Bonded hydrogen in nanocrystalline silicon photovoltaic materials: Impact on structure and defect density

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(Received 30 May 2011; accepted 10 August 2011; published online 22 September 2011)

We have performed a detailed structural and optical investigation of hydrogenated nanocrystalline silicon (nc-Si:H) thin films prepared by plasma-enhanced chemical vapor deposition. The microstructural properties of these thin films are characterized and interpreted physically based on the growth mechanism. Infrared spectroscopy reveals that the bonded hydrogen in a platelet-like configuration, which is believed to be located at grain boundaries, greatly affects oxygen incursions into nc-Si:H thin films, whereas electron spin resonance observations link these incursions to the introduction of dangling bond defects. Consequently, we propose that in nc-Si:H thin films, high bonded-hydrogen content in grain boundaries is of great importance in forming hydrogen-dense amorphous tissues around the small crystalline grains, i.e., compact grain boundary structures with good passivation. Such structures effectively prevent post-deposition oxidation of grain boundary surfaces, which might lead to the formation of dangling bond defects. © 2011 American Institute of *Physics*. [doi:10.1063/1.3638712]

I. INTRODUCTION

Hydrogenated nanocrystalline silicon (nc-Si:H) is a mixed phase material consisting of nanometer grains embedded within a hydrogenated amorphous silicon (a-Si:H) host matrix.¹ This material holds great promise as a low-cost, high-efficiency photovoltaic thin film suitable for tandem cell applications.² Extensive optical and electrical investigations of nc-Si:H thin films have been performed^{3–5} that revealed good properties such as high electron mobility^{3,4} and strong optical absorption with a large photocurrent.⁵

It is generally believed that the optical and electrical properties of nc-Si:H thin films are strongly affected by the bonding configuration of hydrogen as well as its content in the films.⁶ Bonded hydrogen in nc-Si:H thin films has been systematically investigated in several studies,^{7–10} and the hydrides with stretching mode at around 2033 cm⁻¹ are indentified as hydrides in a platelet-like configuration at grain boundaries resulting from the reaction of H-induced crystallization of a-Si:H during film deposition.^{9,10} However, the role of these hydrides within nc-Si:H thin films remains to be further investigated.

In contrast, previous works on microcrystalline silicon thin films have indicated that the post-deposition oxidation of the films, arising from the porosity at grain boundaries, is linked to the introduction of dangling-bond (DB) defects at the Si-O/Si interface (P_b center defects).¹¹ A reduction in the socalled red response of photovoltaic devices has been observed,¹² and thus such porous structures should be avoided. Nonetheless, post-deposition oxidation of nc-Si:H in which grain boundaries not only are unavoidable but also makeup a large volume fraction is still unclear; only recently has a strong correlation been reported between the deep-defect density with oxygen and hydrogen content in nc-Si:H.¹³

In our study, we have performed a detailed structural and optical investigation of nc-Si:H thin films, focusing on bonded hydrogen in a platelet-like configuration at grain boundaries and post-deposition oxidation of the films. We emphasize in this paper the effect of bonded hydrogen in platelet-like configurations on the prevention of the postdeposition oxidation. This arises due to the formation of a hydrogen-dense compact grain boundary structure with good passivation in nc-Si:H thin films. In combination with microstructural characterizations of the films, we discuss the dependence on deposition condition for platelet-like hydrides in terms of the growth mechanism.

II. EXPERIMENTS

The intrinsic nc-Si:H thin films with thicknesses of 0.6–3.0 μ m were prepared on both glass and double-sided-polished intrinsic single crystalline silicon (c-Si) substrates under a radio-frequency (rf, 13.56 MHz) capacitively coupled plasma-enhanced chemical vapor deposition (PECVD) from silane (SiH₄) and hydrogen (H₂) at a temperature of 250 °C, a total gas flow rate of 150 sccm, and a chamber pressure of 150 Pa. The percentage content of silane [SiH₄/(SiH₄+H₂)] was kept constant at about 1%. The rf power density (*P*_W) ranged from 0.17 to 0.61 W/cm² at 0.08–0.09 W/cm² increments; the samples were denoted sequentially RF100, RF150, RF200, RF250, RF300, and RF350 (see Table I).

