



Characterization of microvoids in thin hydrogenated amorphous silicon layers by spectroscopic ellipsometry and Fourier transform infrared spectroscopy



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ABSTRACT

Microstructures of voids in a-Si:H layers on the surface of c-Si wafers were quantitatively analyzed by combining spectroscopic ellipsometry and Fourier transform infrared spectroscopy. A diameter (D) from 0.52 to 2.11 nm and a number density (N_{voids}) from 8.4×10^{18} to $5.4 \times 10^{20} \text{ cm}^{-3}$ were estimated. It was demonstrated large-size voids were formed owing to the network relaxation caused by H^+ etching. Measurements of the minority carrier lifetime revealed both D and N_{voids} affect the passivation performance for a c-Si surface.

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Hydrogenated amorphous silicon (a-Si:H), as the most universal choice to passivate dangling bonds on crystalline silicon (c-Si) surfaces, has increasingly attracted attention over the last several decades. Recently, the conversion efficiency of silicon heterojunction (SHJ) solar cells has approached 25%, which is based on the excellent surface passivation of the a-Si:H layers for the c-Si wafer [1]. To further improve the performance of SHJ solar cells, it is necessary to optimize the optical and electrical properties of a-Si:H layers, which are closely related to their microstructures. For instance, the band gap increases linearly with the hydrogen content (C_{H}) [2], the position of the Fermi energy shifts with the impurity concentration [3], and the open-circuit voltage of an SHJ solar cell decreases drastically when epitaxial growth occurs [4]. Currently, various evaluation tools are widely used to characterize the microstructures of a-Si:H layers. For example, Raman scattering is used to investigate the short- and intermediate-range disorder [5], atomic force microscopy is used to determine the surface morphology [6], electron paramagnetic resonance is used to measure the dangling-bond-type defect density [7], and small-angle X-ray scattering (SAXS) is used to detect the existence of microvoids [8]. Among these, the detection of

microvoids is crucial because they lower the mass density [9] and are correlated with the Staebler–Wronski effect of a-Si:H layers [10,11].

In order to detect the microvoids embedded in a-Si:H networks, the thickness of the a-Si:H layer must be greater than $\sim 1 \mu\text{m}$ in SAXS measurements, which is much thicker than the passivation layer (usually $\sim 10 \text{ nm}$) of an SHJ solar cell. Further, the microstructures of the a-Si:H layers are often inhomogeneous along the growth direction in plasma-enhanced chemical vapor deposition (PECVD) [12,13]. These factors make the investigation of SHJ solar cells much more difficult. So far, the most popular method to evaluate the passivation performance of an a-Si:H layer is to measure the effective minority carrier lifetime (τ_{eff}) of a c-Si wafer covered with a-Si:H layers on both sides or even prepared in SHJ solar cell structures with a transition photoconductance decay method or a quasi-steady-state photoconductance decay method. By these means, it is possible to determine whether or not an a-Si:H layer is good for passivation, but the origin is unknown because of the lack of detailed information about the microstructures. There are still no powerful instruments that can be utilized to detect the microvoids in an a-Si:H layer with a thickness as low as $\sim 10 \text{ nm}$. In this letter, a method for estimating the diameter (D) and number density (N_{voids}) of the microvoids in an ultra-thin a-Si:H layer by spectroscopic ellipsometry (SE) and Fourier transform infrared

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spectroscopy (FTIR) is introduced. The correlation between these parameters (D and N_{voids}) for an ultrathin a-Si:H layer and the passivation performance for a c-Si surface is also summarized.

