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Hydrogen in Si–Si bond center and platelet-like defect configurations in amorphous hydrogenated silicon

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Hydrogen and deuterium in bond-centered (BC) and platelet-like configurations were detected in hydrogenated (and deuterated) amorphous silicon thin films deposited from SiH₄ and SiD₄ plasmas. Infrared absorptions due to these configurations were measured using *in situ* multiple total internal reflection Fourier transform infrared spectroscopy in a differential mode, where changes in the as-deposited *a*-Si:H(D) films were observed during D₂(H₂) plasma exposure. This method coupled with preferential replacement of H(D) by D(H) in BC and platelet-like configurations over the isolated bulk SiH(SiD) configurations enabled detection of these modes without interference from the strong SiH(SiD) absorptions. The Si–H(D) stretching modes for BC hydrogen and BC deuterium were observed at ~ 1950 and ~ 1420 cm⁻¹, respectively, while those for platelet-like hydrogen and deuterium were detected at ~ 2033 and ~ 1480 cm⁻¹, respectively. © 2004 American Vacuum Society. [DOI: 10.1116/1.1824191]

I. INTRODUCTION

Hydrogenated amorphous silicon (*a*-Si:H) films grown by plasma deposition from SiH₄ and H₂ containing discharges are used in photovoltaic devices and in thin film transistors for flat panel displays.^{1,2} The films' hydrogen content and microstructure play a major role in determining their electronic properties. Hydrogen passivates dangling-bond defects in *a*-Si:H, increasing carrier lifetime; however, excessive H incorporation leads to a less dense *a*-Si:H network containing voids and, thus, to inferior electrical properties.³ Moreover, the mobility of hydrogen in *a*-Si:H has also been associated with photodegradation of *a*-Si:H, known as the Staebler–Wronski effect.⁴ A fundamental understanding of how H is bonded in *a*-Si:H is expected to lead to better deposition methods for production of high-quality stable films, as well as a better understanding of the origin of the Staebler–Wronski effect.

The H content and the microstructure of plasma-deposited *a*-Si:H films are strongly influenced by the interaction with the growth surface of the different hydrogen-containing radicals, such as SiH_x ($1 \leq x \leq 3$) and H atoms generated in a SiH₄ plasma, that impinge onto the substrate during growth. Among the various radical and atomic species impinging onto the deposition surface, H atoms are known to play a key role in determining the H content and the structural characteristics of the deposited films.^{5,6} Despite 20 years of re-

search, however, the understanding of the role of H in *a*-Si:H deposition is still incomplete. Nevertheless, fundamental studies of the growth surfaces have revealed various surface reactions that a H atom impinging on the *a*-Si:H surface may undergo. For example, H atoms can abstract an H atom from the surface, passivate a dangling bond, insert into a strained Si–Si bond, or diffuse into the bulk film.^{7–11} Furthermore, repeated insertion of H into Si–Si bonds can lead to the formation of volatile silanes and eventual etching of the *a*-Si:H film.

In this article, we focus on identifying the infrared (IR) absorption modes of two configurations (Fig. 1) that can be formed by insertion of H(D) into strained Si–Si bonds. Insertion of H into Si–Si bonds can lead to the formation of (a) isolated silicon monohydrides where the H atom is bonded to only one Si, (b) silicon hydrides in platelet-like configurations where the Si–H bonds are present along a planar defect such as a crack or a grain boundary, or (c) bond-centered hydrogen (BCH), where a H atom is present between two Si atoms and is bonded to both Si atoms. The platelet-like configurations are similar to the structures observed in crystal-line silicon (*c*-Si) where Si–H bonds are predominantly oriented along {111} crystallographic planes,^{12,13} and the BCH configurations are similar to the BCH in *c*-Si where an H atom is present between two Si atoms forming two Si–H bonds along the [111] axis.¹⁴ The IR absorption due to the stretching mode of isolated Si–H groups in *a*-Si:H is well known and it is centered at ~ 2000 cm⁻¹.^{15,16} The IR peak positions for the stretching modes for the BCH and platelet-

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FIG. 1. Schematic illustration of H atoms present in *a*-Si:H as silicon monohydride in (i) isolated, (ii) bond-centered, and (iii) platelet-like configurations.

like configurations in *a*-Si:H and *c*-Si are expected to be close to the absorption due to isolated Si-H in the bulk. Therefore, it is difficult to isolate these modes because they overlap with the broad isolated SiH absorption band. The isolated SiH groups are the major monohydride species in most *a*-Si:H films and dominate the film IR spectra. Thus, it is difficult to observe other SiH configurations such as those that may be found at the bond-centered location or in platelet-like defects.

