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In situ probing of surface hydrides on hydrogenated amorphous silicon using attenuated total reflection infrared spectroscopy

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An in situ method based on attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) is presented for detecting surface silicon hydrides on plasma deposited hydrogenated amorphous silicon (a-Si:H) films and for determining their surface concentrations. Surface silicon hydrides are desorbed by exposing the a-Si:H films to low energy ions from a low density Ar plasma and by comparing the infrared spectrum before and after this low energy ion bombardment, the absorptions by surface hydrides can sensitively be separated from absorptions by bulk hydrides incorporated into the film. An experimental comparison with other methods that utilize isotope exchange of the surface hydrogen with deuterium showed good agreement and the advantages and disadvantages of the different methods are discussed. Furthermore, the determination of the composition of the surface hydrogen bondings on the basis of the literature data on hydrogenated crystalline silicon surfaces is presented, and quantification of the hydrogen surface coverage is discussed. © 2002 American Vacuum Society. [DOI: 10.1116/1.1469012]

I. INTRODUCTION

Investigation of plasma–surface interactions in plasma deposition of materials and the effect of these interactions on the deposited film properties requires knowledge of both the plasma and surface composition. While there have been many studies on the identity and concentration of gas phase species in SiH₄ containing discharges used for deposition of hydrogenated amorphous silicon (a-Si:H), studies on the composition of the surface during deposition are scarce. For a-Si:H, the hydrogen coverage of the surface is expected to influence the film quality through its effect on the interaction mechanisms of radicals impinging on the surface with the film. Surface reactions can also affect the incorporation of dangling bonds, leading to electronic defects, and the incorporation of hydrogen which influences the opto-electronic properties of the material such as the absorption coefficient and the optical band gap. Furthermore, the interaction of atomic hydrogen from the plasma with the film affects the film morphology, and it is believed that hydrogen in the film plays an important role in the photoinduced degradation of the electronic properties, the so-called Staebler–Wronski effect.

Information on silicon surface hydrides (SiHₓ, x ≤ 3) can be obtained through surface sensitive infrared absorption spectroscopy (in all its diversities), preferentially in situ and real-time monitoring of the film growth. The study of the surface hydrides is made difficult by the fact that the weak absorptions due to surface Si–H stretching modes cannot easily be discerned from the strong absorption by SiHₓ bonds in the a-Si:H bulk film. This problem can be partially solved by studying the absorption during the initial stages of film growth for ultrathin a-Si:H films. These experiments have indicated that mainly higher hydrides (SiH₂ and SiH₃) are present during the initial film growth, but one cannot distinguish whether these higher hydrides are present at the substrate–film interface and/or at the film–vacuum interface (the surface) for thicker films. In fact, these experiments do not reveal information about the surface composition and coverage under steady-state film growth conditions. In an attempt to resolve this information, Miyoshi et al. deposited a-Si:H on as grown a-Si:H films and analyzed the infrared spectra with respect to the spectrum of the as grown films. However, in spectra collected this way possible changes in the bulk SiHₓ bonds cannot be distinguished from changes in

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the newly deposited film and interactions of the plasma with the underlying film are obscured. This problem can be avoided by using methods that rely on isotope substitution. For example, Toyoshima et al. were able to detect the surface hydrides by depositing a-Si:D from a SiD$_4$ plasma on top of an a-Si:H film.$^{13,14}$ In such an experiment, the removal of the surface hydrides initially present on the a-Si:H surface is not obscured by SiD$_4$ absorptions in the newly deposited a-Si:D film. A similar technique relies on the exposure of a-Si:H films to atomic deuterium while monitoring the decrease in SiH$_2$ absorption due to the replacement of surface hydrides with their deuterated counterparts.$^{11,12,15}$

This method also reveals the interactions of atomic deuterium (hydrogen) with a-Si:H films, which are not limited only to hydrogen substitution at the surface.$^{16}$ A method recently applied to study the surface hydrides on amorphous and nanocrystalline silicon films$^{17}$ is the removal of the surface hydrides by low-energy ($\sim$20 eV) ion bombardment using a low ion density Ar plasma. The absorption by the hydrides before and after this Ar plasma was measured by attenuated total reflection Fourier transform infrared spectroscopy (ATR–FTIR). In this article, this technique is described in greater detail and the influence of the Ar plasma on the film is determined. Furthermore, a comparison between this technique and the above-mentioned methods using isotope substitution is given. The validity of the different techniques in terms of probing the surface hydrides is discussed along with their applicability and accuracy.

**II. EXPERIMENTAL SETUP**

The experiments were conducted in an inductively coupled plasma reactor at 13.56 MHz,$^{17}$ and the conditions for deposition, ion bombardment assisted desorption of the surface hydrides, and the isotope exchange experiments with D$_2$ are listed in Table I. For all conditions, the reflected power was less than 5% and the base pressure in the reactor was $10^{-7}$ Torr.