The microstructure and optical properties of these nc-Si:H thin films have been characterized by x-ray diffraction (XRD), Raman, and optical transmission measurements. The respective measurements were performed on a Bruker D-8 XRD system with a Cu K α radiation (40 kV, 60 mA), a Jobin Yvon LabRam HR800 UV micro-Raman spectrometer in

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TABLE I. Parameters for the nc-Si:H thin films prepared under different power densities. P_W is the power density, R_d the growth rate obtained from step profilometer measurements, X_c the crystalline fraction calculated from Raman spectra, d the average grain size derived from XRD (111) peaks, n_{∞} the refractive index in the long wavelength limit deduced from optical transmission spectra, C_H and C_O the bonded hydrogen and oxygen content studied from IR absorption spectra, respectively, and N_S the spin density estimated from ESR measurements.

| Samples No. | $P_{\rm W} ({\rm W/cm}^2)$ | $R_{\rm d}({\rm \AA/s})$ | $X_{\rm c}~(\%)$ | d (nm) | n_{∞} | $C_{\rm H} ({\rm at.}\%)$ | $C_{\rm O}({\rm at.}~\%)$ | $N_{\rm S}~(10^{16}/{\rm cm}^3)$ |
|-------------|-----------------------------|--------------------------|------------------|--------|--------------|---------------------------|---------------------------|----------------------------------|
| RF100 | 0.17 | 0.36 | 44.9 | 6.1 | 3.177 | 8.7 | 7.4 | 11.9 |
| RF150 | 0.26 | 0.36 | 48.5 | 6.5 | 3.184 | 9.1 | 7.7 | 11.8 |
| RF200 | 0.35 | 0.37 | 52.0 | 7.0 | 3.287 | 7.0 | 10.1 | 14.5 |
| RF250 | 0.43 | 0.47 | 48.7 | 6.1 | 3.141 | 12.5 | 3.6 | 7.5 |
| RF300 | 0.52 | 0.66 | 45.0 | 5.6 | 3.085 | 12.3 | 4.3 | 9.0 |
| RF350 | 0.61 | 0.49 | 45.6 | 5.7 | 3.062 | 14.4 | 5.1 | 10.7 |

backscattering configuration mode using an Ar ion laser (514.5 nm), and a Jobin Yvon 460 monochromator in the spectral range of 400–900 nm (0.5 nm resolution). Atomic-scaled micrographs and selected area electric diffraction (SAED) patterns of the nc-Si:H thin films were obtained by transmission electron microscopy (TEM, CM200, Philips).

To obtain detailed information on bonded hydrogen and oxygen within these thin film samples, we performed infrared (IR)-absorption measurements between 400 and 4000 cm⁻¹ with a Nicolet Nexus 870 Fourier transform infrared spectrometer of films deposited on double-sided-polished intrinsic c-Si wafers. Electron spin resonance (ESR) measurements were performed to estimate the defect density of the films in the X-band using a Bruker EMX-8 ESR spectrometer operation at 9.8 GHz. The microwave power used in the ESR measurements was 1 mW, and the powdered samples used were peeled from the thicker films. Moreover, a Dektak 6M profilometer was used to measure the thicknesses of the films. All these measurements were conducted at room temperature about 3 mo after sample preparation.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a typical high resolution TEM (HRTEM) image of sample RF100. The micrograph verifies the presence of approximately 6 nm-sized silicon nanocrys-tallites with the embedded in an amorphous matrix. The inset provides the SAED pattern, showing the diffraction rings of the (111) and (220) planes of silicon. The HRTEM and SAED enable us to have atom-scaled images of the two-phase-mixture to ascertain the nature of nc-Si:H thin films.