The purpose of this article is to demonstrate the presence of the bond-centered (BC) and the platelet-like H configurations in as-deposited *a*-Si:H(D) films through the use of *in situ* multiple total internal reflection Fourier transform infrared (MTIR-FTIR) spectroscopy. Through carefully designed experiments and using isotopic substitution, we have isolated successfully the IR absorptions due to these configurations by observing the compositional changes in as-deposited *a*-Si:H(D) during D(H) exposure from a D₂(H₂) plasma. In these experiments, we were able to remove D(H) in the BC and in platelet-like configurations preferentially over the isolated SiH(D) groups, hence, allowing for clear identification of these less commonly observed modes. Platelet-like H configurations have been detected previously in post-deposition H-exposed *a*-Si:H films.⁹ We show that they are also present in as-deposited films and the planar defects decorated by H in this configuration must therefore form during deposition.

This article is organized as follows. In Sec. II, we review and discuss the previous theoretical and experimental findings in the literature on BCH and the platelet-like H modes. We place emphasis on the structure and stability of these configurations and their expected IR absorption bands in *a*-Si:H based on the literature results. In Sec. III, we describe our experimental procedure and data collection methodology for *a*-Si:H(D) deposition and D₂(H₂) pulsed plasma exposure. In Sec. IV, we present our IR data along with a detailed discussion of our experimental results. The main conclusions of our study are summarized in Sec. V.

II. PREVIOUS WORK

A. BCH in Si

Using density-functional theory (DFT) calculations within the local-density approximation (LDA), Van de Walle and

co-workers¹⁴ determined that the absorption due to the Si-H stretching mode in the BC configuration in *c*-Si, should appear at 1945 cm⁻¹, if H is in a neutral charge state. This is the only calculated value of the stretching frequency of H in the BC configuration. The calculations of Van de Walle and co-workers also showed that the BC configuration is stable in *c*-Si only at temperatures below 100 K due to the energy cost of moving the two Si atoms apart after H insertion. However, if the Si atoms are spaced further apart initially, the energy gain due to the formation of the Si-H-Si bonding configuration would still be the same, but the energy cost involved in moving the Si atoms is lower, thus stabilizing the BC configuration. Such an expansion of the Si-Si bonds is quite possible in *a*-Si:H, and H can be inserted into elongated (stretched) Si-Si bonds.^{11,17,18} Consequently, the BCH configuration could be stable at temperatures much higher than 100 K in *a*-Si:H. *Ab initio* molecular-dynamics (MD) simulations of Yonezawa and co-workers,¹⁹ using a cell size of up to 64 Si atoms and a few percent H atoms, showed that the BCH configuration in *a*-Si:H is stable if the Si-Si bond is elongated by more than 10%. These authors also suggested that defect creation in the Staebler-Wronski effect involves the migration of H in isolated SiH groups to the BC position in strained Si-Si bonds. More recently, Su and Pantelides²⁰ studied the transport of H atoms in an *a*-Si:H supercell, containing 64 Si atoms and two H atoms, through Car-Parrinello MD simulations. However, they did not observe BCH to be a stable configuration at the simulation temperature of 800°C over the time scales captured by the MD simulations.

Recently, we reported the presence of H in the BC configuration in *a*-Si:H films during H(D) exposure.¹¹ These atomic configurations were both observed in MD simulations and detected in the plasma-deposited *a*-Si:H films upon D exposure. Other investigators have recorded absorptions below 2000 cm⁻¹ in *a*-Si:H and in *c*-Si upon exposure to H, but the assignment of these absorption bands is not clear and has not been supported by atomistic calculations. Chabal and co-workers²¹ observed a broadband feature at 1970 cm⁻¹ on a H-exposed Si(111)-(7×7) surface. This absorption was assigned to Si-H bond vibrations inside the bulk Si formed by H diffusion into the subsurface region. Fujiwara and co-workers²² observed a peak at 1937 cm⁻¹ in the *a*-Si:H subsurface upon Ar plasma treatment. This absorption band was assigned to either SiH_n complex in a two-monolayer subsurface region or the SiH₂(Si *d*) vacancy complex based on the work of Shi and co-workers.²³ This is in contradiction with the proposal of Mukashev and co-workers²⁴ that vacancy complexes in H-implanted *c*-Si correspond to frequencies higher than 2000 cm⁻¹. Using IR spectroscopic ellipsometry, Ossikovski and Drevillon²⁵ measured a shift in the Si-H vibrational frequency from 2000 to 1950 cm⁻¹ with decreasing film thickness, in *a*-Si:H films deposited from a SiH₄ plasma. They concluded that the vibrational band at 1950 cm⁻¹ in the *a*-Si:H films was due to bond-angle disorder at the film-substrate interface. Zhao and co-workers²⁶ detected an increase in absorption at 1940 cm⁻¹ in addition