The ATR–FTIR setup is described in detail in Ref. 17. Briefly, GaAs (100) ATR crystals were used to extend the spectral range of the study down to 800 cm$^{-1}$. The number of total reflections at each side is 35, leading to a sensitivity in reflectance $R$ of $\Delta R/R \approx 1.4 \times 10^{-5}$ per reflection. The resolution of the spectrometer was set at 4 cm$^{-1}$ and spectra were collected in the range of 750–4000 cm$^{-1}$. However, this study focuses on the regions containing the stretching vibrations of the hydrides ("deuterides"). This is around 2100 cm$^{-1}$ for hydrogen and 1500 cm$^{-1}$ for deuterium. No polarization dependent studies have been performed. The absorptions are, however, measured with equal sensitivity in both polarizations because the electric field strength is about equal for the three components of the electric field at the a-Si:H surface for the angle of incidence used in this study.$^{18,19}$

**III. PROBING OF SURFACE HYDRIDES BY Ion BOMbardment ASSISTED DESORPTION**

**A. Procedure and identification of surface hydrides**

Approximately 200 Å thick a-Si:H films were deposited on ATR crystals and infrared spectra of the films were monitored in real time. At 200 Å the ratio of the absorption by bulk hydrides at $\sim$2000 cm$^{-1}$ (attributed to isolated SiH) and $\sim$2100 cm$^{-1}$ (attributed to SiD$_2$ and clustered SiD at internal surfaces) had already reached a steady state. Following the deposition, a reference spectrum was collected by averaging 1000 scans, which results in a total collection time of nearly 7 min. Subsequently, an Ar plasma was ignited for 2 s, using the pulse mode of a programmable rf power supply, and a spectrum with 1000 scans was collected with respect to the reference spectrum that was taken immediately after deposition. The 2 s long Ar plasma exposures were usually repeated up to a total exposure time of 10 s, collecting an infrared spectrum each time with respect to the reference spectrum of the as deposited film. This procedure is illustrated schematically in Fig. 1 and as will be shown below the spectrum taken after 10 s of Ar plasma exposure gives a very good indication of the hydrides initially present on the surface.

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**Table I. Experimental conditions for deposition of a-Si:H, ion bombardment assisted desorption of the surface hydrides by an Ar plasma, and the isotope exchange experiments with an Ar–D$_2$ plasma.**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Deposition</th>
<th>Ion bombardment</th>
<th>Isotope exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar flow (sccm)</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Ar/SiH$_4$ (1%) flow (sccm)</td>
<td>50</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>D$_2$ flow (sccm)</td>
<td>...</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Power (W)</td>
<td>50</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>40</td>
<td>20</td>
<td>40</td>
</tr>
</tbody>
</table>

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**Fig. 1. Schematic representation of the method used for probing surface and bulk hydrides in a-Si:H by ATR–FTIR. Hydrogen in both the bulk and on the interfaces is probed with a spectrum (b) during or after deposition with respect to a spectrum (a) of a clean crystal. Surface hydrides are probed by taking a spectrum (c) after ion bombardment, using an Ar plasma, with respect to a spectrum (b) of the film after deposition. In the text, spectrum (b) is referred to as the reference spectrum.**