To obtain structural details of the nc-Si:H films, we performed Raman, XRD, and optical transmission measurements at room temperature; typical results corresponding to sample RF100 are illustrated in Figs. 1(b) to 1(d). As shown in Fig. 1(b), the experimental Raman spectrum (open circles) is decomposed into three Gaussian phonon bands from the amorphous silicon contribution [*viz.*, a longitudinal acoustic (LA) band centered at 300 cm⁻¹, a longitudinal optical (LO) band at 380 cm⁻¹, and a transverse optical (TO₁) band at 480 cm⁻¹], and one asymmetric transverse optical (TO₂) band at around 520 cm⁻¹ from the crystalline silicon contribution calculated from the strain-incorporated three-dimensional phonon confinement model.¹⁴ The Raman crystalline fraction (X_c) of 44.9% is deduced by using the relationship $X_c = I_c/$ ($I_c + \gamma I_a$),¹⁵ in which I_c is the integrated intensity of TO₂ Raman mode whereas I_a is the integrated intensity of TO₁ Raman mode and $\gamma(L_0) = 0.1 + \exp(-L_0/25)$ with L_0 the average defect distance of 5.6 nm.

Figure 1(c) presents the experimental XRD pattern that displays peaks typical of Si atoms in an ordered lattice. The diffraction peaks located at $2\theta = \sim 29.0^{\circ}$, $2\theta = \sim 47.5^{\circ}$, and $2\theta = \sim 57^{\circ}$ correspond to the (111), (220), and (311) planes of silicon, respectively. In accord with the strongest diffraction peak intensity, the (111) plane is considered to be the preferential growth orientation for these films. The large diffraction peak broadening manifests the nanometer-sized grains that appear in the films; for sample RF100 an average grain size (*d*) of 6.1 nm has been obtained using Lorentzian fitting of the (111) peak as well as the Scherrer formula.¹⁶ Figure 2(a) shows the grain sizes obtained from XRD (111) peak for all the studied samples.

Also for sample RF100, Fig. 1(d) displays the experimental optical transmission spectrum (open circles) and the result (solid curve) calculated by the envelop method¹⁷ from which two important parameter values can be obtained, namely the refractive index in the long wavelength limit



FIG. 1. (Color online) Typical results obtained from the nc-Si:H thin film sample RF100. (a) HRTEM image with SAED pattern shown in the inset. (b) Experimental (open circles) and fitted (solid curves) Raman spectra. (c) Experimental XRD spectrum showing diffraction peaks of (111), (220), and (311). (d) Experimental (open circles) and fitted (solid curve) transmission spectra.



FIG. 2. (Color online) (a) Grain sizes and (b) volume fractions within the nc-Si:H thin films under different power densities.

 (n_{∞}) of 3.177 and the film thickness of 0.839 μ m. n_{∞} is an important wavelength-independent optical parameter related to mass density and atomic structure of the film and is discussed further in the following. Meanwhile, a good agreement has been achieved between film thicknesses derived from both the envelope method analyses and step profilometer measurements.

It is well known that nc-Si:H is a two-phase-mixed material with nanocrystallites embedded in an amorphous matrix. However, nanometer-sized voids also exist in nc-Si:H thin films; these should not be neglected when characterizing the microstructure of nc-Si:H.^{18,19} Thus, based on Bruggeman's effective media approximation (BEMA),²⁰ we calculate volume fractions of crystalline silicon (p_c), amorphous silicon (p_a), and voids (p_v) of the films by using the crystalline fraction (X_c , from Raman analysis) and the refractive index (n_{∞} , from transmission analysis).²¹ The variation of these three volume fractions with increasing power density are presented in Fig. 2(b).

It is clear that the rf power density plays an important role in the microstructure of the nc-Si:H thin films during their depositions by PECVD. The change in power density results in a variation of the kinetic energy both for SiH_x (x = 0-3, mainly for x = 3) precursors and for atomic hydrogen, that can be divided into two stages. During the initial period, stage I, in which the power densities are below 0.35 W/cm^2 , the surface diffusion length of the film precursors is enhanced as the power increases that leads to the formation of an atomically flatter growing surface.²² Such processes result in a decrease in the void volume fraction. Meanwhile the H-induced crystallization of a-Si:H^{8,9,23,24} is also reinforced, leading to the increases of crystalline volume fraction as well as grain size. Additionally, the growth rates (R_d) of the films listed in Table I remains unchanged because the source gas SiH₄ is considered to be completely depleted within the power density range of our experiments.²⁵

During the final period, stage II, at still higher power densities, a large number of H atoms and ions on the growing surface with excessively high kinetic energies enhance the H-abstraction reaction, which reduces the surface diffusion length of film precursors,^{26,27} thus clearly increasing the growth rate. High power densities also bring about excessive silicon etching, which together with the H abstraction reaction causes not only decreases in crystallization and grain size but also increases in voids within the film.²⁸ In particular, under power densities as high as 0.61 W/cm², extremely strong silicon etching dramatically influences film growth by decelerating the growth rate and reducing both amorphous and crystalline volume fractions, resulting in further increases in the void volume fraction.