to absorption bands centered at 2000 and 2064 cm^{-1} upon light soaking of *a*-Si:H for 342 h. However, they did not comment on the presence of unexpected absorption bands at 1940 and 2064 cm^{-1} .

B. Platelet-like H in Si

Johnson and co-workers have shown that exposing *c*-Si to a H_2 plasma can lead to the formation of H-stabilized platelets predominantly along the {111} crystallographic planes.²⁷ Nevertheless, the microscopic structure of this configuration is still a matter of debate.²⁸ Van de Walle and co-workers used DFT/LDA calculations to show that H platelets are stable in *c*-Si if a double layer of Si atoms is removed through a vacancy–formation process and the resulting dangling bonds are passivated with H atoms.¹⁴ Presence of analogous platelet-like structures in *a*-Si:H was first suggested by von Keudell and Abelson who observed an increase in the absorption band at 2033 cm^{-1} upon exposure of *a*-Si:H films, deposited by reactive magnetron sputtering, to H atoms generated by a hot tungsten filament.^{8,9} This IR peak assignment was based on the argument that the Si–H groups in such platelets should appear at a frequency higher than that for Si–H bonds in the bulk ($\sim 2000 \text{ cm}^{-1}$) but lower than that for Si–H bonds in internal voids ($\sim 2100 \text{ cm}^{-1}$), since the volume occupied by H in the platelet mode is intermediate of the above two configurations.^{8,9} von Keudell and Abelson also studied the thermal annealing behavior of the platelet-like defects in *a*-Si:H films and found that H atoms in this configuration are released from the film at temperatures greater than 300°C.²⁹ In recent IR studies of *a*-Si:H exposure to H, this absorption mode centered at $\sim 2033 \text{ cm}^{-1}$ has also been reported by Roca i Cabarrocas and co-workers³⁰ and by Fujiwara and co-workers.²²

In this work we have performed isotope exchange and short- and long-term annealing experiments to confirm if the vibrational bands at ~ 1945 and $\sim 2033 \text{ cm}^{-1}$ in *a*-Si:H could be due to the stretching modes of Si–H bonds in BCH and platelet-like configurations. Furthermore, if the absorptions at ~ 1945 and $\sim 2033 \text{ cm}^{-1}$ are due to the stretching modes of Si–H bonds in BCH and platelet-like configurations, respectively, we expect the frequency to shift by an experimentally measured factor of 0.73 for Si–D bonds to ~ 1420 and $\sim 1484 \text{ cm}^{-1}$, respectively;³¹ this factor is approximately equal to the square root of the ratio of the reduced masses of the Si–H and Si–D harmonic oscillators. Hence, in our experiments, we deposited films using both SiH_4 and SiD_4 as feed gases and exposed these films subsequently to a D_2 and H_2 plasma, respectively, to allow for observation of the isotope shift in the peak positions.

III. EXPERIMENT

A. Plasma deposition reactor

The plasma deposition chamber has already been discussed in detail.³² Briefly, the experiments were conducted in a stainless-steel, inductively coupled plasma (ICP) reactor

equipped for *in situ* MTIR-FTIR spectroscopy. The plasma was generated by applying radio frequency (rf) power at 13.56 MHz to a planar spiral coil seated on a quartz window which forms the vacuum seal. The distance between the quartz window and the grounded substrate was $\sim 20 \text{ cm}$. The base pressure of the plasma chamber was $\sim 10^{-5} \text{ Pa}$. The temperature of the substrate was controlled by a feedback controller (Omega 9000A) in combination with a 500 W resistive heater and a K-type thermocouple placed directly under the sample position. The gases were injected through two gas injection rings. SiH_4 (1% in Ar) and SiD_4 (2% in Ar) were injected close to the substrate, while H_2 and D_2 were injected close to the plasma source. The gas flows were controlled by mass flow controllers (BOC Edwards Model 825 Series B). The pressure in the chamber was measured by a capacitance manometer (BOC Edwards Model 655) and regulated by a throttle valve and a downstream adaptive pressure controller (VAT PM-5).

