Direct insertion of SiH₃ radicals into strained Si-Si surface bonds during plasma deposition of hydrogenated amorphous silicon films

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We investigate the interaction of silyl (SiH₃) radicals with hydrogenated amorphous silicon (a-Si:H) films using real time *in situ* infrared spectroscopy in a mode that can detect as little as ~ 0.2 ML of Si-H bonds. The results are directly relevant to the growth of a-Si:H by plasma-chemical vapor deposition. In this paper, a remote silane plasma source is used to generate a pure SiH₃ beam, without any contribution of H or SiH₂. Deuterated (a-Si:D) films are exposed to this beam and the change in the IR absorption caused by the loss of SiD groups and the creation of SiH groups is measured in real time. At the beginning of exposure to SiH_3 radicals, a hydrogen-rich layer is deposited on top of the deuterated sample, but no release of deuterium from SiD surface groups can be observed. This is a surprising result, since it has been assumed in the literature that SiH₃ radicals can easily abstract surface-bonded H atoms, and that abstraction must occur in order to create dangling bond sites on which SiH₃ radicals subsequently adsorb. Our results show that the reaction mechanism with the largest rate coefficient must be the direct insertion of SiH_3 radicals into bonding sites at the film surface, which leads to a hydrogen-rich top layer while preserving the preexisting SiD bonds. After completion of one monolayer of surface Si-H bonds, deuterium atoms from the initial surface are released simultaneously with the creation of SiH bulk groups. We propose a reaction scheme based on the direct insertion of SiH_3 radicals into strained Si-Si bonds. This scheme also predicts that the surface-bonding configurations depend on a dynamic balance between the rates of SiH₃ adsorption and thermal desorption, which is confirmed experimentally as a function of SiH₃ flux. We discuss the implications of this reaction mechanism for the growth of a-Si:H from silane discharges, and for the growth of microcrystalline Si in H₂ diluted SiH₄ discharges. [S0163-1829(99)03508-0]

I. INTRODUCTION

Hydrogenated amorphous silicon films (a-Si:H) are generally prepared from low-temperature plasma-chemical vapor deposition using silane.^{1,2} Understanding the growth mechanism is important for predicting and controlling the resulting film properties, including hydrogen content, film morphology, and defect density. The dominant growth precursor in silane discharges is the SiH₃ radical, if the dissociation of the SiH₄ source gas is kept below $\sim 15\%$.^{3–8} This is consistent with plasma-chemistry calculations,^{7,8} and has been experimentally verified using mass spectrometry,⁹ trench coverage experiments,^{3,4,10} and *in situ* electron spinresonance experiments.¹¹ It has been generally assumed that incoming SiH₃ radicals attach to the growing film surface via adsorption at dangling bonds.¹⁻⁶ It is well established that dangling bonds can be created by hydrogen abstraction from the film surface due to incoming atomic hydrogen, and it has been assumed that the analogous reaction occurs with incoming SiH₃ radicals; however, no direct evidence has been available. At substrate temperatures >350 °C, dangling bonds are also created via thermal desorption of hydrogen.¹²

In this paper we obtain quantitative information about the reaction of SiH_3 radicals with a hydrogenated amorphous silicon surface using *in situ* real-time infrared (IR) spectroscopy. From the change in the IR spectra during exposure of a deuterated (*a*-Si:D) film to a SiH_3 radical source, we determine the temporal relationship between the loss of SiD groups and the creation of SiH groups. As mentioned above,

the reaction mechanism for creation of SiH surface groups is thought to involve the abstraction of deuterium from a SiD surface bond followed by adsorption of a SiH₃ radical at the dangling bond. Thereby the creation of SiH surface groups should occur simultaneously with the removal of SiD surface groups during adsorption of the first monolayer of surface SiH.

In order to resolve the time dependence of the reactions at the growing film surface, the loss and creation of SiD/SiH groups has to be measured with submonolayer resolution. This resolution is usually achieved in IR spectroscopy by sampling over a long period of time (~ 1 h) and averaging the resulting spectra. However, during film growth the time for sampling an IR spectrum has to be smaller than the time for depositing a new Si:H monolayer ($\sim min$).