For the SE and FTIR measurements, (100) float-zone (FZ) Si wafers with mirrored surfaces (thickness: 525 μm and resistivity: $>3000 \Omega \text{ cm}$) were used as substrates. They were cleaned and etched with a diluted HF solution. a-Si:H layers ($\sim 20 \text{ nm}$) were deposited onto the substrates with PECVD operating at a radio frequency of 13.56 MHz. A wide range of plasma parameters, i.e., a H_2 -to- SiH_4 flow-rate ratio from 0 to 18 and a gas pressure from 0.15 to 2.48 Torr, were applied, the substrate temperature was fixed at 200 $^\circ\text{C}$. The as-deposited films were measured with SE (J. A. Woollam, M-2000XI) in the wavelength range from 246 to 1689 nm at different incident angles (50 $^\circ$, 60 $^\circ$, and 70 $^\circ$). An ambient/roughness layer/bulk a-Si:H layer/c-Si substrate optical model was used to fit the measured (ψ , Δ) curves to obtain the thickness and refractive index of the a-Si:H layers, where the Tauc-Lorentz model was used for the bulk a-Si:H layer [14], and the Bruggeman effective medium approximation (BEMA) combining 50 vol% bulk a-Si:H and 50 vol% ambient was used for the roughness layer. For the FTIR (Perkin Elmer, Spectrum 100) measurements, a bare FZ wafer was first measured using the background model; then, the as-deposited samples were measured using the sample model, and the transmittance spectra of the a-Si:H layers were directly obtained by subtracting the background. The transmittance spectra were then transformed into absorption spectra. C_{H} in an a-Si:H layer was calculated from the integrated value of the Si–H stretching modes at ~ 2000 and $\sim 2080 \text{ cm}^{-1}$. To evaluate the passivation effect of the a-Si:H layers, solar-grade czochralski (CZ) Si wafers (thickness: 200 μm , resistivity: 1–10 $\Omega \text{ cm}$) with surface texture were utilized. They were cleaned with the standard RCA process. a-Si:H layers with a constant thickness of 15 nm ($\pm 1 \text{ nm}$) were successively deposited onto both sides of the Si wafers using the same PECVD parameters as those for the deposition of the SE and FTIR measurement samples. τ_{eff} (s) were measured with Sinton's tester (Sinton, WCT-120) at a carrier injection level of $1.0 \times 10^{15} \text{ cm}^{-3}$.

Figure 1(a) shows the FTIR absorption spectra of two typical samples (referred to as A and B). The absorption in the wavenumber range of 1800–2250 cm^{-1} is attributed to Si–H stretching

modes, and can be fitted with two Gaussian functions around $\sim 2000 \text{ cm}^{-1}$ (LSM) and $\sim 2080 \text{ cm}^{-1}$ (HSM). Using the method in Ref. [15], the values of C_{H} for A and B are calculated to be 14.2 at.% and 13.2 at.%, respectively. However, their refractive indexes (Fig. 1(b)) are apparently different, especially at wavelengths $\lambda > 450 \text{ nm}$, the higher refractive index of A indicates a denser microstructure. Multiple-quantum nuclear-magnetic-resonance measurements revealed both device-quality and nondevice-quality a-Si:H films contain clusters of $\sim 6 \text{ H}$ atoms [16]. This indicates H clusters prefer to form divacancies. On the other hand, optical studies revealed the mass deficiency of a-Si:H layers is affected by not only divacancies but also microvoids, which originate from LSM and HSM networks, respectively [15,17,18]. Therefore, by comparing the results in Figure 1, we deduce the differences in the refractive indexes of two typical specimens are caused by the different microstructures due to the dissimilar distribution proportion of bonded H between divacancies and microvoids instead of the slightly different C_{H} .

Figure 1(c) shows every divacancy “misses” two Si atoms, replaced by six bonded H atoms [15,17]. Thus, the mass deficiency caused by divacancies can be expressed as $(2m_{\text{Si}}N_{\text{LSM}}/6) - m_{\text{H}}N_{\text{LSM}}$, m_{Si} and m_{H} are the atomic masses of Si and H, respectively, N_{LSM} is the bonded H density in the divacancies. To the best of our knowledge, the inner surface of a microvoid can be interpreted as a passivated surface decorated by both monohydrides (SiH) and dihydrides (SiH₂) (Fig. 1(c)). Mui and Smith deduced the density ratio between Si–Si₃H and Si–Si₂H₂ tetrahedrons can be expressed as $P_{\text{Si-Si}_3\text{H}}/P_{\text{Si-Si}_2\text{H}_2} = (4x - 1)/(1 - x)$ for an a-Si:H film with $C_{\text{H}} = (1 - x) \times 100\%$ [19]. That is, $P_{\text{Si-Si}_3\text{H}}/P_{\text{Si-Si}_2\text{H}_2} \geq 16$ when $C_{\text{H}} \leq 15 \text{ at.}\%$. Thus, the monohydrides have the largest contribution to the HSM infrared absorption. This is in agreement with the conclusion of Smets et al. [15].