B. *In situ* MTIR-FTIR spectroscopy

Hydrogenated or deuterated amorphous silicon films were deposited on trapezoidal GaAs crystals with dimensions 50 mm $\times$ 10 mm $\times$ 0.6 mm; the short faces of the crystals were beveled at 45°. IR radiation from a spectrometer (Nicolet 550) was directed by a series of mirrors and focused by a lens through a KBr window onto the beveled edge of the internal reflection crystal (IRC). In this setup, the IR beam undergoes multiple total internal reflections in the IRC, emerges from the opposite beveled edge, and is focused onto a HgCdTe (MCT A) detector. We chose GaAs as the substrate material because the refractive index of GaAs is closely matched with *a*-Si:H and, hence, total internal reflection occurs at the film–vacuum interface. Consequently, the bulk hydrides and deuterides in the *a*-Si:H and *a*-Si:D films were probed through multiple internal transmission and the surface hydrides and deuterides were probed by the attenuated field that decays exponentially into vacuum. Moreover, GaAs is transparent in the IR up to 750 cm^{-1} : this makes possible the simultaneous observation of the stretching modes of silicon hydrides and deuterides, which appear at ~ 2100 and $\sim 1500 \text{ cm}^{-1}$, respectively. In our geometry, the IR beam undergoes approximately 40 internal reflections on each flat face of the IRC and, hence, passes through the growing film 80 times, greatly enhancing the signal-to-noise ratio. The sensitivity of our setup in reflectance R was $\Delta R/R \sim 10^{-5}$ and the resolution of the spectrometer was set at 4 cm^{-1} .

C. *a*-Si:H(D) deposition and post-deposition D_2 (H_2) plasma treatment

Experiments were conducted over various substrate and plasma conditions for the film deposition and post-treatment steps. However, the process conditions described below are for experiments where the IR modes for the BC and platelet-like H (D) were observed clearly. The plasma conditions suitable for observing the BC and platelet-like modes are different for the *a*-Si:H and *a*-Si:D films, most likely be-

cause of the different dissociation of a SiH_4/Ar and a SiD_4/Ar plasma for identical conditions of chamber pressure and input rf power. However, in both $a\text{-Si:H}$ and $a\text{-Si:D}$ films, the BC and platelet-like configurations were detected at the same substrate temperature.

$a\text{-Si:H}$ films were deposited from a SiH_4/Ar plasma while keeping the substrate temperature and power to the plasma source at 333°C and 15 W, respectively. On the other hand, during $a\text{-Si:D}$ deposition from a SiD_4/Ar plasma, the substrate temperature and the power to the plasma source were maintained at 200°C and 50 W, respectively. In both cases, the flow rate of the feed gas mixture was 50 standard cm^3/min (sccm) and the pressure in the plasma chamber was maintained at 26 Pa. The total deposition time was 1 h for the $a\text{-Si:H}$ film and 2 h for the $a\text{-Si:D}$ film. After deposition, the $a\text{-Si:H}$ and $a\text{-Si:D}$ films were exposed to a series of 1 s pulses of D_2 or H_2 plasma and reactions induced by D(H) were observed using *in situ* MTIR-FTIR spectroscopy. During post-deposition plasma exposure, the $\text{D}_2(\text{H}_2)$ flow rate was set at 10 sccm, while the chamber pressure was maintained at 26 Pa. The power to the plasma source was 15 and 25 W for the D_2 and H_2 plasmas, respectively. The substrate temperature during D exposure of $a\text{-Si:H}$ was 333°C (i.e., the same as the deposition temperature). For $a\text{-Si:D}$ films, the temperature was ramped up to 333°C for H_2 plasma exposure. The time difference between deposition and $\text{D}_2(\text{H}_2)$ plasma treatment was ~ 1 h. During the temperature increase from 200 to 333°C before hydrogenation, changes in the IR absorption of the $a\text{-Si:D}$ film were observed. No changes were observed in the IR spectrum for the $a\text{-Si:H}$ films during the 1 h period between deposition and deuteration. After the $\text{D}_2(\text{H}_2)$ plasma exposure, the thermal stability of the films was monitored over a period of several hours. The differences in the deposition conditions and the post-treatment steps for the $a\text{-Si:H}$ and $a\text{-Si:D}$ films do not affect the conclusions of this study.