We obtain excellent IR signal enhancement for SiH and SiD vibrational modes using a multilayer "optical cavity" substrate,^{13–17} which consists of a double-polished *c*-Si wafer with a thermal-oxide thickness of 1040 nm on both sides and an Al backside coating.^{15–18} We have shown that this type of substrate configuration provides superior signal enhancement compared to metal substrates;¹³ and we recently measured the depletion and repopulation of the hydrogen density of states (HDOS) in *a*-Si:H with ~0.2 ML resolution.^{15–17} A key advantage of the optical-cavity substrate configuration is its equivalent sensitivity to both surface and bulk SiH groups. This is important since the concentration of SiH groups can vary not only at the physical surface but also in the bulk of the growing film due to the

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FIG. 1. Schematic of the experimental setup.

eventual transformation of the growth layer into the *a*-Si:H network.

II. EXPERIMENT

A sketch of the experimental setup is shown in Fig. 1. A remote dc plasma source using SiH₄ as source gas is used to generate SiH₃ radicals, as described in Ref. 10. The pressure in the discharge is ~100 m Torr at a flow rate of 5.5 sccm. Using these parameters at a low dc power, the depletion of the SiH₄ source gas in the discharge is small (~10%), as measured by mass spectrometry.¹⁰ Consequently, SiH₃ (silyl) is the dominant radical.^{3–8} Through a small orifice (diameter 3 mm) in the grounded electrode, a directed radical beam effuses into a growth chamber, which is equipped with an *in situ* Fourier-transform infrared spectrometer. This directed beam can be blocked with a beam stop in order to reduce the growth flux towards the substrate, i.e., only radicals with low-sticking probability (SiH₃) can reach the substrate via multiple reflection off the Si-coated chamber walls.

The pressure in the growth chamber is 2 m Torr during film deposition and the substrate temperature is 230 °C for all experiments. In a previous paper we grew *a*-Si:H films with good electronic properties using this remote plasma source operating at the same discharge parameters listed above.¹⁰ Uniform coverage of trench-shaped substrates was observed, indicating that the remote plasma source produces radicals with a small sticking coefficient, consistent with the effusion of predominantly SiH₃ radicals.

To produce deuterated samples, *a*-Si:H films are deposited by the remote plasma source and then exposed to atomic deuterium, generated by a hot tungsten filament at a molecular D_2 pressure of 3 m Torr. The filament power is ~30 W and the filament is mounted at a distance of ~30 cm without line of sight to the sample. The substrate temperature during exposure is also 230 °C. In a previous paper, we quantified the HD exchange in very thin *a*-Si:H films using these parameters.^{15–17} The abstraction and replacement of surface bonded H atoms by gas phase D atoms was detected at a level of 1.5×10^{14} atoms/cm².

IR absorption spectra are measured in reflectance mode using 128 scans if the radical beam impinges directly on the substrate, and using 500 scans if the beam stop is closed. This takes \sim 36 s at 128 scans and \sim 98 s at 500 scans. The infrared background spectra are taken with 1000 scans prior to initiating film growth. The signal-to-noise ratio is $\Delta R/R$



FIG. 2. Change of the extinction coefficient during growth of an a-Si:H film from a SiH₃ radical-beam source without beam stop (high flux).