Aside from its effects on microstructure, the rf power also largely affects hydrogen content and its bonding configuration in nc-Si:H thin films.³ Therefore we have employed room-temperature IR-transmission measurements to better understand hydrogen incorporation of the nc-Si:H thin film samples we studied. Figure 3 shows the IR-absorption spectra of the samples prepared under different power densities, in which absorption peaks of the Si-H rocking-wagging mode, bending mode, and stretching mode can be observed at around 630 cm⁻¹, 880 cm⁻¹, and 2090 cm⁻¹,^{29,30} respectively. Also, we see an absorption peak at 1000-1200 cm^{-1} related to the Si-O stretching mode,^{31,32} which indicates the unwelcomed incorporation of oxygen in the samples. The bulk oxidation was considered to be linked to the introduction of Si-O/Si interface DB (Pb center) defects¹¹ as well as a reduction in the so-called red response of photovoltaic devices.¹² A strong dependence of the deep defects on oxygen content has also been observed in our nc-Si:H thin films; this will be discussed later.

The bonded-hydrogen content $C_{\rm H}$ is obtained by numerical integration of the Si-H rocking-wagging mode at around 630 cm⁻¹. The complete procedure^{29,33} can be expressed as:



FIG. 3. IR-absorption spectra of the nc-Si:H thin films prepared under different power densities as marked; the spectra are shifted vertically for clarity.

$$C_{\rm H} (\text{at. \%}) = \frac{A_{\rm W}}{N_{\rm Si}} \int_{\upsilon/w} \frac{\alpha(\upsilon)}{\upsilon} d\upsilon$$
(1)

where $\alpha(\nu)$ stands for the absorption coefficient of the film at the wave number ν , ν/w the rocking-wagging bands around 630 cm⁻¹, and $N_{\rm Si} = 5 \times 10^{22}$ cm⁻³ the atomic density of pure silicon. We fixed the proportionality constant as $A_{\rm W} = 2.1 \times 10^{19}$ cm⁻² to determine the hydrogen content.³⁴ Similarly, the bonded-oxygen content $C_{\rm O}$ can be deduced from the numerical integration of the fitted band of the Si-O stretching mode at 1000-1200 cm⁻¹ with $A_{\rm W} = 2.8 \times 10^{19}$ cm⁻².^{30,31}

From the hydrogen and oxygen content of the nc-Si:H samples listed in Table I, an interesting inverse correlation has been found in which higher oxygen content appears in films with lower hydrogen content and vice versa. Similar results have been found recently,^{13,35} although no further investigation leading to a convincing explanation for such phenomenon had been conducted. The variation of the crystalline volume fraction was suggested to be a possible factor that influences the hydrogen and oxygen content;¹³ nevertheless, our experimental data provide no evidence for such a conclusion. Hence to better understand the correlation between the bonded hydrogen and oxygen in nc-Si:H thin films, we turn to investigate the stretching mode of Si-H at around 2090 cm⁻¹, which provides detailed information about the different bonding configurations of hydrogen.