D. Data collection procedure

IR absorbance spectra were collected during deposition using *in situ* MTIR-FTIR spectroscopy to monitor the film composition during growth and subsequent $\text{H}_2(\text{D}_2)$ plasma exposure. All the IR spectra were collected in a differential mode, where the spectra were recorded with respect to a suitable reference spectrum (background). This method enables the observation of small changes in the film composition due to the last process the IRC and the film have undergone. IR spectra were collected during growth to monitor the film composition. To avoid the initial deposition stage on a bare GaAs crystal, a new reference spectrum (100 averages) was collected after 30 min of film growth after the bulk deposition and surface coverage had reached a steady state. IR spectra were collected subsequently at intervals of ~ 3 min. Since the surface composition was expected to remain the same during the next 15 min of growth, the IR spectra represent absorption only due to the bulk features in the film.³³ A similar approach was adopted for $a\text{-Si:D}$ deposition. In this case, the duration of initial deposition was 1 h,

FIG. 2. IR absorbance spectra of as-deposited $a\text{-Si:H}$ and $a\text{-Si:D}$ films: (a) $\text{SiH}_x (1 \leq x \leq 3)$ stretching modes in $a\text{-Si:H}$ with each spectrum collected at 3 min intervals during the last 15 min of $a\text{-Si:H}$ film growth at a substrate temperature of 333°C ; (b) the $\text{SiD}_x (1 \leq x \leq 3)$ stretching modes in $a\text{-Si:D}$ with each spectrum collected every 12 min during the last 60 min of $a\text{-Si:D}$ film growth at a substrate temperature of 200°C .

after which a new reference spectrum (100 averages) was collected. Spectra were collected at 6 min intervals during film growth for 1 h.

During $\text{D}_2(\text{H}_2)$ plasma exposure, the reference spectrum (500 averages) was taken to be the spectrum of the IRC and the $a\text{-Si:H(D)}$ film at the temperature of D(H) exposure (333°C). The amount of D(H) exposure was controlled by generating 1-s-long $\text{D}_2(\text{H}_2)$ plasma pulses as described in Ref. 33. Absorbance spectra were collected between the $\text{D}_2(\text{H}_2)$ plasma pulses to monitor the compositional changes in the films. After the pulsing sequence, another reference spectrum was collected (500 averages) and the changes in film composition were monitored over a period of several hours with the substrate temperature maintained at 333°C .

IV. RESULTS AND DISCUSSION

A. IR Spectra during deposition of $a\text{-Si:H}$ and $a\text{-Si:D}$

Figure 2(a) shows the absorbance spectra in the $\text{SiH}_x (1 \leq x \leq 3)$ stretching region recorded approximately every 3 min in the bulk film during the last 15 min of $a\text{-Si:H}$ growth at a substrate temperature of 333°C . In the as-

FIG. 3. Change in IR absorbance in the SiD_x ($1 \leq x \leq 3$) stretching region during heating of the $a\text{-Si:D}$ film from the deposition temperature of 200–300 °C. All spectra are presented with respect to the spectrum of the film taken at 200 °C. The spectra were averaged as the substrate temperature was ramped slowly at $\sim 4^\circ\text{C/min}$. The ranges shown in the figure for each spectrum show the substrate temperature at the beginning and at the end of the averaging period.

deposited $a\text{-Si:H}$ film spectra, absorption modes corresponding to BCH at $\sim 1945\text{ cm}^{-1}$ and platelet-like H at $\sim 2033\text{ cm}^{-1}$ cannot be identified readily. A similar observation was made for other deposition conditions. However, this does not necessarily imply the absence of these modes in the $a\text{-Si:H}$ film, since IR absorption due to the BCH and platelet-like modes may be masked by the large broadband absorption due to the isolated SiH groups in the bulk film centered at $\sim 2000\text{ cm}^{-1}$. Hydrogen is primarily incorporated in $a\text{-Si:H}$ films as isolated SiH groups. Figure 2(b) shows the IR absorption of the $a\text{-Si:D}$ film in the SiD_x ($1 \leq x \leq 3$) stretching region during the last 1 h of film growth. As in the IR spectra of the $a\text{-Si:H}$ film, no distinct bands corresponding to BCD and platelet-like D vibrational modes can be resolved. The broadband absorption centered at $\sim 1460\text{ cm}^{-1}$ is the stretching mode of bulk SiD and the band at $\sim 1525\text{ cm}^{-1}$ is due to bulk SiD_2 and SiD in internal voids. The ratio of D present in isolated SiD groups to D present in bulk SiD_2 and SiD in internal voids in the $a\text{-Si:D}$ film is smaller than the ratio of the corresponding absorptions in the $a\text{-Si:H}$ film. This is due to the different experimental conditions for deposition of the $a\text{-Si:H}$ and $a\text{-Si:D}$ films as discussed in Sec. III C.