 $\sim 5 \times 10^{-4}$. The change in the extinction coefficient κ of the sample is calculated from the measured change in reflectance R during growth or exposure to atomic deuterium using a rigorous optical model.¹³ An increase in reflectivity corresponds to the removal of SiH/SiD groups and a decrease in reflectivity corresponds to the creation of SiH/SiD groups. The change in the extinction coefficient $\Delta \kappa$ is plotted as $\Delta \kappa$ times film thickness in order to obtain a spectrum proportional to the areal density of hydrogen in the sample. From fitting the extinction coefficient to Gaussian peaks for the individual SiH vibrations, the integrated absorption coefficient for each vibrational mode is determined. The line positions for the SiH and SiD surface and bulk groups are taken from the literature: $^{19-23} \sim 2000 \text{ cm}^{-1}$ for the SiH bulk mode, and at the surface $\sim 2083 \text{ cm}^{-1}$ for the SiH monohydride, \sim 2110 cm⁻¹ for the dihydride and \sim 2140 cm⁻¹ for the trihydride; \sim 1455 cm⁻¹ for the SiD bulk mode, and at the surface $\sim 1515 \text{ cm}^{-1}$ for the SiD monodeuteride, ~ 1525 cm^{-1} for the dideuteride and ~1550 cm^{-1} for the trideuteride. From the integrated extinction coefficient the hydrogen areal density is calculated using known oscillator strengths.²⁴ It should be mentioned that only the oscillator strengths of the SiH bulk and the SiH surface monohydride modes are known for a-Si:H. Therefore, the oscillator strengths for the SiD bonds are assumed to be the same as for the SiH bonds, and the oscillator strengths for the SiH diand trihydride surface modes are assumed to be the same as for the SiH surface monohydride mode. If any of these oscillator strengths is different, then the calculated concentrations must be rescaled, but the conclusions of this paper remain unchanged.

III. RESULTS

A. Growth of *a*-Si:H films from the radical source

An *a*-Si:H film is deposited on the optical-cavity substrate using the radical source with the beam stop open, and



FIG. 3. Increase of the areal density of hydrogen in SiH bulk groups, SiH monohydride, and higher hydride surface groups during growth of an a-Si:H film from a SiH₃ radical beam source.

the IR reflectance spectra are measured in real time. The corresponding changes in the extinction coefficient are fit with Gaussian peaks for the SiH bulk and surface modes, as shown in Fig. 2. Up to 144 s, absorption peaks at \sim 2083, 2110, and 2140 cm^{-1} become visible, which correspond to the creation of surface SiH mono-, di-, and trihydride groups, respectively. During further film growth, absorption at 2000 cm⁻¹ also becomes visible, which corresponds to the creation of SiH bulk groups. The maximum of the spectra after 180 s is at $\sim 2080 \text{ cm}^{-1}$, indicating that the dominant surface group during steady-state growth is monohydride. The increase in the areal densities of hydrogen in the bulk monohydride, surface monohydride, and higher hydride groups is determined from the changes in the extinction coefficients and shown in Fig. 3. Approximately 2×10^{15} -cm⁻² SiH surface groups are created before the onset of the formation of SiH bulk groups at 144 s. The contribution of surface monohydrides increases during bulk-film growth, whereas the contribution of higher hydrides saturates at a value of ~ 2.5 $\times 10^{15}$ cm⁻², indicated by the dotted line in Fig. 3. The data can be explained as follows: at the onset of film growth a hydrogen-rich Si:H layer is formed consisting of SiH mono-, di-, and trihydride groups. SiH bulk groups are formed only after deposition of 1-2 ML of this hydrogen-rich layer. The increase in surface monohydrides scales linearly with growth time, i.e., film thickness, which indicates that the bulk a-Si:H film contains internal surfaces. The higher hydride modes, however, exist only at the physical film surface and saturate at $\sim 2.5 \times 10^{15}$ cm⁻². This is consistent with 1 ML of SiH₂ or SiH₃. This variation of the hydrogen content during growth is in excellent agreement with the results of Toyoshima et al. using real-time reflection IR and a metal substrate, which provides high sensitivity to surface modes only.25-27

This *a*-Si:H film is then exposed to atomic deuterium. The changes in the IR spectra are shown in Fig. 4. After 98 s, the reflectivity around $\sim 2100 \text{ cm}^{-1}$ increases, representing a removal of SiH surface groups from the film. However, the reflectivity around 1500 cm⁻¹ does not decrease, which indicates that the SiH groups are removed by etching the film surface rather than by creation of SiD groups via the HD exchange. After 196 s the reflectivity around 1500 cm⁻¹



FIG. 4. Change in reflectivity during exposure of the as-grown *a*-Si:H film to atomic deuterium.

