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Absolute *in situ* measurement of surface dangling bonds during *a*-Si:H growth

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Hydrogenated amorphous silicon (*a*-Si:H) is regarded as a model system in mechanistic studies of amorphous semiconductor film growth, where the key reactive site is generally considered to be a surface “dangling bond.” Employing an ultrahigh- Q ($\approx 10^{10}$) monolithic optical resonator, the authors probe the creation of dangling-bond defects during growth of *a*-Si:H from a predominantly SiH_x ($x=0-3$) radical flux by detecting the associated near-IR subgap absorption with evanescent wave cavity ringdown spectroscopy. They find the apparent dangling-bond creation rate $[(5 \pm 3) \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}]$ and steady-state surface density $[(5 \pm 2) \times 10^{11} \text{ cm}^{-2}]$ to be considerably lower than expected from dangling-bond-based growth mechanisms. © 2007 American Institute of Physics.

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Widely used in electronic and optoelectronic devices, hydrogenated amorphous silicon (*a*-Si:H) has unique properties derived from structural disorder and may enable the development of large-area low-cost flexible solar cells.¹ In mechanistic studies of amorphous semiconductor film growth, *a*-Si:H also serves as a model system, where surface defects are generally thought to play a key role by providing reactive sites for binding of vapor-phase radical precursors.²⁻⁴ Based on epitaxial growth studies of *c*-Si (Ref. 5) and vibrational spectroscopy of *a*-Si:H,⁶ the primary defect site has long been considered to be an undercoordinated Si atom possessing a singly occupied sp^3 -hybridized orbital or “dangling bond” (DB), which binds radical precursors through a facile radical-radical coupling.^{2-4,7} However, the bulk DB density in device-grade *a*-Si:H is typically $\approx 10^{16}/\text{cm}^3$, while a surface defect density as low as $\approx 10^{11}/\text{cm}^2$ is conceivably compatible with DB-based growth mechanisms. Therefore, highly sensitive *in situ* techniques are required to probe DB defects and yield decisive mechanistic insight.

Photothermal deflection,⁸ constant photocurrent,⁹ electron spin resonance (ESR),¹⁰ and cavity ringdown¹¹ spectroscopic techniques have been applied to DB detection. Although constant photocurrent and photothermal deflection methods provide the requisite sensitivity, these techniques are not easily adapted to *in situ* studies under growth conditions. ESR has been applied during growth and H-atom exposure of *a*-Si:H films,¹⁰ although surface, bulk, and interface defects are not readily distinguished. By probing the subgap DB defect absorption,^{8,9,12} cavity ringdown spectroscopy (CRDS) enables determination of very low absolute defect densities.¹¹ However, the conventional implementa-

tion of CRDS using a linear resonator is not readily adapted to *in situ* studies of *a*-Si:H growth.

Alternatively, by employing an ultrahigh- Q miniature monolithic optical resonator, evanescent wave CRDS (Refs. 13 and 14) enables *in situ* studies with high sensitivity, as the concomitant evanescent wave at a total-internal reflection (TIR) surface serves as an ideally suited thin-film probe. The application of high- Q monolithic resonators to probe surfaces, films, and nanoscale materials shows considerable promise. For example, we demonstrated detection of a three-quantum vibration-combination transition on atomically smooth SiO_2 , revealing a unique quasi-ice monolayer at ambient temperature.¹⁴ Moreover, Borselli *et al.*¹⁵ used a monolithic microresonator to detect surface defect states on crystalline Si, revealing the role of surface passivation in the performance of microphotonic components. Here, we employ a monolithic folded resonator^{13,14} to probe the DB defect states during growth of *a*-Si:H from a predominantly SiH_x ($x=0-3$) radical flux on atomically smooth SiO_2 . Assuming an absorption cross section of $10^{-16} \text{ cm}^2/\text{defect}$,¹² a minimum detectable surface DB defect density of $\approx 10^8/\text{cm}^2$ is predicted, enabling mechanistic details to be elucidated.