The complex dielectric functions of a-Si:H thin layers, obtained by fitting the (ψ , Δ) curves measured by SE at different incident angles, are almost the same (not shown here). This implies the as-deposited a-Si:H films have isotropic homogeneity. Thus, the microvoids are randomly shaped or have spherical shapes. Here, we assume they are spherical, as assumed by many other scientists. It is noted that every Si atom on (111) surface has one dangling bond, which is appropriate for forming a monohydride structure. Considering that monohydrides have the largest contribution to the HSM infrared absorption, we believe the bonded H density on the inner surfaces of the microvoids is approximately the same as the Si density on the (111) plane, which is equal to $7.83 \times 10^{14} \text{ cm}^{-2}$. Then, the following equations are used to describe the microvoids in an a-Si:H network:

$$N_{\text{HSM}} = 4\pi \left(\frac{D}{2}\right)^2 N_{\text{voids}} \rho_{\text{S}}, \quad (1)$$

$$(\rho_{\text{Si}} - \rho_{\text{a-Si:H}})V_{\text{unit}} = \left[\frac{2N_{\text{LSM}}m_{\text{Si}} - N_{\text{LSM}}m_{\text{H}}}{6} + \left[\frac{4}{3}\pi \left(\frac{D}{2}\right)^3 N_{\text{voids}} \rho_{\text{Si}} - N_{\text{HSM}}m_{\text{H}} \right] \right], \quad (2)$$

N_{HSM} the bonded H density originating from HSM; $\rho_{\text{S}} = 7.83 \times 10^{14} \text{ cm}^{-2}$ the bonded H density on the inner surfaces of the microvoids; $\rho_{\text{Si}} = 2.35 \text{ g cm}^{-3}$ the mass density of c-Si and is used to represent the mass density of an ideal a-Si without vacancies and microvoids; V_{unit} the unit volume. Eq. (1) describes the total bonded H density on the inner surfaces of microvoids in the unit volume, whereas Eq. (2) denotes the quantitative decrease in the mass density of a-Si:H (compared to ideal a-Si) caused by mass deficiencies including divacancies and microvoids. The mass density of a-Si:H is given by [15,17]

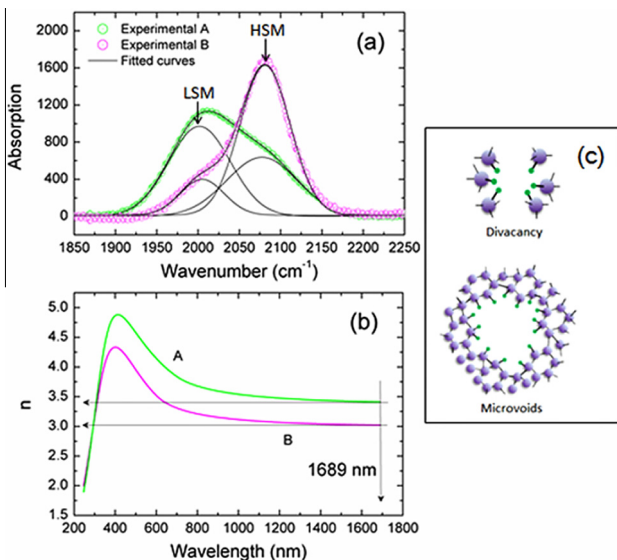


Figure 1. (a) FTIR absorption spectra and (b) refractive index spectra of two typical a-Si:H thin layers; (c) schematic diagram of divacancy and microvoid, the large and small balls represent Si and H atoms, respectively.

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