starts to decrease, corresponding to the onset of the HD exchange. The reflectivity at ~1550 cm⁻¹ does not decrease even though the reflectivity at ~2140 cm⁻¹ increases; this indicates that no SiD₃ groups are created during exposure to atomic deuterium. The change in the IR background (not shown) corresponds quantitatively to the etching of 7-nm of film during exposure for ~3000 s. Summarizing, the interaction of the *a*-Si:H film with atomic deuterium leads to the formation of SiD bulk and SiD surface monohydride groups via the HD exchange, whereas the higher hydrides at the physical surface are etched away. The preferential etching of higher hydrides during exposure of *a*-Si:H to atomic hydrogen is fully consistent with findings in the literature.^{28–30}

HD exchange experiments on crystalline silicon have shown that the total hydrogen coverage remains close to unity $(0.68 \times 10^{15} \text{ cm}^{-2})$ during atomic H or D exposure.³¹ Since the *a*-Si:D is created by exposing an *a*-Si:H film to atomic deuterium, we assume that the monodeuteride at the physical surface consists of $\approx 0.7 \times 10^{15} \text{ cm}^{-2}$ D atoms, and that the local structure is similar to the 2×1 reconstruction of Si(100), since this represents the stable configuration for a hydrogen-terminated silicon surface exposed to atomic H at a substrate temperature of 230 °C.¹²

B. Reaction of SiH₃ radicals with *a*-Si:D

The *a*-Si:D film described above is then exposed to SiH₃ radicals generated by the remote-plasma source with the beam stop open, and an *a*-Si:H film is deposited on top. The measured changes in the IR spectra are shown in Fig. 5. The decrease in reflectivity at $\sim 2100 \text{ cm}^{-1}$ after 36 s corresponds to the formation of $0.94 \times 10^{15} \text{ cm}^{-2}$ SiH surface groups. The decrease in reflectivity at $\sim 2000 \text{ cm}^{-1}$ after 72 s indicates the formation of SiH bulk groups. During further exposure, the amount of created SiH bulk and surface groups increases continuously, indicating steady-state film growth.



FIG. 5. Change in reflectivity during exposure of the a-Si:D film to the SiH₃ radical beam.

However, the increase in reflectance around $\sim 1515 \text{ cm}^{-1}$, indicating the removal of surface-monodeuteride groups, is only visible beginning at 72 s. The loss in surfacemonodeuteride groups corresponds to $0.47 \times 10^{15} \text{ cm}^{-2}$ after 72 s and to $0.68 \times 10^{15} \text{ cm}^{-2}$ after 144 s, equivalent to the removal of 1 ML of SiD. During further film growth, no more SiD groups are released. This supports our assertion that the flux emanating from the remote-plasma source does not contain atomic hydrogen, since it would produce a fast HD exchange reaction with the bulk of the *a*-Si:D film, as we have previously observed using an atomic-hydrogen source.^{15–18} This would be manifest by a fast initial increase in reflectivity at ~1455 cm⁻¹ due to the loss in SiD bulk groups, which is not detected.

We interpret the spectra as follows: an *a*-Si:H film is deposited on top of the *a*-Si:D film by adsorption of SiH₃ radicals. SiD groups from the physical surface of the *a*-Si:D film are removed either by abstraction from the incoming radical flux or by the transformation of the initial *a*-Si:D surface into bulk film. As shown in Fig. 5, the increase in reflectivity at ~1515 cm⁻¹ indeed corresponds to the removal of 1 ML of SiD surface groups.

However, the detailed time sequence of the creation of surface SiH groups vs the removal of surface SiD groups is difficult to resolve from the spectra in Fig. 5 because the growth rate is relatively large. Therefore we reduce the flux of incoming radicals by placing a beam stop between the radical source and the *a*-Si:D film. Since SiH₃ radicals have a surface-loss coefficient of only ~0.26 on *a*-Si:H films and the chamber walls are coated with *a*-Si:H, the radicals are able to survive several wall collisions and still reach the substrate.^{3–5} This is, of course, exactly what happens when *a*-Si:H uniformly coats a trench of high-aspect ratio and small dimensions compared with the mean free path in the gas phase.¹⁰ We have already argued that the plasma source



FIG. 6. Change in the reflectivity during exposure of the a-Si:D film surface to the radical beam source with beam stop (low flux). The SiH/SiD bulk and surface modes are fitted with Gaussian peaks.

produces only SiH₃ radicals. With the beam stop in place, any residual contribution of ions or radicals with large sticking coefficient—such as SiH₂, SiH, or Si—can be completely excluded, since they cannot reach the sample after several wall collisions. The beam stop reduces the flux towards the surface by one order of magnitude.