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crystalline silicon (c-Si) surfaces of various crystal orientations and surface reconstructions.\textsuperscript{20–30} These studies are also used for assigning the different absorption peaks due to the different silicon hydride configurations present on the surface. Some of the assignments are still under debate, but most literature agrees on the following division. Absorption peaks at wave numbers between \(~2070\) and \(~2100\) \text{cm}^{-1} correspond to silicon monohydrides (SiH) on the surface, between \(~2100\) and \(~2130\) \text{cm}^{-1} to silicon dihydrides (SiH\textsubscript{2}), and between \(~2130\) and \(~2150\) \text{cm}^{-1} to silicon trihydrides (SiH\textsubscript{3}). A complication is the observation of SiH\textsubscript{2} vibrations at \(2091\) \text{cm}^{-1} (symmetric stretch) and \(2097\) \text{cm}^{-1} (isolated) on the Si(100)-(3 \times 1) surface\textsuperscript{24} and the observation of SiH\textsubscript{3} vibrations at \(2126\) \text{cm}^{-1} (asymmetric stretch) on the Si(111)-(7 \times 7) surface.\textsuperscript{25} Yet these are exceptions to the aforementioned division, which is expected to give a good approximate indication of the surface composition. For \(a\)-Si:H some controversy about the assignment of surface \text{Si–H} stretching modes still exists in the literature, but the majority of the studies are in approximate agreement with the above-mentioned assignments.\textsuperscript{11,12,14,15} Some minor discrepancies exist for the assignment of absorptions around \(2100\) \text{cm}^{-1},\textsuperscript{11,14} but cases in which absorptions by SiH are assumed to have higher wave numbers than absorptions by SiH\textsubscript{2} (at, respectively, \(2115\) and \(2091\) \text{cm}^{-1})\textsuperscript{31} may be erroneous on the basis of the data available for hydrogenated c-Si.\textsuperscript{20–30} The composition of the \(a\)-Si:H surface in terms of mono-, di-, and trihydrides is obtained by adding the total integrated absorbances peaking in the three aforementioned regions. This lumping of absorptions makes the determination of the surface composition less sensitive to the details of the deconvolution procedure. In terms of absorbance, the dihydride mode is dominant on the \(a\)-Si:H surface at \(230^\circ\text{C}\) as can be seen in Fig. 2.\textsuperscript{17,32} Expressed in absorbance, the distribution of hydrogen in the different hydrides is approximately 13\% in SiH, 51\% in SiH\textsubscript{2}, and 36\% in SiH\textsubscript{3}. Whether the surface contains mainly SiH\textsubscript{3} at \(230^\circ\text{C}\) depends on the relative oscillator strengths for the different stretching modes at the surface. This information is not available for SiH\textsubscript{3} bondings at the surface. The oscillator strengths for bulk hydrides are available, but not completely unambiguous. For the ratio of oscillator strengths of the bulk hydrogen stretching modes at \(~2000\) and \(~2100\) \text{cm}^{-1}, values ranging between 1 and 3 have been proposed.\textsuperscript{33–36} On the other hand, for hydrogen stretching modes in silane gases, it is found that the oscillator strength per Si–H bond is roughly the same for all the silanes.\textsuperscript{37} Thus the distribution of the SiH\textsubscript{3} absorbance may be presumed to be representative and a good approximation of the surface composition, as also indicated by the results in Ref. 32. For the \(a\)-Si:H surface at \(230^\circ\text{C}\), this would mean that 26% of the surface Si atoms are bonded to one hydrogen atom (SiH), 50\% to two hydrogen atoms (SiH\textsubscript{2}), and 24\% to three hydrogen atoms (SiH\textsubscript{3}). This in turn, the final composition of the surface can be determined reproducibly within 5\% accuracy as calculated from the standard deviation of experiments carried out at least in triplicates.

Figure 2 shows the spectrum of the surface silicon hydrides for a film deposited at 230^\circ\text{C}\) obtained using the method described above with 10 s Ar plasma exposure. Note that this spectrum is collected with respect to the reference spectrum of the as deposited film and that the spectrum only shows the changes that have taken place due to the Ar plasma exposure. The absorption is expressed in absorbance \[\text{absorbance} = -10 \log(I/I_{\text{ref}}),\] where \(I/I_{\text{ref}}\) is the ratio of the infrared radiation intensity after and before ion bombardment, respectively. Thus negative values of absorbance correspond to absorbing species removed from the film while positive values of absorbance correspond to newly generated absorptions. The absorption band between \(~2070\) and \(~2150\) \text{cm}^{-1} is therefore due to surface hydrides removed by ion bombardment. The peak centered at \(~1970\) \text{cm}^{-1} is related to Ar plasma induced changes in the bulk \(a\)-Si:H, which appear at lower wave numbers and which are much broader. Fortunately, these absorptions do not interfere with the higher frequency surface hydride modes. The absorption between \(2070\) and \(2150\) \text{cm}^{-1} shows some features and it can be deconvoluted into several narrow Gaussians with a full width half maximum in the range of \(6–14\) \text{cm}^{-1}, although sometimes on the level of noise, the features are expected to correspond to different configurations of hydrogen present at the surface and are therefore narrow. This has been supported by the fact that the features were consistently present, for all sputtering times and also under different plasma conditions and substrate temperatures. In fact, the exact deconvolution procedure involved an iterative approach in which multiple spectra were fitted using nonlinear least-squares optimization with different numbers of peaks. The total number of peaks and their positions were decided based on the need to include them to reproduce the features consistently observed in different spectra. Although some influence of noise cannot be excluded, it is believed that by far most of the features are real and that the deconvolution is appropriate. This is also corroborated by the agreement between the peak positions (within the resolution) and those obtained by numerous infrared absorption spectroscopy experiments on hydrogenated
present at 160 °C, along with an increase in contribution from wave numbers above 10 s, a rather abrupt increase in absorbance is observed. However, when the film is exposed to the Ar plasma longer than 10 s, a rather abrupt increase in absorbance is observed as well after ~10 s of Ar plasma exposure. The film used for generating this figure was deposited at 160 °C.