Fabricated from ultralow-OH amorphous silica (Suprasil 300; Heraeus Tenevo), the folded resonator (Fig. 1, inset) has two orthogonal planar highly-refractive mirror surface ($R=99.998\%$ at 1200 nm) separated by a 2 cm unfolded path and a convex TIR surface. Having 0.05 nm rms roughness, the TIR surface forms the working surface for deposition, where an approximately 0.04 mm^2 region is sampled at the apex by the resonator modes. The idler beam of a seeded-tripled-neodymium-doped-yttrium-aluminum-garnet-pumped optical parametric oscillator (30 Hz, $\approx 0.5 \text{ mJ/pulse}$, 6 ns, linewidth $<10 \text{ cm}^{-1}$) was employed to generate orthogonally polarized ringdown transients, which were simultaneously detected by free-space-coupled, high-speed, 125 MHz, In-GaAs detectors. The resonator was mounted in a high-vacuum chamber ($<10^{-9} \text{ mbar}$) and maintained at 150°C

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FIG. 1. (Color online) (a) Base line spectra for an ultrahigh- Q monolithic folded resonator (inset) are shown for p and s polarizations at 150°C . In (b), the solid and dashed lines show the polarized absorption arising from dangling bonds in $a\text{-Si:H}$ films having thicknesses of 25 and 60 nm, respectively.

by radiative heating. The $a\text{-Si:H}$ film was deposited by thermal decomposition of SiH_4 at 4×10^{-3} mbar on a hot tungsten filament ($\sim 2050^\circ\text{C}$) located at a distance of 6.8 cm from the TIR surface, producing primarily SiH_3 as the growth precursor.¹⁶ Separate real-time spectroscopic ellipsometry measurements under identical conditions determined the growth rate to be 3.5 nm/min. The growth process was studied by performing many growth cycles (flux on/growth/flux off), resulting in a final thickness of 800 nm.

Figure 1(a) shows the absolute intrinsic loss per pass of the resonator prior to deposition for s and p polarizations between 1170 and 1245 nm using a 0.05 nm step size. Each data point is an average of 75 measurements, which yielded a typical 1σ noise level of 2×10^{-8} optical loss. The loss per pass reaches a minimum of 18×10^{-6} at 1205 nm, which yields a base ringdown time of 5.3 μs and a quality factor of $Q = 8.3 \times 10^9$. At 150°C in vacuum, the spectral dependence of the intrinsic loss arises mostly from mirror reflectance, although very weak features can be seen (arrows) at 1229, 1232, and 1236 nm, which we tentatively attribute to residual (100)- and (111)-cristobalite-like surface hydroxyl species.¹⁴ In Fig. 1(b), the solid and dashed plots show the intrinsic-loss-subtracted, polarized absorption spectra for 25 and 60 nm $a\text{-Si:H}$ films, respectively, obtained after termination of growth. As the DB defect state produces a very broad absorption, only a portion of the spectrum is accessible within the coating bandwidth. The trend observed in Fig. 1(b) is consistent with the DB signature, which shows an increasing absorption toward 1.2 eV.^{8,9,11,12} For both the intrinsic and film-coated resonator measurements we observed excellent stability (<1 ppm drift over 3 weeks at 150°C) and reproducibility, while environmental effects (e.g., surface heating by the filament) during experiments induced only very small variations in loss having relatively long time scales. Furthermore, no light induced degradation of the $a\text{-Si:H}$ thin film by the radiation from the filament or lamps was observed in control experiments.¹⁷

The spectra in Fig. 1(b) show distinct polarization anisotropy and a decrease in the optical loss for the 60 nm film compared to the 25 nm film, which derive from the thickness-dependent electric field structure in the film. The total optical loss of the film as a function of wavelength

FIG. 2. (Color online) s -polarized absorption when a radical flux is incident on the surface of a 60 nm film during a growth cycle of $a\text{-Si:H}$; the base resonator loss has been subtracted. The right ordinate shows the equivalent surface DB density induced by the radical flux.