A fresh *a*-Si:D film is prepared by exposing the *a*-Si:H film of Fig. 4 to atomic deuterium until saturation. This film is then exposed to the radical source with the beam stop in place. Figure 6 shows the resulting changes in the reflectivity spectra, which are taken with 500 scans to achieve a better signal-to-noise ratio. The decrease in reflectivity at ~ 2090 cm⁻¹ after 98 s indicates the creation of SiH surface groups consisting predominantly of monohydrides; the decrease in reflectivity at $\sim 2000 \text{ cm}^{-1}$ at 392 s indicates the creation of SiH bulk modes and corresponds to the onset of bulk-film growth. This is the same sequence as shown in Figs. 2 and 3. The increase in reflectivity at 1515 cm⁻¹ indicating the removal of SiD surface groups becomes visible only after 392 s, and saturates after 780 s. The reflectivity at 1455 cm^{-1} increases slightly during longer exposure times, indicating a slow release of SiD bulk groups.

The spectra are converted to $\Delta \kappa$ and fit with Gaussian peaks for the SiH and SiD bulk and surface modes. For this quantification we use only one Gaussian peak for the SiH(SiD) bulk mode and the sum of the SiH(SiD) surface modes. The resulting changes in the areal density of hydrogen(deuterium) are shown in Fig. 7. Initially, ~0.5 $\times 10^{15}$ -cm⁻² SiH surface groups are created before the onset of the formation of SiH bulk modes. Interestingly, the onset



FIG. 7. Variation of the areal density of hydrogen during exposure of the deuterated film to a SiH_3 radical source. (a) Increase of the areal density of SiH surface groups and SiH bulk groups; (b) decrease in the areal density of SiD surface groups and SiD bulk groups.

of the removal of SiD surface groups after 392 s occurs simultaneously with the creation of the SiH bulk modes, i.e., the onset of bulk-film growth. The loss of SiD surface groups saturates exponentially during film growth as illustrated by the solid line in Fig. 7. The data taken at small radical fluxes thereby confirm the interpretation of the data taken at a large radical flux shown in Fig. 5: during exposure of an *a*-Si:D film to SiH₃ radicals, SiH surface groups are created *before* deuterium from SiD surface groups is released. In the following section, we present a reaction scheme that is able to explain this result as well as the consequences for *a*-Si:H film growth.

IV. DISCUSSION

It has generally been assumed that the attachment of SiH₃ radicals to the growing film surface occurs via chemisorption at Si dangling bonds. These dangling bonds are thought to be created when incoming SiH₃ radicals abstract hydrogen.^{1–6} However, the exact reaction mechanisms are unknown, due to the lack of detailed experimental data. The creation of 1 ML of SiH groups implies the removal of 1 ML of SiD, if it is necessary to create dangling bonds by deuterium abstraction from the initial film surface. The experimental results, as shown in Figs. 5 and 7, directly contradict the above assumption: SiH surface groups are created with no release of surface SiD groups. This asymmetry is illustrated in Fig. 6 for the spectrum taken after 294 s: 0.55×10^{15} -cm⁻² SiH monohydride groups are created and according to the reaction scheme 0.55×10^{15} -cm⁻² SiD groups should be released.

This would lead to an increase in reflectivity at 1515 cm^{-1} as shown by the calculated dotted line, but the data show no such change well within the measurement uncertainty. Therefore, the dominant mechanism for SiH₃ insertion during the initial exposure of an *a*-Si:D film does not require deuterium abstraction.