B. Effect of Ar plasma exposure time

The influence of the plasma exposure time on the spectra and the selection of an exposure time of 10 s for the determination of the surface composition are addressed next. Ideally, the films should be exposed to the Ar plasma only for the time necessary to remove all the hydrides present on the surface. This time is, however, not easily defined and we have explored the optimum Ar plasma exposure time by studying the changes in the infrared spectrum of the surface as a function of the exposure time. Figure 3 shows the integrated absorbances as a function of Ar plasma exposure time for the three wave number regions mentioned above for a film deposited at 160 °C. During the first 10 s of Ar plasma exposure only the surface hydrides (only SiH₂ and SiH₃ are present at 160 °C) are removed. This is evidenced by slight increases in their absorbances with increasing exposure time while their relative distribution remains roughly constant. However, when the film is exposed to the Ar plasma longer than 10 s, a rather abrupt increase in absorbance is observed along with an increase in contribution from wave numbers <2100 cm⁻¹. The latter is due to the appearance of a broad absorption at these lower wave numbers and this corresponds to removal of bulk-like SiH₄ bonds. This indicates that at these longer times, not only the surface hydrides are desorbed but that H is removed from the subsurface or from the bulk of the film as well. In fact, bulk SiH₄ bonds have absorptions centered at ~2015 and ~2100 cm⁻¹ for films deposited at 160 °C and the fact that after 16 min of Ar plasma exposure the SiH₄ absorption is still not centered at ~2015 cm⁻¹ but at slightly higher wave numbers indicates that still no real bulk a-Si:H has been sputtered but only the subsurface layer. It can be concluded that at up to ~10 s of Ar plasma exposure only the surface hydrides are removed. This conclusion is corroborated by spectroscopic ellipsometry measurements where for Ar plasma exposure times up to 10 s no changes in the film thickness have been observed. Figure 3 shows that even for shorter Ar plasma exposure times a good indication of the surface composition can be obtained, but at ~10 s the best signal-to-noise ratio is achieved because the absorbance corresponding to the removed surface hydrides is at a maximum. The integrated absorbance at this time will correspond approximately to the total amount of hydrogen present on the surface, i.e., the hydrogen surface coverage. Yet an accurate determination of this coverage will suffer from the difficulty in exactly determining the integrated absorbance corresponding to surface hydrides. This will be discussed in Sec. V. Finally, it should be noted that the time of Ar plasma exposure necessary to remove only the surface hydrides depends strongly on the properties of the plasma used for ion bombardment assisted desorption. Under the presented conditions, the ion energy and flux are approximately 20 eV and 2 × 10¹⁵ cm⁻² s⁻¹, respectively. Thus a 10 s Ar plasma exposure corresponds to an ion dose of 2 × 10¹⁶ cm⁻², which is in the expected order of magnitude to remove approximately 1 monolayer of adsorbates.

IV. COMPARISON WITH METHODS USING ISOTOPE SUBSTITUTION

A. Deposition of a-Si:H on a-Si:D

In this section the method of probing the surface hydrides by Ar ion bombardment as described in Sec. III is compared with other methods presented in the literature. First a comparison is made with the method used by Toyoshima et al. and Toyoshima who obtained the surface composition by depositing a-Si:H on an a-Si:D film while monitoring the surface deuterides removed from the initial surface. In the present study, SiD₄ was not available to exactly duplicate this procedure, and a-Si:D films were created by exposing a-Si:H films to an Ar–D₂ plasma for 1 min. This leads to an exchange of the hydrogen in a large fraction of the film and certainly in the topmost regions as evidenced by infrared spectra taken in real time. Subsequently, a-Si:H was deposited onto this film and information on the surface composition was obtained. The surface spectra cannot directly be compared with those of Toyoshima because the Ar–D₂ plasma treatment can also induce other changes in the bulk and at the surface, such as deuterium insertion in Si–Si bonds and a-Si:H etching. For the present purpose, which is to compare different methods for obtaining the surface composition, the effect of these changes is made irrelevant. This is done by comparing the surface spectrum obtained by the above mentioned method with a spectrum obtained by ion assisted desorption of deuterium from an a-Si:D film prepared by Ar–D₂ plasma treatment as well. Information about the assignments of the absorption peaks in the stretching region has been obtained from data available for deuterated c-Si surfaces.

