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Characterization of microvoids in device-quality hydrogenated amorphous silicon by small-angle x-ray scattering and infrared measurements

A. H. Mahan
Solar Energy Research Institute, 1617 Cole Boulevard, Golden, Colorado 80401

D. L. Williamson
Physics Department, Colorado School of Mines, Golden, Colorado 80401

B. P. Nelson and R. S. Crandall
Solar Energy Research Institute, 1617 Cole Boulevard, Golden, Colorado 80401

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The size, shape, and number density of microvoids in device-quality glow discharge deposited hydrogenated *a*-Si has been obtained by small-angle x-ray scattering (SAXS). By combining the SAXS results with infrared measurements, we deduce that the interior surfaces of these microvoids are largely unhydrogenated, containing at most 4–9 bonded H atoms. We suggest that these H atoms are the clustered H atoms previously detected by multiple-quantum NMR.

Microstructure in hydrogenated amorphous silicon (*a*-Si:H) has been extensively studied in the past few years. Probes of microstructure include multiple-quantum nuclear magnetic resonance (NMR),[1] calorimetry experiments involving H_2,[2] infrared spectroscopy,[3–5] positron-annihilation spectroscopy,[6] H evolution experiments,[7] scanning electron microscopy (SEM),[8] and small-angle scattering.[9–11] All of these techniques suggest or demonstrate the existence of microvoids in nondevice-quality *a*-Si:H. However, it is unclear whether device-quality *a*-Si:H has microvoids, or can be considered a homogeneous material. Evidence to date on device-quality material is at best indirect and conflicting. Calorimetry experiments indirectly suggest 10–40 Å diameter microvoids, SEM suggests columnar microstructure, and multiple-quantum NMR indicates clustered H. Nevertheless, device-quality *a*-Si:H shows no low-temperature H evolution peak indicative of a heterogeneous microstructure,[7] and previous small-angle x-ray scattering (SAXS) measurements[10,11] showed no detectable scattering, suggesting a homogeneous media. Earlier, we used SAXS (Refs. 12 and 13) to measure microvoids in *a*-SiC:H and in *a*-Si:H.

In the present study we extend and quantify preliminary results reported earlier[12,13] on device-quality glow discharge *a*-Si:H. We find a small but distinct SAXS signal indicative of microvoids in every device-quality glow discharge sample. We analyze these data to obtain the microvoid size, shape, and number density. By combining the SAXS results with infrared measurements, we deduce that the interior surfaces of the microvoids are largely unhydrogenated, containing at most 4–9 bonded H atoms. We suggest that these H atoms are one source of clustered H atoms previously detected by multiple-quantum NMR. Finally, a comparison of microvoid number densities with gap state densities indicates that the unhydrogenated bonds must reconstruct to reduce the number of dangling bonds to the levels observed in device-quality *a*-Si:H.

The Solar Energy Research Institute (SERI) *a*-Si:H samples used in this study were deposited on the anode of an rf (13.56 MHz) glow discharge reactor using device-quality conditions,[14] i.e., substrate temperature of 250 °C, flow rate of 70 cm^3/min at standard temperature and pressure (SCCM) SiH_4, chamber pressure 700 mT, and rf power 30 mW/cm^2, in a cross-flow geometry. For each sample, two sequential depositions were made. The first was made onto 10-μm-thick iron-free aluminum foil and a single polished crystalline silicon substrate. After deposition, the foil was cut into eight strips and stacked for the SAXS measurements. Details of our SAXS method can be obtained elsewhere.[13] No attempt was made to account for the shape of the radial distribution function in this scattering regime, since its shape for a material without microvoids is unknown. Infrared measurements on the sample deposited on crystalline silicon determined both the total bonded-H content from the Si-H bending mode (H_{630}) and the integrated intensities of the Si-H stretch modes centered at 2070 cm^{-1} [$I(2070)$] and 2000 cm^{-1} [$I(2000)$]. $I(2070)$ has been linked to microvoids.[3,5,12,13,15–18] The second deposition on 7059 glass was used for photothermal-deflection-spectroscopy (PDS) measurements of the midgap state density.[19] Film thicknesses were typically 2–4 μm. We also obtained a device-quality *a*-Si:H sample from Energy Conversion Devices, Inc. (ECD), for SAXS analysis. To demonstrate the quality of the *a*-Si:H material used in this study, the efficiencies of single-junction solar cells, fabricated using identically prepared material as the intrinsic layer, are greater than 10% for both the SERI (Ref. 14) and ECD (Ref. 20) samples under *AM* 1 illumination.