Figure 4(a) presents the IR-absorption spectrum (open circles) of sample RF100 in the range of the hydride stretching modes; five modes can be identified that relate to the hydrides in different bonding configurations. The stretching mode frequency position of a hydride in the bulk depends on the unscreened eigen-frequency of the hydride, bulk screening, local hydride density, and possible mutual dipole interactions of the hydrogen incorporation configuration.³⁶ The low stretching mode (LSM), in the range 1980-2010 cm⁻¹, and the high stretching mode (HSM), in the range 2070-2100 cm⁻¹, originate from the a-Si:H tissue of nc-Si:H thin film,

in which the monohydrides in vacancies contribute dominantly to the LSM, whereas both the monohydrides and the dihydrides on void surfaces contribute significantly to the HSM.⁷ The extreme HSM (EHSM), between 2140 and 2150 cm⁻¹, arises from the trihydrides in the film deposited under high hydrogen dilution condition.⁸ The stretching mode at ~2250 cm⁻¹ (O_xSi-H_y SM) corresponds to the hydride O_xSi-H_y vibration in which the oxygen atoms are back-bonded to silicon atoms,³⁷ and thus, together with the Si-O stretching mode at 1000-1200 cm⁻¹, reflect the bulk oxidation of the film. The middle stretching mode (MSM) at ~2033 cm⁻¹ is due to hydride vibrations located in a platelet-like configuration at the amorphous-crystalline interfaces, *i.e.*, the grain boundaries.⁸⁻¹⁰

Figure 4(b) illustrates the integrated absorptions of the LSM (I_{2000}) , MSM (I_{2033}) , and HSM (I_{2090}) for all the samples studied; these are deduced from the decomposition of the stretching bands illustrated in Fig. 4(a). Let us first discuss the evolutions of I_{2000} and I_{2090} , which indicate changes in hydrogen-bonding configurations in the amorphous tissue of nc-Si:H thin films. In the earlier-mentioned stage I, decreases of both I_{2000} and I_{2090} with increasing power density have been observed. These can be explained by decreases in the amorphous volume fraction of the films as power increases. Moreover, the decrease in I_{2090} , which reflects the hydride presence on a-Si:H void surfaces, also corresponds well with the reduced void volume fraction of the films discussed in Fig. 2. In stage II, the obvious higher I_{2090} is considered to be caused by the excessively high kinetic energy of H atoms and ions during film deposition. As depicted in Fig. 2, the excessive silicon etching reaction together with the H-abstraction reaction leads to a less compact a-Si:H tissue with more voids in this stage; at the same time, H atoms and ions with higher kinetic energy enhance the H diffusion into the bulk, thus more H atoms and ions permeate into the sub-surface region of the film during its deposition. Therefore, DBs on the surfaces of the increased voids are passivated by diffusing H atoms and ions, leading to the



FIG. 4. (Color online) (a) A close-up of the measured Si-H stretching modes (open circles) of the nc-Si:H thin film sample RF100. The solid curve represents the total fit, whereas the dashed curves are the five Gaussian-shaped stretching modes. (b) Bar graph of integrated absorptions of the LSM, HSM, and MSM. (c) Integrated absorption of the MSM and oxygen content within the nc-Si:H thin films prepared under different power densities.

formation of the HSM hydrides. Such processes explain the dramatically high I_{2090} as well as the total bonded hydrogen content listed in Table I in stage II, and both of these integrated absorptions keep increasing as the power density is further increased. Moreover, more dihydrides are formed in this stage, which can be reflected by their reinforced bending mode at around 880 cm⁻¹ (see Fig. 3); these dihydrides are considered to be responsible for the deterioration of the nc-Si:H thin film solar cell efficiency stability.³⁸ Similarly, it is easy to understand the decrease in I_{2000} that reflects hydrides located in vacancies of the a-Si:H tissue.

We move our attention next to the MSM corresponding to the vibration of hydrides in a platelet-like configuration; so far few studies have focused on this. We start with the formation of those hydrides in such a mode. The process of Hinduced crystallization of a-Si:H by the insertion of H into the strained Si-Si bonds, both on the surface and in the bulk of the film, leads to the formation of (a) a bond-centered hydrogen, where a H atom is present between two Si atoms and is bonded to both Si atoms, (b) an isolated silicon monohydrides where the H atom is bonded to only one Si leaving a DB on the other Si after the break of the strained Si-Si bond, or (c) a Si-Si bond with bond length close to the equilibrium c-Si bond length (2.35 Å) where the H atom is bonded to only one Si atom after the relaxation of the strained Si-Si bond.^{10,39} Silicon hydrides in a platelet-like configuration in which the Si-H bonds are present along a planar defect, i.e., the grain boundaries, are formed just after the passivation of DBs in condition (b) mentioned above by H diffusion. Such a platelet-like configuration is similar to the structures observed in c-Si where Si-H bonds are predominantly oriented along {111} crystallographic planes.⁴⁰

