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Changes in the vacancy size distribution induced by non-bonded hydrogens in hydrogenated amorphous silicon

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ABSTRACT

It was demonstrated that the presence of large amounts (≥2.8 at.%) of non-bonded hydrogens (NBHs) in hydrogenated amorphous silicon (a-Si:H) resulted in changes in the vacancy size distribution, where the vacancy size distribution was determined using positron annihilation lifetime spectroscopy. NBHs in small vacancies induced large nanovoids (>~1 nm), via the relaxation of internal stresses in the a-Si network, without decreasing the atomic number density of the silicon.

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) [1] shows a low defect density because of the hydrogen termination of dangling bonds (DBs); because of this low defect density, a-Si:H has been applied in thin film transistors and solar cells [2,3]. Recently, the silicon heterojunction structure adopted in photovoltaic modules HIT® has received much attention [3]. The hydrogen passivation of DBs at the a-Si/crystalline (c-) Si interface is one of the most important techniques for efficiency enhancement in these devices. DBs in an a-Si network appear with defects such as vacancies and voids, and Si—H_x ($x = 1$ to 3) bonds are formed as a result of the termination of DBs. With reference to the characteristics of such defects, it has been reported that Si—H and/or Si—H_2 bonds [4–12] exist within vacancies and/or voids [13–16], and that non-bonded hydrogens (NBHs), most likely H_2 molecules, also exist in the voids [14,16–20], and are positioned in *T*-like sites [20–22]. The NBHs have a possibility to enter various sizes of vacancies [13,23] in addition to voids.

When considering how hydrogen will affect an a-Si network, the solubility limit of bonded hydrogen (C_{SLBH}) has to be considered. It has been pointed out that the solubility of hydrogen is associated with the defect-related trap concentration inherent to the network [24]. C_{SLBH} values of 3–4 at.% [24] and ~5 at.% [25] for a-Si:H, and 2–4 at.% (bonding to Ge) for a-SiGe:H [26] have been suggested. The a-Si network becomes unstable when the hydrogen solubility limit is exceeded. The solubility limit of NBH (C_{SLNBH}), however, has not been studied in detail. As for non-bonded hydrogen contents (C_{NBH}), the values of ≤2 at.% in a-Si:H films have been reported [27–29]. Danesh et al. [29] found that the C_{NBH} content of 6 at.% determined by Kroll et al. [30] was reduced to 2 at.% when the *A* factor was changed. If an a-Si network containing NBHs exceeds this limit, structural inhomogeneity may be introduced into the network. Kroll et al. found that with a high total hydrogen content (C_T), C_{NBH} and the compressive stress reached a maximum in or near the amorphous-to-microcrystalline transition zone [30]. Their experimental data implied that the incorporation of NBHs affected the a-Si network. However, because it was not only C_{NBH}, but also the bonded hydrogen content (C_{BH}), that became large in or near the transition zone, it was not clear what portion of the influence derived from the NBHs.

It is known that increases in the optical band gap (E_{opt}) can result from changes in C_{BH} [31–34] and the film thickness (d) [35]. In particular, Smets and coworkers suggested that incorporated divacancies and nanovoids induced anisotropic volumetric compressive stress in an a-Si network, resulting in larger E_{opt} values [34]. In addition, the tensile stress due to the collapse of nanovoids [36] must be a significant factor. If NBHs produce some sort of structural change in a-Si network, E_{opt} will be changed.

In this paper, we report the influence of NBHs on an a-Si network, working from the results of positron annihilation lifetime (PAL) spectroscopy [19,37–41], Raman spectroscopy [29,42–44], and transmittance (T) and reflectance (R) measurements [45]. C_{NBH} is quantitatively determined using C_T (determined via Rutherford backscattering

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Table 1
Hydrogen plasma treatment (HPT) and deposition conditions for PECVD equipment A and B.

	Equipment A			Equipment B	
	HPT	Deposition		Deposition	
		Samples A1 to A4	Sample A5	Sample B1	Sample B2
Substrate temperature (°C)	200	200	200	200	180
Excitation frequency (MHz)	40	40	40	27	27
Reaction pressure (Pa)	150	50	25	31	173
Power density (mW/cm^2)	221	18	12	37	1667
Hydrogen dilution ratio	–	4.8	4.8	0	25

spectrometry/hydrogen forward scattering (RBS/HFS)), and C_{BH} (determined using Fourier transform infrared spectroscopy – the attenuated total reflection (FTIR-ATR) method) [46–48]. The C_T determined using RBS/HFS was verified using thermal desorption spectrometry (TDS) [28,49,50]. $C_{NBH} = C_T - C_{BH}$.

2. Experimental details

The a-Si:H films were deposited using plasma-enhanced chemical vapor deposition (PECVD), using two kinds of equipment (A and B), with SiH_4 and/or H_2 gasses. The deposition conditions are summarized in Table 1. Samples A1 to A5 were fabricated on glass substrates (EAGLE XG, Corning) using PECVD equipment A. Samples A1 to A4 were deposited under the same deposition conditions, and for samples A2 to A4, hydrogen plasma treatment (HPT) [51] was carried out on the substrate before the deposition was performed. Sample A5 was deposited under low pressure and low power, compared with samples A1 to A4. Sample AQ3 was fabricated on a quartz substrate using PECVD equipment A, under the same conditions used to produce sample A3. Samples B1 and B2 were fabricated on a glass substrate using PECVD equipment B in order to investigate the influence of hydrogen dilution. Sample B1 was deposited from pure SiH_4, without dilution with H_2. Sample B2 was deposited under high H_2 dilution, high pressure, very high power, and low temperature conditions, compared with sample B1.