The spectrum for the surface silicon deuterides, obtained by exposing an a-Si:D film deposited at 230 °C to an Ar plasma for 10 s, is shown in Fig. 4(a). The spectra obtained by depositing a-Si:H on top of the a-Si:D are shown in the
same figure: Figures 4(b) and 4(c) correspond to \( a\)-Si:D deposition times of 4 and 28 s, respectively. Comparison of the spectra shows that Fig. 4(b), recorded after 4 s of \( a\)-Si:H deposition on \( a\)-Si:D, resembles Fig. 4(a) both in absolute magnitude of absorbance and in peak positions. On the other hand, Fig. 4(c), recorded after 28 s of \( a\)-Si:H deposition on \( a\)-Si:D, shows a much higher magnitude of absorbance and, more importantly, peak positions different from those in Figs. 4(a) and 4(b). In Fig. 4(c), the dominant absorption is centered at 1528 cm\(^{-1}\) instead of 1534 cm\(^{-1}\), as is the case for both Figs. 4(a) and 4(b). Furthermore, the shoulder at higher wave numbers is less pronounced in Fig. 4(c). From a comparison with a spectrum of bulk \( a\)-Si:D [Fig. 4(d)], which has broad absorption peaks centered at 1475 and 1525 cm\(^{-1}\), it can be concluded that during the 28 s of \( a\)-Si:H deposition in Fig. 4(c) the underlying \( a\)-Si:D bulk is influenced by the SiH\(_4\) plasma. The fact that the absorption peaks are not yet centered at the positions of the bulk deuterides indicates that only the probably less dense region close to the surface is influenced. Apparently, depositing \( a\)-Si:H on top of an \( a\)-Si:D film eventually not only removes the surface deuterides but also induces changes in the bulk \( a\)-Si:D. This can occur by hydrogen diffusion or by penetration of the film by radicals or ions from the plasma. In fact, this experiment shows that the reactions that lead to deposition and hydrogen incorporation take place not only on the surface but most likely in a thin reaction zone that includes subsurface layers. These changes are not observable for short deposition times when the SiH\(_4\) plasma has only had time to affect the surface. Indications for bulk modification already appear after 7 s. This illustrates that caution is required when this method is applied: when the film is exposed too long to the SiH\(_4\) plasma (\( \geq 7\) s for the present experimental conditions and consequently more sensitive to time than Ar ion bombardment), not only are the deuterides on the surface removed but also the underlying film is changed. This can complicate the determination of the surface composition when this method is used.

From Figs. 4(a) and 4(b) the surface composition of the \( a\)-Si:D film at 230 °C can be determined by deconvoluting the SiD\(_2\) absorption band with absorption peaks centered at 1510, 1525, 1535, and 1550–1570 cm\(^{-1}\) (See Fig. 5). These absorptions are attributed to SiD, SiD\(_2\)/SiD\(_3\), SiD\(_2\), and SiD\(_3\) stretching modes, respectively.\(^{21-23}\) As both SiD\(_2\) and SiD\(_3\) contribute to the absorption at 1525 cm\(^{-1}\), the absorbance at this position is divided among SiD\(_2\) and SiD\(_3\) on the basis of the ratio of their absorbances at 1535 and 1550–1570 cm\(^{-1}\), respectively. For the surface composition of the \( a\)-Si:D films at 230 °C this means that, in terms of absorbance, \( \sim 15\%\) of the surface deuterium is bonded as SiD, \( \sim 35\%\) as SiD\(_2\), and \( \sim 50\%\) as SiD\(_3\). Compared to the \( a\)-Si:H surface at 230 °C, the \( a\)-Si:D surface contains relatively more SiD\(_3\) at the expense of SiD\(_2\). This can possibly be attributed to the preparation method of the \( a\)-Si:D film (Ar–D\(_2\) exposure of \( a\)-Si:H) also causing insertion of deuterium in Si–Si bonds at the surface.

We note that, if one assumes that spectrum (c) shows a pure “surface spectrum” with no contribution of the bulk, one would most probably draw roughly the same conclusion about the dominant bonding configuration of the surface deuterides, yet on a wrong basis. This can lead to erroneous interpretations, especially in attempts to quantify the surface composition. In conclusion, the method of depositing \( a\)-Si:H on \( a\)-Si:D (or vice versa) also requires a careful examination of the influence of deposition time (more so than for the ion bombardment assisted desorption method) as changes in the bulk are easily induced.