Clearly the reactions of H insertion and H diffusion are fundamental in forming the MSM hydrides. The strikingly higher I_{2033} in stage II can be explained in that the H atoms and ions with higher kinetic energy enhance the H diffusion into the bulk of film, especially diffusion along the grain boundaries, which as a result leads to higher hydride content in a platelet-like configuration. In contrast, the H diffusion reaction is relatively weak over the power density range existing in stage I. However, H atoms and ions with extremely high kinetic energy also turn MSM hydrides into HSM hydrides by excessive silicon etching, which can be obviously observed at the power density of 0.61 W/cm². Furthermore, we attribute the slight decrease in I_{2033} during stage I as power density increases to the increase in grain size which reduces the grain boundary volume fraction.

It is well known that grain boundaries makeup a large volume fraction in nc-Si:H because the crystalline fraction of nc-Si:H is made of nanometer-sized crystalline grains. Thus we need to investigate further the role of MSM hydrides located within grain boundaries on nc-Si:H thin films. As shown in Fig. 4(c), the oxygen content depends strongly on the integrated absorption of the MSM; a higher integrated absorption signifies lower oxygen content. To explain this, we suggest that the MSM hydrides help to form a hydrogen-dense amorphous tissue around the small crystalline grains, i.e., a compact grain boundary structure with good passivation. Consequently, the permeation of oxygen into grain boundaries during preservation of the films that results in the post-deposition oxidation of the grain boundary surface can be effectively prevented. Moreover, films of higher integrated absorptions of the MSM have grain boundaries with more H molecules adsorbed on the surfaces, namely H-rich regions within grain boundaries⁴¹ that are also beneficial in preventing post-deposition oxidation.

To relate the unwanted incursion of oxygen in nc-Si:H thin films to the deterioration in electrical properties, we employed room-temperature ESR measurements which basically detect the density of neutral DBs with unpaired spins. Figure 5(a) shows the ESR spectra of the nc-Si:H samples prepared under different power densities, each normalized to the sample mass so that the signal amplitude is proportional to spin density. All spectra show an asymmetric line shape believed to be caused by a superposition of several resonances due to DB types in different environments.⁴² However, the identification and location of the possible different defects, which mainly determines the g-value as well as the peak-to-peak width of the ESR spectrum, is still a matter of debate that we will not discuss further. We shall focus here on the spin density (N_S) , as compared to a spin standard, of our nc-Si:H samples calculated from a numerical doubleintegration over the entire signal of the spectrum. As illustrated in Fig. 5(b), a strong correlation between the spin density (from ESR) and the oxygen content (from absorption in Fig. 4) of the nc-Si:H thin films can be observed. This indicates that oxygen incursions result in the formation of DB defects, the Si-O/Si interface DB defects (Pb center defects) being the most likely candidates.¹¹ Considering that the density of DB defects in amorphous tissues is relatively low $[\sim 10^{15} \text{ cm}^{-3} \text{ (Ref. 43)}]$ due to the effective passivation by hydrogen during deposition under a high hydrogen dilution condition, as well as the induced DB densities caused by the increased voids in a-Si:H tissue [$\sim 10^{15}$ cm⁻³ (Ref. 26)], we submit that post-deposition oxidation of grain boundary surfaces mainly results in the increase of DB defects in the nc-Si:H thin films that we have studied. Verification of this fact is supported by the clear proportionality between oxygen content and spin density in Fig. 5(b).



FIG. 5. (a) ESR spectra of the nc-Si:H thin films prepared under different power densities normalized by sample mass. (b) The correlation between spin density and oxygen content.