The as-deposited $a\text{-Si:D}$ film was heated from 200 to 333 °C. Changes in the film's IR spectrum upon heating were recorded at three different temperatures as shown in Fig. 3. As the film temperature rises, IR absorption at $\sim 1420\text{ cm}^{-1}$ increases while absorption at higher wavenumbers decreases. In $a\text{-Si:D}$ films, the absorption feature at $\sim 1420\text{ cm}^{-1}$ corresponds to the BCD configuration¹¹ while the feature at $\sim 1470\text{ cm}^{-1}$ corresponds to both isolated and clustered SiD groups in the bulk. The IR absorptions at frequencies greater than 1530 cm^{-1} are due to the Si–D stretching vibrations in higher bulk and surface deuterides (SiD_2 , SiD_3).^{34–36} The IR spectra in Fig. 3 show that there is a decrease in the number of Si–D bonds in the film, especially for the higher silicon

deuterides, as the substrate temperature is elevated from 200 to 333 °C. Decreasing H incorporation into plasma-deposited films at higher substrate temperatures is well established in the $a\text{-Si:H}$ literature. This decrease in the film H concentration with increasing deposition temperature is attributed partly to the thermal decomposition of higher hydrides on the films surface.^{6,37–39} When Si–D bonds in the film break, D atoms are released into the bulk film and diffuse in the $a\text{-Si:D}$ matrix until they find another energetically favorable location or until they diffuse to the surface of the film, recombine, and desorb into the gas phase. It has been shown previously that the BC location is contained in the pathway with the lowest activation energy barrier for the diffusion of H(D) in $c\text{-Si}$ and $a\text{-Si:H(D)}$.^{14,40} If the released D atoms, diffusing through the $a\text{-Si:D}$ film, sample a BC site where the Si–Si bond is considerably elongated compared to the equilibrium $c\text{-Si}$ bond length, the BCD configuration can be stable at the temperature of the experiment^{17,19,40} and prevent further diffusion of D in the film. In such a case, the IR spectra collected would show an increase in absorption at $\sim 1420\text{ cm}^{-1}$ corresponding to an increase in BCD in the $a\text{-Si:D}$ film. The above mechanism is the most plausible explanation for the increase in absorption at $\sim 1420\text{ cm}^{-1}$, with concomitant decrease in absorption for all other Si–D bonding configurations in the film and supports the assignment of the $\sim 1420\text{ cm}^{-1}$ frequency to BCD. These spectra show that the BCD configuration in $a\text{-Si:D}$ can be stable enough to be observed at low concentrations compared to isolated SiD. The experiments shown in Fig. 3 could also be produced for $a\text{-Si:H}$ films. Such an experiment which has been performed was done by Marra.³⁸ The results of this experiment also show changes in the vibrational modes at ~ 1950 and 2033 cm^{-1} , in addition to other bulk and surface modes.

B. IR spectra during $\text{D}_2(\text{H}_2)$ plasma exposure: BCH (BCD) and platelet-like H(D) configurations in as-deposited films

The as-deposited $a\text{-Si:H}$ film and the heated $a\text{-Si:D}$ film were subsequently exposed to a D_2 and H_2 plasma, respectively, under the conditions stated in Sec. III C. The changes in the IR absorbance due to plasma exposure for $a\text{-Si:H}$ and $a\text{-Si:D}$ films are shown in Figs. 4(a) and 4(b), respectively. Figure 4(a) shows the change in absorbance for $a\text{-Si:H}$ films for three different D exposure times: 5, 13, and 52 s. The IR spectra were deconvoluted using Gaussian line shapes based on the IR peak assignments available in the literature for the different surface and bulk silicon hydride and deuteride stretching modes, recently summarized in Ref. 33. The lower wavenumber region (1900 to 2050 cm^{-1}) of the spectra could be best fitted with three Gaussians centered at 1950, 2000, and 2033 cm^{-1} . The presence of the feature at 1950 cm^{-1} is also obvious from the shoulder at this wavenumber for shorter D exposure times (5 and 13 s). The features at 1950 and 2033 cm^{-1} correspond to Si–H stretching absorptions in the BCH and platelet-like configurations, respectively. The higher-frequency region was fitted with peaks centered at 2091, 2099, and 2135 cm^{-1} , corresponding to bulk SiH_2 , sur-