B. D/H exchange by Ar–D\(_2\) plasma exposure

Another method of probing the surface hydrides on \( a\)-Si:H is by replacing them with atomic deuterium generated from a D\(_2\) plasma.\(^{11,12,15}\) We investigated this method by exposing an \( a\)-Si:H film deposited at 230 °C to an Ar–D\(_2\) plasma for different amounts of time. In Fig. 6, the spectra of this film taken after 0.2 s [Fig. 6(b)] and after 7 s [Fig. 6(c)] of Ar–D\(_2\) plasma exposure are given. It is expected that for a properly chosen exposure time, atomic deuterium will replace the hydrogen atoms on the surface, and that the corresponding decrease in absorbance due to the removed hydrides yields an indication of the composition of the surface. On the other hand, the increased absorbance due to the newly created surface deuterides does not give a good indication of...
the surface composition because atomic deuterium can also induce other changes at the surface.\(^{16}\) This has no implications for the absorbance corresponding to the disappearing hydrides as this region of the spectrum shows only what has been removed from the surface. However, the fact that this technique does not work out properly can be seen in Fig. 6. A comparison between the spectrum taken after 0.2 s Ar–D\(_2\) plasma [Fig. 6(b)] and that taken after 10 s Ar plasma exposure [Fig. 6(a)] shows a discrepancy in the positions of the (dominant) absorbances. The main peak in Fig. 6(a) is positioned at 2112 cm\(^{-1}\), while the main peak after deuterium substitution is positioned at 2102 cm\(^{-1}\). This shift to lower wave numbers is also observed for longer exposure times [e.g., in Fig. 6(c)] and implies that hydrogen in the bulk is affected by the Ar–D\(_2\) plasma exposure. Deuterium substitution is apparently very fast compared to the removal of the surface hydrides by ion bombardment or by deposition. The fact that the total absorbance of Fig. 6(b) is roughly of the same order of magnitude as for Fig. 6(a) implies that modifications in the bulk occur before the hydrogen on the surface is completely substituted by deuterium. This fast bulk change is possibly due to fast diffusion of deuterium in a-Si:H and/or to deuterium ions in the Ar–D\(_2\) plasma, which can easily penetrate the film. Because of this simultaneous modification of the bulk, spectra showing only the surface hydrides cannot be obtained by an Ar–D\(_2\) plasma, not even when the exposure time is decreased. An interaction by deuterium ions can be circumvented by using atomic deuterium, e.g., created on a hot filament. However, thus far mainly plasmas have been used to create atomic deuterium for probing the surface hydrides.\(^{11,12,15}\)

V. DISCUSSION

From the results, it can be concluded that absorptions by surface hydrides and by bulk hydrides can be distinguished by comparing infrared spectra before and after Ar ion assisted desorption of surface hydrides and that this method gives an accurate and unambiguous representation of the surface composition. Furthermore, this method is easier to apply than the techniques that utilize isotope substitution. The surface deuterium removal by depositing a-Si:H on top of an a-Si:D film is also a viable method for determining the surface hydride composition and results obtained using this method are in good agreement with the ion bombardment assisted desorption method. However, deuterium removal by depositing a-Si:H on a-Si:D is more sensitive to exposure time due to fast deuterium substitution in the bulk. Probing the surface composition by substituting hydrogen with deuterium using an Ar–D\(_2\) plasma is complicated for the same reason. Moreover, bulk hydrogen substitution can occur on even shorter time scales, even before all surface hydrides have been replaced, rendering this method unfeasible. Furthermore, using an Ar plasma to probe the surface hydrides has a practical advantage of eliminating the need for D\(_2\) or, very expensive, SiD\(_4\). Moreover, the ion assisted desorption technique can also be used in a broad range of (plasma) deposition and surface modification processes, even in cases where isotope substitution experiments are unfeasible, e.g., in the study of fluorine surface termination. A disadvantage common to all three techniques is that no real time information on the surface composition during film growth is obtained. In all three cases the film deposition has to be stopped to take a reference infrared spectrum. Complications can arise especially when thermal hydrogen desorption from the surface takes place. The time between deposition and probing of the surface can, however, be shortened by using a technique with enhanced sensitivity like attenuated total reflection infrared spectroscopy.

Concerning the determination of the surface composition by Ar ion bombardment, the best accuracy has been obtained after an Ar plasma exposure of 10 s. This corresponds roughly to the time necessary to completely remove the hydrides from the surface (see Fig. 3). Although easier than the methods using isotope substitution, it is still difficult to decide accurately on the time necessary to remove exactly all surface hydrogen. This complicates the determination of the hydrogen surface coverage from the infrared absorbance. Another problem in calculating the surface coverage is the lack of knowledge about oscillator strengths or proportionality constants of the different hydride configurations that relate the hydrogen areal density to the infrared absorbance. Two approaches have been used in the literature for estimating the a-Si:H hydrogen surface coverage.

In the first approach, the proportionality constants for hydrogen in the bulk of a-Si:H determined by, for example, Langford et al.\(^{33}\) have been used. This procedure has been applied by Katiyar et al.,\(^9\) Toyoshima et al.,\(^{14}\) and von Keudell and Abelson\(^{41}\) who all used data on the bulk stretching mode at 2100 cm\(^{-1}\). The number of hydrogen bonds is related to the integrated absorption coefficient \[I(\alpha/\omega)d\omega\), where \(\alpha\) is the absorption coefficient and \(\omega\) is the frequency\] by the proportionality constant \(A\). \(A\) is theoretically defined as\(^{33,37}\)

\[
A = \frac{cn\mu\omega}{2\pi^2e^*},
\]