IV. CONCLUSIONS

In summary, the microstructure of nc-Si:H thin films prepared by PECVD has been identified using Raman spectroscopy, XRD, optical transmission spectroscopy, and TEM measurements. IR absorption spectroscopy has been performed to obtain detailed information on bonded-hydrogen and oxygen content as well as bonding configurations of hydrogen in nc-Si:H thin films. The evolution of the microstructure and bonded hydrogen in terms of content and bonding configuration can be explained by the variation in kinetic energy of hydrogen atoms and ions during film deposition under different power densities. Moreover, we have found a strong correlation between oxygen incursion and bonded hydrogen in a platelet-like configuration, i.e., hydrides in grain boundaries, in which more platelet-like hydrides lead to less oxygen incorporation. We attribute such phenomenon to the role of bonded hydrogen in platelet-like configurations in the prevention of post-deposition oxidation by forming a hydrogen-dense compact grain boundary structure with good passivation in nc-Si:H thin films where grain boundaries makeup a large volume fraction. The deterioration in electrical properties of nc-Si:H thin films from oxygen incursions by the introduction of DB defects has been further verified using ESR measurements. Therefore, we submit that hydrides in grain boundaries are of great importance to the property of nc-Si:H thin films, special attention of which could provide benefits in improving the performance of nc-Si:H-based thin-film solar cells. Nevertheless, according to our experimental data, the higher power densities needed to initiate platelet-like hydride formations during film deposition also leads to higher voids volume fractions in amorphous tissues and higher dihydride content, both of which should be avoided in nc-Si:H thin film solar cell manufacture. Consequently, further investigation is necessary to determine precise optimal growth conditions that yield nc-Si:H thin films with not only compact grain boundary structures but also compact amorphous tissues with less dihydrides.

ACKNOWLEDGMENTS

This work was supported by the National Major Basic Research Project of 2012CB934302 and Natural Science Foundation of China under Contract Nos. 11074169 and 11174202.

- ¹Y. L. He, C. Z. Yin, G. X. Cheng, L. C. Wang, X. N. Liu, and G. Y. Hu, J. Appl. Phys. **75**, 797 (1994).
- ²J. Yang, B. Yan, and S. Guha, Thin Solid Films **487**, 162 (2005).
- ³X. Y. Chen, W. Z. Shen, H. Chen, R. Zhang, and Y. L. He, Nanotechnology 17, 595 (2006).
- ⁴X. Y. Chen, W. Z. Shen, and Y. L. He, J. Appl. Phys. 97, 024305 (2005).
- ⁵R. Zhang, X. Y. Chen, K. Zhang, and W. Z. Shen, J. Appl. Phys. **100**, 104310 (2006).
- ⁶A. M. Funde, N. A. Bakr, D. K. Kamble, R. R. Hawaldar, D. P. Amalnerkar, and S. R. Jadkar, Sol. Energy Mater. Sol. Cells **92**, 1217 (2008).