Therefore, we propose an alternative reaction pathway for SiH₃ adsorption, namely, that *the preferred adsorption sites* are strained Si-Si bonds at the film surface. It is known that atomic hydrogen can easily insert into strained dimers at the 2×1 reconstructed Si(100) surface to form the 1×1 reconstruction.¹² At elevated substrate temperatures this 1×1 reconstruction. ¹² We propose that the incoming SiH₃ radical follows an analogous reaction pathway. The insertion of a SiH₃ radical into strained Si-Si bonds on the growing *a*-Si:H film surface will form at first a transition state consisting of a pentacoordinated SiH₃ site:

$$\operatorname{SiH}_{3(g)} + \operatorname{Si-Si}_{(s)} \to \operatorname{Si-SiH}_3 - \operatorname{Si}_{(s)}, \qquad (1)$$

the indices (*s*) and (*g*) denote the surface and gas phase, respectively. The existence of pentacoordinated silicon atoms is well known as a transition state in nucleophilic substitution reactions, and these types of chemical reactions have been recently proposed for the dissociative adsorption of Si_2H_6 at dangling bonds on crystalline silicon surfaces.^{32–35} The role of the nucleophile reactant is played by the open surface bond, which acts as the donor for the charge transfer and the silicon atom in Si_2H_6 acts as the acceptor.³⁵ The pentacoordinated silicon atoms are bonded through their dsp³ orbitals as known for fivefold coordinated Si compounds in the gas phase.³⁶ In the case of adsorption of SiH₃ at the hydrogenated surface, this situation is reversed, since now the dangling bond of the SiH₃ radical acts as the acceptor for the charge transfer during bonding.

We assume that the lifetime of the pentacoordinated SiH₃ transition state should be sufficient to lead to a nonzero steady-state coverage at the growing film surface. It is known that adsorbed SiH₃ can only dissociate to form adsorbed SiH₂ and adsorbed H if a dangling bond is nearby.³³ This leads to a lifetime of minutes at room temperature for silicon surfaces with a large hydrogen coverage corresponding to a low density of dangling bonds.³³ Since the *a*-Si:H film surface remains hydrogenated during growth,^{25–27,37} such that the surface-dangling bond concentration is smaller than 1%,¹¹ the assumption of a finite lifetime for an isolated SiH₃ site is reasonable.

We postulate further that neighboring SiH_3 sites can reconstruct by directly forming a surface monohydride and releasing two H_2 molecules:

$$2Si-SiH_3-Si_{(s)} \rightarrow Si_2-SiH-SiH-Si_{2(s)} + 2H_{2(g)}.$$
(2)

This mechanism has important implications for the surface configurations during SiH₃ adsorption. In general, an amorphous film surface is different than a crystalline surface; however, it is reasonable to assume that the same reaction mechanisms occur on the local atomistic scale. To illustrate the reaction pathway for adsorption of SiH₃ radicals, we therefore use the 2×1 reconstructed and H passivated Si(100) surface as a model system.



FIG. 8. Reaction scheme for the insertion of SiH₃ radicals into strained surface bonds on the 2×1 reconstructed Si(100) surface.

The reaction scheme is illustrated in Fig. 8 by three reaction steps, which connect surface configurations I to IV: (I) two neighboring dimers on the 2×1 reconstructed Si(100) surface; (II) two SiH₃ radicals insert into the strained Si-Si surface bonds and form pentacoordinated SiH₃ transition states; (III) neighboring pentacoordinated SiH₃ sites reconstruct to create a new strained Si-Si surface bond and release two H₂ molecules; and (IV) one SiH₃ radical inserts in the new strained Si-Si surface bond. Overall, this reaction pathway leads to the attachment of three SiH₃ radicals, the release of two H₂ molecules, and the relaxation of two strained bonds on the initial film surface. *No hydrogen abstraction* from the film surface and no creation of dangling bonds is involved in this reaction scheme.

The surface configuration IV represents the maximal concentration of SiH surface groups in the absence of H abstraction, because no *neighboring* pentacoordinated SiH₃ sites are then available and no further reconstruction can occur. However, the pentacoordinated SiH₃ site in IV is metastable and can thermally dissociate by the reformation of a strained bond and the desorption of the SiH₃ radical back into the gas phase. We therefore postulate an equilibrium for the surface between configurations III and IV. This equilibrium depends on the relative rate of thermal desorption of the SiH₃ radicals vs the rate for SiH₃ insertion, which is a function of the incoming flux of SiH₃ radicals. This equilibrium should be observable in the IR spectra because configuration III consists solely of SiH monohydride groups, whereas IV contains SiH monohydride groups as well as higher hydride groups.