FIG. 4. Change in IR absorbance of (a) *a*-Si:H film during exposure to D from a D₂ plasma and (b) *a*-Si:D film during exposure to H from a H₂ plasma for three different exposure times, *t*, at a substrate temperature of 333°C. The solid line (—) is the IR spectrum, the dashed line (---) is the overall fit, and the dotted lines (·····) are the individual Gaussian fits for the three different silicon monohydride (-deuteride) stretching modes. In each case, the reference spectrum was collected before the D₂(H₂) plasma treatment. The individual peaks correspond to (1) BCH (1950 cm⁻¹), (2) isolated bulk SiH (2000 cm⁻¹), (3) SiH in platelets (2033 cm⁻¹), (4) BCD (1423 cm⁻¹), (5) isolated bulk SiD (1463 cm⁻¹), and (6) SiD in platelets (1486 cm⁻¹).

face SiH₂, and surface SiH₃, respectively. For clarity, only the three Gaussians in the lower wavenumber region (1900–2050 cm⁻¹) are shown in the deconvoluted spectra in Fig. 4(a) and the fit in this region is independent of the peak positions in the high wavenumber region of the IR spectrum. Since the spectra in Fig. 4(a) represent change in absorbance of the *a*-Si:H film due to D exposure, we conclude that the Si-H configurations corresponding to the 1950 and 2033 cm⁻¹ absorption bands must have been present in the as-deposited *a*-Si:H film prior to D exposure, even though they could not be resolved in Fig. 2(a) due to interference from bulk isolated SiH absorption as discussed previously. The fact that they can be resolved in Fig. 4(a) implies that during D exposure, the 1950 and 2033 cm⁻¹ modes corresponding to BCH and platelet-like configurations, respectively, are removed preferentially over the isolated SiH groups. Since the 1950 mode and 2033 cm⁻¹ modes, are removed faster than the 2000 cm⁻¹ mode, the change in absorbance in the above three modes is comparable and, hence, enables the deconvolution of the IR spectra in Fig. 4(a) into the above three distinct bands in the 1900–2050 cm⁻¹ region. In contrast, in Fig. 2(a) the absorbance in the 1900–2050 cm⁻¹ region can be fitted with a single Gaussian centered at 2000 cm⁻¹.

Preferential removal of the BCH and the platelet-like H mode over the isolated SiH mode is possible if these modes are present along fast diffusion pathways for atomic D in the *a*-Si:H films or if the activation energy barrier for H-D exchange or H abstraction by D is lower for these defect configurations. The fast diffusion pathways can be micropores in *a*-Si:H or grain boundaries in hydrogenated nanocrystalline silicon films. It is reasonable to expect that there is a higher concentration of strained Si-Si bonds in these locations and,

FIG. 5. Change in IR absorbance of (a) *a*-Si:H film after 5 and 90 min of annealing at 333°C, respectively, and (b) *a*-Si:D film after 300 min of annealing at 333°C. The solid line (—) is the IR spectrum, the dashed line (---) is the overall fit, and the dotted lines (·····) are Gaussian fits for the three different silicon monohydride (-deuteride) stretching modes. The reference spectrum was collected before the initiation of the annealing experiment. The individual peaks correspond to (1) BCH (1945 cm⁻¹), (2) isolated bulk SiH (2004 cm⁻¹), (3) SiH in platelets (2033 cm⁻¹), (4) BCD (1417 cm⁻¹), (5) isolated bulk SiD (1460 cm⁻¹), and (6) SiD in platelets (1480 cm⁻¹).

hence, it is more likely for H atoms to be present in the BCH configuration. Platelet-like defects also provide fast diffusion pathways and the H atoms bonded to Si along a platelet defect are more accessible to be replaced with D atoms. This rapid exchange of H by D or abstraction of H by D, compared to slower removal of H in isolated SiH in the bulk, enables preferential removal and detection of Si-H vibrations in BCH and platelet-like configurations and supports the peak assignment for these configurations. As D exposure time increases, bulk isolated SiH groups are also exchanged or abstracted by D and the IR spectra begin to resemble those in Fig. 2(a) with the BCH and platelet-like modes overshadowed by the isolated SiH absorption.