where \(c\) is the speed of light, \(n\) is the refractive index, \(\mu\) is the reduced mass, and \(e^*\), is the effective charge of the
dipole in the solid. Values for $A$ between $1.4 \times 10^{20}$ and $2.2 \times 10^{20}$ cm$^{-2}$ have been reported in the literature for the 2100 cm$^{-1}$ bulk absorption peak in $a$-Si:H and from these values, an effective charge of $\sim 0.3$–0.4 has been calculated.33,36 It is claimed$^{36,37}$ that the effective charge of the dipole in the solid $e^*_S$ is related to the effective charge $e^*_G$ of the same oscillator in a gas molecule by a local field correction. This local field correction, which is still under discussion,$^{36,37}$ causes the effective charge of a dipole to be larger than the corresponding one in a gaseous molecule.$^{37,42}$ When the above $A$ values for bulk hydrogen are used to calculate the hydrogen surface coverage, it is assumed that the required local field correction and therefore also the effective charge for the surface hydrides are identical to those for the bulk hydrides. This assumption is not trivial because there is a large shift (up to $\sim 80$ cm$^{-1}$) in absorption frequencies for bulk hydrogen as compared to surface hydrogen and this frequency shift depends, among other factors, on the effective charge of the dipole.$^{30}$ Another aspect is that the refractive index in Eq. (1) is lower in the surface region than in the bulk. Assuming 50% voids and using Bruggeman’s effective medium theory,$^{43}$ a 40% lower refractive index is estimated on the surface. Neglecting these aspects and applying the proportionality constants for hydrogen in bulk $a$-Si:H to convert the surface infrared absorbance data in Fig. 2 to surface hydrogen coverage yields a surface hydrogen areal density of $(3.0–4.6) \times 10^{14}$ cm$^{-2}$.

In the second approach, surface infrared absorbance data on hydrogenated $c$-Si surfaces have been used to obtain the hydrogen surface coverage on $a$-Si:H surfaces. $^{17}$ Jakob $et$ $al.$ have reported an integrated absorbance of $2.27 \times 10^{-3}$ cm$^{-1}$ for the stretching mode at 2086 cm$^{-1}$ due to 1 monolayer of hydrogen on a ideally terminated Si(111) surface ($7.83 \times 10^{14}$ cm$^{-2}$ H atoms).$^{30}$ When this absorbance is expressed as the integrated absorption coefficient $[\int (\alpha/\omega) \omega d\omega]$ and linked to the monolayer coverage, the corresponding proportionality constant $A$ for a Si(111) surface can be calculated to be $3.13 \times 10^{20}$ cm$^{-2}$. Using this proportionality constant yields an amount of hydrogen removed from the surface of the film in Fig. 2 of $6.7 \times 10^{14}$ cm$^{-2}$. This coverage is larger than the one found when applying the values proposed for bulk hydrogen. An important difference in this respect is that the effective charge of the SiH oscillators on the Si(111) surface as calculated by Jakob $et$ $al.$ is $0.120 \pm 0.005$. $^{30}$ This is much smaller than the values of the effective charge proposed for bulk hydrogen.

This second approach, using the literature data on a hydrogenated Si(111) surface, seems to be more appropriate. It gives a higher hydrogen coverage and it would therefore correspond better to the fact that the hydrogen surface coverage is expected to be close to unity for $a$-Si:H (see below).$^{44,45}$ The approach is also more straightforward in the sense that no important assumptions need to be made about the local field correction, because basically the local field is expected to be similar for both the $a$-Si:H and the Si(111) surface. There is however a complication. The SiH oscillators on a Si(111) surface are aligned, and therefore the electric field experienced by one oscillator is screened by the dipole fields of all the other oscillators. This leads to a screened effective charge by a macroscopic screening factor $e^*_\infty$: $^{19}$

$$e^*_\text{screened} = e^*_\text{unscreened}/e^*_\infty.$$  

The macroscopic screening factor for the fully hydrogenated Si(111) surface calculated by Jakob $et$ $al.$ is $2.0 \pm 0.4$, $^{30}$ while for the Si(100)-(2×1) surface, Chabal has estimated a macroscopic screening factor $e^*_\infty$ of $\sim 1.4$. $^{19}$ The amount of screening is actually expected to be approximately equal for both the Si(111) and Si(100)-(2×1) surface and the rather large uncertainties in these values should be taken into account in this respect.$^{46}$ No information is available about screening on an $a$-Si:H surface, but taking the above considerations into account, the screening for the $a$-Si:H surface might be somewhat lower than for $c$-Si surfaces due to the amorphous nature of the $a$-Si:H. Large differences are not expected because no shift in the frequencies of the different SiH$_x$ stretching absorptions has been observed (within the resolution) compared to $c$-Si surfaces.