$\Gamma(\lambda)$ is obtained by integrating the product of the relative electric field intensity $I_{s,p}(z, \lambda)$ and the position-dependent DB-density distribution function $N_{\text{DB}}(z)$ over the film thickness h ,

$$\Gamma(\lambda) = \int_0^h I_{s,p}(z, \lambda) N_{\text{DB}}(z) \sigma_{\text{DB}} dz, \quad (1)$$

where the DB absorption cross section σ_{DB} is assumed to be position independent. We approximate $I_{s,p}(z, \lambda)$ using a plane-wave matrix formalism,¹⁸ which adequately describes the bulk fields, including excitation of quasiwaveguide modes having broad radiative linewidths associated with coupling into the resonator half-plane. Specifically, the polarization anisotropy observed in Fig. 1(b) arises from the influence of the quasi- TE_0 mode, which leads to a larger average electric field intensity inside the film for s compared to p polarization for both h values considered. Similarly, a larger optical loss is observed for the 25 nm compared to the 60 nm film as optimal coupling into the broad quasi- TE_0 mode occurs at a thickness of <20 nm. Furthermore, Eq. (1) accounts for the surface contribution to the optical loss through $N_{\text{DB}}(h)$ and $I_{s,p}(h, \lambda)$. We use the s -polarized field to evaluate the DB defect contribution to the growth mechanism, since for the p -polarized field Fresnel analysis¹⁸ implies a large discontinuity in the normal component of the surface electric field. Using the s -polarized field provides therefore a quantitative description that is insensitive to the precise relationship between the chemical versus optical surface.¹⁸

Employing the single-laser-shot minimum detectable absorption of 10^{-7} , we probed the film growth kinetics with a repetition-rate-limited time resolution of 33 ms. Figure 2 shows the s -polarized optical response of a 60 nm $a\text{-Si:H}$ film to a 20 s radical flux exposure, where the base loss of the resonator has been subtracted. Figure 3 shows the optical loss for both s and p polarizations up to a film thickness of 800 nm, as obtained by combining sequential growth cycles similar to the growth cycle shown in Fig. 2. The large variation in the optical loss as a function of thickness in Fig. 3 derives from excitation of aforementioned quasi-waveguide modes, while the gradual increase in optical loss with thickness is caused by absorption by DBs in the bulk $a\text{-Si:H}$. The

FIG. 3. (Color online) Optical loss during growth of the *a*-Si:H film for (a) *p* polarization and (b) *s* polarization as a function of the film thickness; the base resonator loss has been subtracted. The sequential growth cycles are indicated by vertical tick marks in (a).

noise level in the data is enhanced at high optical loss values due to the reduced *Q* factor of the resonator+film configuration. Figure 2 shows that the film response to the radical flux attains steady state within several seconds of exposure, followed by comparatively slow recovery after flux termination. Using the measured DB absorption cross section, a *radical flux-induced* surface DB density can be obtained as shown on the right ordinate, where a local field correction has been applied using the electric field intensity just below the film surface [i.e., $I_s(h_-, \lambda)$]. Because the *s*-polarized electric field is continuous across the surface region, DB defects on the surface cannot be distinguished from those just inside the surface, although clearly defects on the surface are relevant to growth. However, the measured *s*-polarized loss is at least the sum of the true surface+subsurface contributions, which provides an *upper bound* for the steady-state surface DB density and the DB creation rate during growth.

Figure 4 shows the radical flux-induced surface DB density, as obtained from data in Figs. 2 and 3 at different film thicknesses. A thickness-independent steady-state surface DB density of $(5 \pm 2) \times 10^{11}$ DB/cm² is found, which corresponds to a fractional surface coverage of $\approx 5 \times 10^{-4}$. Such a low coverage precludes a mechanism based on the *direct* precursor-defect binding, as a coverage of ≈ 0.1 is required to account for typical *a*-Si:H growth rates, assuming a sticking probability for radical-radical coupling of 0.1.⁴ However, a low surface coverage does not eliminate mechanisms involving surface diffusion of weakly bound precursors²⁻⁴ or a direct insertion mechanism.^{19,20} Yet the role of the DB is significantly different for these latter two mechanisms. For precursor-mediated growth, the creation rate of DB defects is critical and must at least equal the growth rate (DB passivation rate), while for direct insertion the DB defect is not specifically relevant. As also shown in Fig. 4, the initial DB creation rate, which was obtained from many growth cycles at various film thicknesses, is found to be $(5 \pm 3) \times 10^{12}$ DB/cm² s. Comparing this value with the actual growth rate of 2.9×10^{14} Si/cm² s, assuming a Si density of 5×10^{22} cm⁻³ in *a*-Si:H, the DB creation rate is