Figure 9(a) shows the change in extinction coefficient after completion of the hydrogen-rich overlayer in the open beam stop (high flux) experiment. The spectrum is fit with Gaussian peaks for the surface hydrides. The quantification of the data yields the creation of 0.53, 0.42, and 0.45 $\times 10^{15}$ -cm⁻² hydrogen atoms in SiH mono-, di-, and trihy-



FIG. 9. Change in the extinction coefficient at the time corresponding to the formation of the hydrogen-rich overlayer in the case of (a) no beam stop (large flux of SiH_3 radicals) and (b) with beam stop (small flux of SiH_3 radicals). The insets show surface configurations III and IV as illustrated in Fig. 8.

dride groups, respectively. This is in good agreement with the areal densities in model configuration IV, illustrated in the inset, which has 0.34×10^{15} -cm⁻² hydrogen in SiH monohydrides and 0.52×10^{15} -cm⁻² hydrogen in pentacoordinated SiH₃ sites. As stated earlier, we use oscillator strength of the monohydride mode to quantify the higher hydrides modes. This might overestimate the higher hydride population, since higher hydride groups usually have a larger oscillator strength than monohydride groups in gas-phase molecules.

Figure 9(b) shows the change in the extinction coefficient after completion of the hydrogen-rich overlayer in the closed-beam stop (low flux) experiment. The spectrum is fit with Gaussian peaks of the same peak positions and widths, yielding the creation of 0.4, 0.1, and 0.04×10^{15} -cm⁻² hydrogen in SiH mono-, di-, and trihydride groups, respectively. This quantification is in good agreement with the areal density in model configuration III, shown in the inset, which has 0.34×10^{15} -cm⁻² hydrogen in SiH monohydrides and no higher hydrides. The spectra show that the hydrogenrich overlayer contains much less higher hydrides in the limit of low SiH₃ flux than in the limit of high SiH₃ flux. Therefore, we conclude that an equilibrium does exist between configuration III, which dominates in the case of a small SiH₃ flux, and configuration IV, which dominates in the case of a high SiH₃ flux.

In Fig. 9(a), the change in the extinction coefficient at 2110 cm^{-1} indicates the formation of SiH₂ groups, although the reaction scheme illustrated in Fig. 8 includes only SiH and SiH₃ groups. The SiH₂ groups might form by the following additional reactions. (i) An incoming SiH₃ radical might abstract a hydrogen atom from the pentacoordinated site to form a surface-dihydride group. (ii) Two neighboring penta-

coordinated sites might reconstruct by the formation of two SiH_2 sites and the release of a H_2 molecule. (These two sites could further reconstruct by the release of a second H_2 molecule and the formation of the stable-surface monohydride.) (iii) A SiH₃ might insert into a strained Si-Si bond and directly form a stable SiH₂ group and a free hydrogen atom. The hydrogen atom would presumably be able to abstract a neighboring surface-hydrogen atom, which would reduce the deuterium coverage during initial SiH₃ adsorption on *a*-Si:D. However, the latter is not observed experimentally, so reaction (iii) must be unfavorable. And of course, the surface morphology of the growing *a*-Si:H film must be more complex than the Si(100) 2×1 reconstruction, allowing bond rearrangements that we have not considered.

After completion of this hydrogen-rich surface layer, further growth can only proceed if deuterium is abstracted from SiD groups on the initial film surface. The rate coefficient for deuterium abstraction must be smaller than for SiH₃ insertion; indeed, the data shown in Figs. 3 and 7 indicate that the hydrogen-rich overlayer forms 4-5 times faster than the rate of continuous film growth.

The fact that direct insertion of SiH_3 radicals into strained Si-Si surface bonds is the dominant adsorption pathway has several consequences for our understanding of *a*-Si:H film deposition:

(i) The existence of a hydrogen-rich surface layer follows directly from the large rate coefficient for SiH_3 insertion into strained bonds: SiH_3 is attached without abstracting existing surface hydrogen, thereby increasing the hydrogen concentration at the growing film surface.