From the above discussion, it is clear that calculating the amount of hydrogen on the $a$-Si:H surface is a complicated matter. Different approaches have been applied in the literature each with their own uncertainties. Although we have a preference for the second approach, not enough information is available to decide on which approach is the most appropriate for the $a$-Si:H surface. An additional difficulty is that the number of Si surface sites is unknown for the $a$-Si:H films. This inhibits an exact calculation of the hydrogen surface coverage of $a$-Si:H, which is considered to be a very relevant parameter in $a$-Si:H film growth.$^{1,2}$ Assuming the $a$-Si:H surface to be Si(100)-(1×1) like [i.e., a Si surface site density equal to that of Si(100)] with also on average 2 hydrogen atoms per surface Si atom] a hydrogen surface coverage of $\sim 0.2$–0.3 equivalent monolayer is obtained when applying the bulk proportionality constants and $\sim 0.5$ monolayer when using the data on hydrogenated Si(111). These values of the coverage are not close to unity for both cases as is expected for $a$-Si:H.$^{44,45}$ But this can be due to a lower Si surface site density of the $a$-Si:H compared to $c$-Si surfaces (especially here, where we used a very diluted Ar–SiH$_x$ mixture to deposit the $a$-Si:H). Interestingly, calculations of the hydrogen surface density on $a$-Si:H films “grown” by molecular dynamics simulations using SiH$_4$ as the sole precursor,$^{44}$ have revealed a hydrogen surface areal density of $5–7 \times 10^{14}$ cm$^{-2}$ for a substrate temperature of 230°C. This is in good agreement with the experimental value when applying the second approach with the data for hydrogenated $c$-Si surfaces. Moreover, the simulations revealed a relatively low surface dangling bond density while the simulated and experimental surface composition in terms of hydrides showed very good agreement.$^{45}$ This suggests that the second approach is most appropriate for calculating areal densities of hydrogen on $a$-Si:H surfaces. Furthermore, the rather low experimental and simulated hydrogen surface coverage can also indicate a considerable degree of surface
reconstruction; for example, the hydrogen coverage of the reconstructed Si(111)-(7×7) surface is only \(3 \times 10^{11} \text{ cm}^{-2}\).

Finally, it should be mentioned that the surface is not well defined for a-Si:H and it should be taken into account that the surface site density and thus the hydrogen coverage increase with increasing surface roughness. The surface hydrogen areal density can therefore depend on, e.g., the substrate temperature and film thickness.\(^3\) The main conclusion of this discussion is therefore also that the calculation of surface coverage of a-Si:H from infrared absorption data is not as straightforward as sometimes presented.\(^9\)\(^,\)\(^4\)\(^1\) This also complicates the determination of the surface coverage of hydrogen as a function of substrate temperature in order to draw conclusions about the surface dangling bond density as done in Ref. 14.

VI. CONCLUSIONS

A recently developed method\(^1\)\(^7\) to determine the surface hydride composition on plasma deposited a-Si:H by means of in situ attenuated total reflection infrared spectroscopy has been studied in detail. In this method, absorptions due to surface hydrides are distinguished from absorptions by hydrides in the bulk a-Si:H by removing the hydrogen at the surface with an Ar plasma and by comparing the infrared spectra of the film taken before and after ion bombardment. Herein, the influence of Ar plasma exposure has been investigated and the time necessary to remove only surface hydrides has been established. The determination of the surface composition in terms of mono-, di-, and trihydrides on the basis of data available for hydrogenated c-Si surfaces is addressed and the quantification of the hydrogen surface coverage by using data from ideally hydrogen terminated c-Si surfaces and from bulk a-Si:H has been discussed.

Furthermore, the method of Ar ion bombardment has been compared with other techniques using isotope substitution. A good agreement has been found with the method in which a-Si:H is deposited on a-Si:D to reveal the surface deuterides. However, it is shown that the Ar ion bombardment method is preferable for the experimental conditions used, particularly in comparison with isotope substitution by means of an Ar–D\(_2\) plasma. In this case, fast substitution of bulk hydrogen has been observed even before the substitution of surface hydrogen was completed. Another advantage of the Ar ion bombardment method is that it is applicable in a much wider range of (plasma) deposition and surface modification processes.

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\(^3\) W. Luft and Y. S. Tsuo, Hydrogenated Amorphous Silicon Alloy Deposition Processes (Dekker, New York, 1993).
\(^32\) D. C. Marra, W. M. M. Kessels, M. C. M. van de Sanden, K. Kashefi-zadeh, and E. S. Aydil (unpublished).
\(^38\) A-Si:H surface is not very well defined and it is not excluded that Si atoms bonded to the surface hydrogen are desorbed. This has no direct implications for the interpretation of the data.
46 P. Jakob (private communication).