FIG. 4. (Color online) Experimental DB surface density induced by the radical flux (left ordinate) and the corresponding DB creation rate (right ordinate, solid line) for a range of film thicknesses. The DB creation rate is contrasted with the calculated value (dashed line) needed to account for the actual growth rate based on a “dangling-bond” dependent growth mechanism.

$60 \times$ too small to account for the actual growth rate. Therefore, we conclude that the DB defect is not crucial in growth mechanism of a Si:H from radical precursors.

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- ¹A. Shah, P. Torres, R. Tscharnner, N. Wyrsh, and H. Keppner, *Science* **285**, 692 (1999).
- ²G. Ganguly and A. Matsuda, *Phys. Rev. B* **47**, 3661 (1993).
- ³J. Perrin, M. Shiratani, P. Kae-Nune, H. Videlot, J. Jolly, and J. Guillon, *J. Vac. Sci. Technol. A* **16**, 278 (1998).
- ⁴W. M. M. Kessels, A. H. M. Smets, D. C. Marra, E. S. Aydil, D. C. Schram, and M. C. M. van de Sanden, *Thin Solid Films* **383**, 154 (2001).
- ⁵S. M. Gates and S. K. Kulkarni, *Appl. Phys. Lett.* **58**, 2963 (1991).
- ⁶Y. Toyoshima, K. Arai, A. Matsuda, and K. Tanaka, *J. Non-Cryst. Solids* **137**, 765 (1991).
- ⁷T. Umeda, S. Yamasaki, J. Isoya, and K. Tanaka, *Phys. Rev. B* **59**, 4849 (1999).
- ⁸W. B. Jackson, D. K. Biegelsen, R. J. Nemanich, and J. C. Knights, *Appl. Phys. Lett.* **42**, 105 (1983).
- ⁹M. Vanecek, J. Kocka, A. Poruba, and A. Fejfar, *J. Appl. Phys.* **78**, 6203 (1995).
- ¹⁰S. Yamasaki, T. Umeda, J. Isoya, and K. Tanaka, *Appl. Phys. Lett.* **70**, 1137 (1997).
- ¹¹I. M. P. Aarts, B. Hoex, A. H. M. Smets, R. Engeln, W. M. M. Kessels, and M. C. M. van de Sanden, *Appl. Phys. Lett.* **84**, 3079 (2004).
- ¹²N. Wyrsh, F. Finger, T. J. McMahon, and M. Vanecek, *J. Non-Cryst. Solids* **137**, 347 (1991).
- ¹³A. C. R. Pipino, *Phys. Rev. Lett.* **83**, 3093 (1999).
- ¹⁴I. M. P. Aarts, A. C. R. Pipino, J. P. M. Hoefnagels, W. M. M. Kessels, and M. C. M. van de Sanden, *Phys. Rev. Lett.* **95**, 166104 (2005).
- ¹⁵M. Borselli, T. J. Johnson, and O. Painter, *Appl. Phys. Lett.* **88**, 131114 (2006).
- ¹⁶E. C. Molenbroek, A. H. Mahan, and A. Gallagher, *J. Appl. Phys.* **82**, 1909 (1997).
- ¹⁷D. L. Staebler and C. R. Wronski, *Appl. Phys. Lett.* **31**, 292 (1977).
- ¹⁸K. Ohta and H. Ishida, *Appl. Opt.* **29**, 1952 (1990).
- ¹⁹A. von Keudell and J. R. Abelson, *Phys. Rev. B* **59**, 5791 (1999).
- ²⁰S. Agarwal, M. S. Valipa, B. Hoex, M. C. M. van de Sanden, D. Maroudas, and E. S. Aydil, *Surf. Sci.* **598**, 35 (2005).