(ii) The creation of the hydrogen-rich overlayer is a selflimiting process, since the insertion of SiH_3 radicals into strained bonds consumes adsorption sites. In the case of a crystalline surface, this limit is reached after adsorption of the second monolayer.

(iii) The hydrogen-rich overlayer consists of isolated pentacoordinated SiH_3 sites, as illustrated in Fig. 8. However, the steady-state creation of bulk *a*-Si:H requires the removal of hydrogen from the SiH surface groups. The present experiments do not rule out the possibility that SiH_3 radicals can, at a small rate, abstract hydrogen from the surface, creating a dangling bond and a SiH_4 molecule. However, it is probable that this abstraction reaction can be blocked by the presence of the hydrogen-rich overlayer, which implies that the morphology of the growing film surface influences the rate of hydrogen incorporation in the film.

(iv) The SiH₃ radicals, which have inserted into strained Si-Si surface bonds, may be mobile. We suggest that these adsorbed SiH₃ radicals are able to migrate through the bond centers of the strained Si-Si bonds; this is a direct analogy to the diffusion of hydrogen through bond-centered sites in c-Si.^{38,39} This provides a possible reaction path for surface diffusion, which is necessary to explain the observation of nucleation phenomena.⁴⁰ The surface diffusion length would depend on the density and morphology of strained bonds on the film surface. On c-Si surfaces, hydrogen diffusion is fast along the dimer rows and slow perpendicular to the dimer rows.¹²

(v) The electronic properties of a-Si:H films are usually optimized at substrate temperatures between 200-300 °C. c-Si (100) surfaces have the 2×1 reconstruction in this temperature range; under H exposure at lower temperatures the surface becomes 1×1 reconstructed (additional H atoms break the Si-Si dimers), which reduces the number of strained bonds. Assuming the same behavior for local reconstructions on a-Si:H implies that the surface diffusion length of adsorbed SiH₃ radicals should decrease at temperatures <200 °C because the number of strained bonds decreases. At substrate temperatures >300 °C the hydrogen thermally desorbs; this also diminishes the surface-diffusion length because incoming radicals can easily adsorb at surfacedangling bonds and then cross link (form Si-Si bonds) as more hydrogen evolves. Thereby a large surface diffusion length of SiH₃ is only expected in the temperature range between 200 and 300 °C, and surface diffusion is believed to be favorable for the formation of high-quality films.

(vi) The hydrogen-rich overlayer is etched by an incoming flux of atomic hydrogen as shown in Fig. 4. The consequence is a surface with a large coverage of strained bonds, which is the stable surface under atomic hydrogen exposure at this substrate temperature (230 °C). The deposition of microcrystalline silicon from hydrogen-diluted silane discharges corresponds to the simultaneous interaction of atomic hydrogen and SiH₃ with the film-growth surface. In such depositions the strained bond density at the surface is expected to be considerably larger than in pure silane discharges, due to the permanent reetching of higher hydrides. Consequently, the surface migration for adsorbed SiH₃ radicals through strained surface bonds is facilitated; highsurface diffusion has been postulated to promote the evolution of crystallinity, along with a certain hydrogen coverage and the absence of a higher hydrides.^{5,29,30}

V. CONCLUSION

We analyzed the interaction of SiH₃ radicals, produced by a remote silane-plasma source, with a deuterated a-Si:D film at 230 °C using in situ real-time IR spectroscopy. 1-2 ML of SiH surface groups are created during adsorption of SiH₃ radicals before the removal of deuterium from the surface is observed. This experimental observation directly conflicts with the assumption that SiH_3 radicals abstract surface D atoms and leave open dangling bond sites on which other SiH₃ radicals attach. This experimental result is explained by postulating a reaction scheme based on insertion of SiH₃ radicals into strained Si-Si surface bonds forming metastable pentacoordinated Si-SiH₃-Si sites. These metastable sites can further reconstruct by the desorption of H₂ molecules. This reaction mechanism leads to a hydrogen-rich overlayer present during film growth, which is observed in this paper as well as in the literature. This reaction scheme forms a new basis for the development of realistic growth models for a-Si:H growth from low-temperature silane discharges, as well as for the evolution of microcrystallinity in H₂ diluted SiH₄ discharges.

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