribution of large open volume deficiencies in comparison to the 50 °C sample. This means that the latter material has a broader mix of large vacancies and nanosized voids than the 10 °C sample, most likely because the agglomeration and/or effusion of large vacancies takes place less efficiently in the 50 °C sample. Finally, it should be stressed that it is surprising that well-passivating layers can be achieved after a short annealing treatment for a highly porous type of a-Si:H, as opposed to the common notion that dense material with a very low \( R^* \) is a prerequisite for obtaining a high level of surface passivation. When taking a description of the a-Si:H nanostructure involving open volume deficiencies into account, the high level of passivation provided by annealed porous a-Si:H can likely be understood as the migration of hydrogen towards the a-Si:H/c-Si interface from the a-Si:H bulk either coming from Si-bonded hydrogen or molecular hydrogen that can both be present in open volume deficiencies. In contrast, for dense a-Si:H the surface passivation is probably already provided in the as-deposited state due to the much lower defect density and thus better dangling bond passivation in comparison to a nanosized void-rich material which typically has a relatively high defect density. Following this reasoning it can be argued that the migration of hydrogen in nanosized void-rich a-Si:H takes place more efficiently in comparison to dense a-Si:H, such that ample hydrogen atoms can reach the a-Si:H/c-Si interface and provide good surface passivation, even despite the likely lower electronic quality of the a-Si:H bulk that is typically associated with the presence of nanosized voids.

Since many processes are taking place simultaneously during annealing, as manifested in the discussion of Figs. 1–5, it is not straightforward to understand all the changes in the nanostructure that are taking place during annealing. Yet, in order to explain these changes in the various a-Si:H materials, a schematic illustration of the different processes that are taking place during annealing is depicted in Fig. 6. In this illustration, we distinguish three different time scales: (I) a short time scale on the order of seconds, (II) a medium range time scale on the order of minutes to a few hours, and finally (III) a long time scale on the order of tens of hours or more. During time period (I), there is a rapid improvement in
the a-Si:H/c-Si interface passivation due to the migration of hydrogen towards the interface which is most likely responsible for the vast increase in the minority carrier lifetime. Although this is the dominant process during time period (I), there is likely also some clustering of open volume deficiencies and hydrogen effusion, as described elsewhere for bulk a-Si:H, but these processes appear not to play a dominant role on such short timescales. Subsequently, on the moderate time scale (II), the DB passivation by hydrogen at the a-Si:H/c-Si interface stays approximately intact despite the more dominant role of open volume deficiency clustering and hydrogen effusion. This means that these three processes are rather equilibrated, although the loss of hydrogen from the film is already becoming apparent in the slow decrease of the minority carrier lifetime. Finally, the depassivation of the a-Si:H/c-Si interface clearly sets in on the long time scale (III) due to the outdiffusion of large open volume deficiencies and significant effusion of hydrogen from the film. This visualization correlates the a-Si:H nanostructure to the physical mechanism behind the a-Si:H/c-Si interface passivation mechanism that stands at the basis of the success of SHJ solar cells. Furthermore, this structural model can form a useful starting point for a more specific model on the hydrogen passivation mechanism of the c-Si surface. With this model, activation energies of the various processes which are dominant on different time scales could be evaluated to reach a more complete understanding of the passivation of the a-Si:H/c-Si interface.

Finally, for the application of the developed a-Si:H passivation scheme to c-Si solar cells, it is instructive to also investigate the passivation quality on Si (111) wafers, as Si (111) surfaces are obtained when a Si (100) wafer is wet-chemically random-pyramid textured. To this end, a set of symmetrical lifetime samples was prepared at 50 °C on both (100) and (111) wafers and these samples were subsequently annealed at 300 °C for 2 min. Minority carrier lifetimes of 7.9 and 5.0 ms were obtained on the (100) and (111) wafers, respectively. This underlines the ability of the process to achieve excellent surface passivation quality on both Si surfaces. Note that the lifetime achieved on the (100) wafer is even higher than achieved in the earlier described experiments, which could be due to a difference in chamber conditions and/or wafer quality as the Si (100) wafers that were used in this experiment originated from a different wafer batch.

CONCLUSIONS

ICP CVD with a remote plasma is used to deposit a-Si:H films on c-Si at low temperatures (10, 25, and 50 °C) such that the amorphous-to-nanocrystalline phase transition is not approached. At higher temperatures (75 and 100 °C), local epitaxy occurs as evidenced by poor surface passivation reflected in the minority carrier lifetimes provided by the samples. Despite the very low temperatures (<50 °C) which yield relatively high values of the nanostructure parameter R* as a classical indication of porous, defect-rich a-Si:H, it is nevertheless possible to achieve a good level of passivation of the c-Si surface by using a short rapid thermal annealing treatment (<1 min). This surprising finding can be understood in terms of a nanostructural description of a-Si:H in which open volume deficiencies play a critical role. More specifically, open volume deficiencies such as nanosized voids can aid the migration of hydrogen towards the a-Si:H/c-Si interface, especially in a-Si:H layers that contain a significant amount of such large open volume deficiencies. The nanostructure of the a-Si:H films prepared at different temperatures and their passivation quality is systematically investigated using spectroscopic ellipsometry, Raman spectroscopy, and quasi steady state photoconductance measurements. The result of this systematic investigation of the a-Si:H passivation layers is a qualitative model that describes how the passivation and depassivation of the a-Si:H/c-Si interface take place during annealing over a large range of timescales, explicitly involving the role of open volume deficiencies and migrating hydrogen. This model is expected to
be valuable in the further development of thin a-Si:H films, c-Si surface passivation layers, and SHJ solar cells.

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