The d and the E_{opt} values were determined using an $(\alpha h\nu)^{1/3}$ vs $h\nu$ plot, using $T/(1-R)$ [45]. Because the $(\alpha h\nu)^{1/3}$ vs $h\nu$ plot showed better linearity than Tauc's plot [52], E_{opt} values could be obtained with greater accuracy.

RBS/HFS measurements were carried out using a Pelletron instrument (National Electronics Corp.), using a helium ion beam (2.3 MeV). The incident angle of the beam was 75°, and the detection angles were 160° for RBS, and 30° for HFS. No hydrogen desorption was detected during the RBS/HFS experiments. The atomic number density (determined using RBS/HFS) was corrected for Si (N_{Si}) and H (N_H), using real d values. Here, it was ensured for all samples that the concentration of Si and H was constant throughout the depth of the samples. The C_T and C_{BH} values were expediently calculated for each N_H value by dividing by 5×10^{22} cm^{-3}, which was the N_{Si} for c-Si. The results are summarized in Table 2.

For sample AQ3, the TDS measurement was performed using a mass spectrometer and an infrared heating furnace, for temperatures from room temperature to 900 °C. The heating rate used was 10 °C/min, and a vacuum of 4×10^{-5} Pa was used.

Raman spectra were recorded at room temperature using an inVia Raman microscope (Renishaw) equipped with a YAG laser (λ = 532 nm), a single monochromator, and a charge-coupled device detector. It has been reported that the TO peak width (Δ_{TO}) at approximately 480 cm^{-1} is related to the bond angle distortion [43,44]. Simulations have indicated that bond angle distortion increases film density, which is proportional to N_{Si}, of a-Si:H more than that of c-Si [53], while the N_{Si} decreases with increasing void concentrations [13,36,53].

FTIR-ATR analysis was performed using a Spectrum 100 instrument (PerkinElmer), using a single reflection ATR accessory and a germanium prism. The refractive indices of the a-Si:H films were corrected using literature values for the hydrogen content dependence of the refractive index [6], with attention given to the different definitions of the hydrogen content [7]. Absorption peaks attributed to the low stretching mode (LSM) of Si—H bonds and high SM (HSM) of Si—H_2 bonds were measured at approximately 2000 and 2100 cm^{-1}, respectively [4]. These SMs are related to the ambient environment of the Si—H bond: LSM for vacancies and HSM for nanovoids [13,23,34]. The HSM-to-LSM peak height ratio ($R_{H/L}$) provides an index for the light-induced degradation of an a-Si:H film [5,9]. $C_{BH} = (A/N_{Si}) \int (\alpha'/\omega)\, d\omega$, where α' is the absorption coefficient, and ω is the wavenumber. We used two A factors of $(9.0 \pm 1.0) \times 10^{19}$ cm^{-2} for LSM and $(2.2 \pm 0.2) \times 10^{20}$ cm^{-2} for HSM [7]. C_{LSM} and C_{HSM} are the hydrogen content contributing to LSM and HSM, respectively. $C_{BH} = C_{LSM} + C_{HSM}$.

PAL spectra were measured using a ^{22}Na-based pulsed-positron beam system (PALS-200A, Fuji Imvac Inc.), using a positron incident energy of 1 keV in vacuum at room temperature. The penetration depth of the positrons was estimated as approximately 50 nm. The accumulated positron count was approximately 5×10^6. The PAL curves could be analyzed using only one component, using the nonlinear least-square program "POSITRONFIT" [54], and the average PAL τ values of the component were estimated. For each PAL curve, the distribution of the PAL values was calculated using the program "CONTIN", based on the inverse Laplace transform method [55]. In this study, the Doppler broadening spectra of the positron annihilation radiation [12,39,56–59] were not measured.

3. Results and discussion

3.1. Non-bonded hydrogen content

Estimated hydrogen contents are summarized in Table 2. For sample A1 only, the RBS/HFS measurements were performed twice, and very

Table 2
Deposition rate (DR), film thickness (d), number density of Si (N_{Si}) and H (N_H), optical band gap (E_{opt}), TO peak width (Δ_{TO}), peak height ratio of HSM and LSM ($R_{H/L}$), and total (C_T), bonded (C_{BH}), LSM (C_{LSM}), HSM (C_{HSM}), and non-bonded hydrogen contents (C_{NBH}), and average PAL (τ). An asterisk represents a sample produced with HPT being performed on the substrate before film deposition.

Sample number	DR (nm/s)	d (nm)	Number density (10^{22} cm^{-3})		E_{opt} (eV)	Δ_{TO} (cm^{-1})	$R_{H/L}$	Hydrogen content (at.%)					τ (ns)
			N_{Si}	N_H				C_T	C_{BH}	C_{LSM}	C_{HSM}	C_{NBH}	
A1	0.16	245	4.86	0.589	1.61	64	0.139	11.8	10.3	7.9	2.4	1.5	0.309
			4.83	0.578				11.6	10.3	7.9	2.4	1.3	0.310
A2*	0.17	125	5.11	0.612	1.69	65	0.106	12.2	8.5	7.0	1.4	3.8	0.301
A3*	0.17	255	5.06	0.644	1.62	–	0.117	12.9	9.1	7.2	1.9	3.8	–
AQ3*	0.16	245	5.05	0.636	1.61	64	0.109	12.7	8.9	7.2	1.7	3.9	0.303
A4*	0.17	510	4.86	0.631	1.62	–	0.119	12.6	10.3	8.1	2.2	2.3	–
A5	0.13	131	4.88	0.647	1.66	65	0.138	12.9	10.2	7.8	2.4	2.8	0.302
B1	0.17	169	4.61	0.541	1.59	64	0.160	10.8	9.5	6.9	2.7	1.3	0.317
B2	1.2	290	4.05	1.28	1.76	64	0.838	25.6	25.6	7.7	17.9	0.0	0.315

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