The spectra obtained during H exposure of *a*-Si:D films at 333°C are shown in Fig. 4(b) for three different H exposure times; 80, 400, and 880 s. We used a longer plasma exposure in this case, since the H flux per 1 s pulse was

lower than D flux at the plasma conditions mentioned in Sec. III C. The IR spectra for the H-exposed *a*-Si:D film shown in Fig. 4(b) are qualitatively similar to the spectra for *a*-Si:H shown in Fig. 4(a). In the case of *a*-Si:D, we see the expected shift in the stretching modes for the monodeuterides by the experimentally measured factor of 0.73. The BCD mode, the isolated SiD mode, and the platelet-like D modes are shifted to 1423, 1463, and 1486 cm^{-1} , respectively. In Fig. 4(b), a shoulder is clearly visible at $\sim 1423 \text{ cm}^{-1}$ corresponding to the BCD mode. For clarity, in Fig. 4(b), we have shown the Gaussian fits only for the above three modes; the fit in the low wavenumber region ($1350\text{--}1500 \text{ cm}^{-1}$) is independent of the modes present at higher wavenumbers. For the *a*-Si:D films, some of the BC and the platelet-like modes may have been created solely by the heating of the film from 200 to 333 °C as was discussed above and demonstrated in Fig. 3.

C. IR spectra during thermal annealing

The changes in the IR spectra of the *a*-Si:H and *a*-Si:D films during annealing were monitored *in situ* at 333 °C for 90 and 300 min, respectively. The IR spectra of the *a*-Si:H film obtained after 5 min and after 90 min of annealing are shown in Fig. 5(a). During thermal annealing, we expect preferential removal of BCH and platelet-like H configurations as these configurations are expected to be less stable than isolated monohydride species in the film. The IR spectra of the *a*-Si:H film show a clear shoulder at 1945 cm^{-1} , in addition to changes at 2000 and 2033 cm^{-1} . Similar spectra were obtained for *a*-Si:D with these spectral features shifted by a factor of ~ 0.73 ; one such spectrum collected after annealing the film for 300 min at 333 °C is shown in Fig. 5(b). The *a*-Si:D spectrum shows a clear decrease in absorbance for the BCD and platelet-like D modes at 1417 and 1480 cm^{-1} , respectively. The decrease in the BC mode in Figs. 5(a) and 5(b) is in contrast with Fig. 3, where there was an increase in BCD during heating. This suggests that the BC configuration is not stable over longer time scales and it may only be an intermediate configuration for H(D) elimination from the film. From the data in Figs. 5(a) and 5(b), we can further conclude that as the film is annealed, there must be structural rearrangement of the Si atoms along the cracks and microvoids to eliminate the H(D) atoms in the BC and platelet-like configurations.

V. CONCLUSIONS

We have detected the presence of Si–H(D) bonds in BC and platelet-like structures in *a*-Si:H and *a*-Si:D films by exposing these films to D and H atoms and studying the changes in their IR spectra through the use of *in situ* MTIR-FTIR spectroscopy. The vibrational modes for Si–H and Si–D bonds in the BC configuration were detected at ~ 1950 and $\sim 1420 \text{ cm}^{-1}$, respectively. In addition, Si–H and Si–D stretching modes for H and D atoms in platelet-like defects in *a*-Si:H and *a*-Si:D films and were detected at ~ 2033 and $\sim 1480 \text{ cm}^{-1}$, respectively. Changes in the IR absorbance of these structures were also observed during thermal annealing

of the *a*-Si:H(D) film at 333 °C. The BCH structure has been proposed to play an important role in the H-induced crystallization of *a*-Si:H and the photodegradation of *a*-Si:H known as the Staebler–Wronski effect.⁴ Recently, an increase in absorbance at 1940 cm^{-1} has been observed during light soaking of *a*-Si:H films.²⁶ Based on our IR peak assignments, we propose that this change in absorbance is due to a change in the BCH configurations in light-soaked *a*-Si:H.

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