- ⁷A. H. M. Smets, W. M. M. Kessels, and M. C. M. van de Sanden, Appl. Phys. Lett. **82**, 1547 (2003).
- ⁸D. C. Marra, E. A. Edelberg, R. L. Naone, and E. S. Aydil, J. Vac. Sci. Technol. A **16**, 3199 (1998).
- ⁹A. V. Keudell and J. R. Abelson, J. Appl. Phys. 84, 489 (1998).
- ¹⁰S. Agarwal, B. Hoex, M. C. M. van de Sanden, D. Maroudas, and E. S. Aydil, J. Vac. Sci. Technol. B 22, 2719 (2004).
- ¹¹F. Finger, R. Carius, T. Dylla, S. Klein, S. Okur, and M. Günes, IEE Proc.: Circuits Devices Syst. 150, 4 (2003).
- ¹²T. Matsui, A. Matsuda, and M. Kondo, Sol. Energy Mater. Sol. Cells 90, 3199 (2006).
- ¹³P. G. Hugger, J. D. Cohen, B. J. Yan, G. Z. Yue, J. Yang, and S. Guha, Appl. Phys. Lett. **97**, 252103 (2010).
- ¹⁴M. Yang, D. M. Huang, P. H. Hao, F. L. Zhang, X. Y. Hou, and X. Wang, J. Appl. Phys. **75**, 651 (1994).
- ¹⁵E. Bustarret, M. A. Hachicha, and M. Brunel, Appl. Phys. Lett. **52**, 1675 (1988).
- ¹⁶M. R. Fitzsimmons, J. A. Eastman, M. Müller-Stach, and G. Wallner, Phys. Rev. B 44, 2452 (1991).
- ¹⁷H. Chen, M. H. Gullanar, and W. Z. Shen, J. Cryst. Growth **260**, 91 (2004).
- ¹⁸S. C. Moss and J. F. Graczyk, Phys. Rev. Lett. 23, 1167 (1969).
- ¹⁹H. C. Lee, S. I. Lee, H. Lee, S. H. Choi, J. I. Ryu, and J. Jang, J. Korean Phys. Soc. **39**, S30 (2001).
- ²⁰D. A. G. Bruggeman, Ann. Phys. 24, 636 (1935).
- ²¹J. Mullerova, P. Sutta, G. Vanelzakker, M. Zeman, and M. Mikula, Appl. Surf. Sci. 254, 3690 (2008).
- ²²A. Matsuda, Thin Solid Films **337**, 1 (1999).
- ²³S. Sriraman, S. Agarwal, E. S. Aydil, and D. Maroudas, Nature 418, 62 (2002).
- ²⁴S. Sriraman, S. Agarwal, E. S. Aydil, and D. Maroudas, J. Appl. Phys. 100, 053514 (2006).
- ²⁵E. Amanatides, S. Stamou, and D. Mataras, J. Appl. Phys. **90**, 5786 (2001).
- ²⁶A. H. Mahan, Y. Xu, D. L. Williamson, W. Beyer, J. K. Perkins, M. Vanecek, L. M. Gedvilas, and B. P. Nelson, J. Appl. Phys. **90**, 5038 (2001).
- ²⁷J. Robertson, J. Appl. Phys. 87, 2608 (2000).
- ²⁸S. C. Saha, A. K. Barus, and S. Ray, J. Appl. Phys. 74, 5561 (1993).
- ²⁹M. H. Brodsky, M. Cardona, and J. J. Cuomo, Phys. Rev. B **16**, 3556 (1977).
- ³⁰G. Lucovsky, R. J. Nemanich, and J. C. Knights, Phys. Rev. B 19, 2064 (1979).
- ³¹E. C. Freeman, and W. Paul, Phys. Rev. B 18, 4288 (1978).
- ³²D. V. Tsu, G. Lucovsky, and B. N. Davidson, Phys. Rev. B 40, 1795 (1989).
- ³³U. Kroll, J. Meier, A. Shah, S. Mikhailov, and J. Weber, J. Appl. Phys. 80, 4971 (1996).
- ³⁴A. A. Langford, M. L. Fleet, B. P. Nelson, W. A. Lanford, and N. Maley, Phys. Rev. B 45, 13367 (1992).
- ³⁵J. Kočka, H. Stuchlíkováa, M. Ledinskýa, J. Stuchlíka, T. Matesa, and A. Fejfar, Sol. Energy Mater. Sol. Cells 66, 1444 (2009).
- ³⁶A. H. M. Smets and M. C. M. van de Sanden, Phys. Rev. B **76**, 073202 (2007).
- ³⁷M. Niwano, J. Kageyama, K. Kurita, K. Kinashi, I. Takahashi, and N. Miyamoto, J. Appl. Phys. **76**, 2157 (1994).
- ³⁸M. Kondo and A. Matsuda, Curr. Opin. Solid State Mater. Sci. 6, 445 (2002).
- ³⁹M. S. Valipa, S. Sriraman, E. S. Aydil, and D. Maroudas, J. Appl. Phys. 100, 053515 (2006).
- ⁴⁰N. H. Nickel, G. B. Anderson, N. M. Johnson, and J. Walker, Phys. Rev. B 62, 8012 (2000).
- ⁴¹S. Vignoli, R. Butté, R. Meaudre, M. Meaudre, and R. Brenier, J. Phys.: Condens. Matter 15, 7185 (2003).
- ⁴²K. Lips, P. Kanschat, and W. Fuhs, Sol. Energy Mater. Sol. Cells 78, 513 (2003).
- ⁴³C. Manfredotti, F. Fizzotti, M. Boero, P. Pastorino, P. Polesello, and E. Vittone, Phys. Rev. B 50, 18046 (1994).