In Fig. 1 we show Guinier plots[21] for three SERI samples and the ECD sample, where $I(h)$ is the SAXS signal from the *a*-Si:H film, $h \equiv (2\pi/\lambda)(2\theta)$ is the scattering parameter, $\lambda = 1.54$ Å, and 2θ is the scattering angle. The data reduction procedure used to obtain $I(h)$ is discussed elsewhere.[13] Since in a Guinier approximation, $I(h) = I_0 \exp(-R_g^2 h^2/3)$, the slope of a linear fit in such a plot yields the radius of gyration R_g, which characterizes the size of the electron density fluctuations. Previous SAXS

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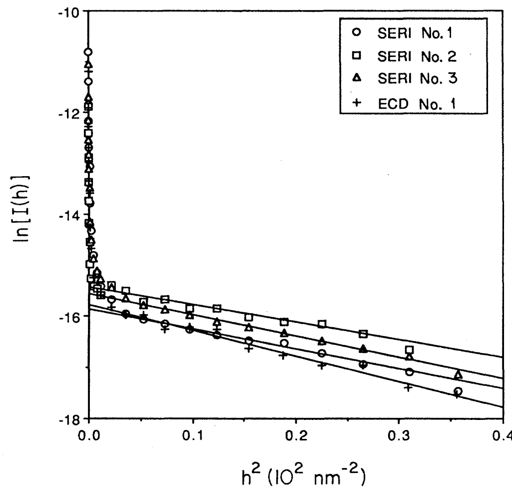

FIG. 1. Guinier plots for the device quality a-Si:H films. The open symbols (□,△,○) represent SAXS results for the three SERI samples, while the symbol (+) represents SAXS data for the ECD sample.

publications[22,23] have argued that the observed signals were due to microvoids and not low-density, H-rich tissue-like material; we agree with this interpretation and have also addressed this issue in a SAXS study of a-SiC:H.[12,13] To explore the shape of the microvoids, SAXS scans were made on two of the samples tilted at an angle of 45° with respect to the beam axis and compared to the nontilted data. The SAXS curves were identical, suggesting that the microvoids are either spherical or randomly oriented.[21] If a spherical shape is assumed, the microvoid radii are $(5/3)^{1/2}R_g \sim 4.4$ Å for the SERI samples and ~ 5.0 Å for the ECD sample. For a randomly oriented ellipsoid, with the ratio of major to minor axes equal to 2, values of a (6.2 Å, 5.1 Å) and b (3.1 Å, 2.6 Å) are obtained for "cigarlike" and "pancakelike" microvoids respectively, with $R_g = 3.4$ Å.[24]

To obtain the microvoid number density, we use the formula[13]

$$\int hI(h)\,dh = K(\Delta\rho)^2 v_f(1-v_f)\,,$$

where the left-hand side is the integrated SAXS signal appropriate for a line source, $\Delta\rho$ the difference in electron densities for our two phase material, and v_f the microvoid volume fraction. To obtain the constant K, we determined the density deficiency of a sample deposited at 125 °C ($v_f = 0.06$) by the flotation method[25] and equated this density deficiency to the integrated SAXS intensity of that sample.[13,26] Thus, the v_f's of the present samples can be determined.[27] In addition, using these values of v_f, we calculate the total number of missing atoms per microvoid and the resultant microvoid number densities.[13] These results are presented in Table I, where both spherical and ellipsoidal ($a = 2b$, numbers in parentheses) microvoid shapes are assumed.[28] The microvoid densities lie in the low to mid 10^{19} cm^{-3} range.

It is not clear why SAXS signals were not obtained previously[10,11] from device quality a-Si:H. We suggest that the small scattering signal from the iron-free aluminum foil, the low background counting rate (0.19–0.20 counts/s), the high efficiency of the x-ray detector in the 8 keV (Cu anode) region, and the use of long counting times (~ 8 h per scan) enable the present small SAXS signals to be detected.

Several comments can be made from correlations between the SAXS and infrared results. First, we have calculated the total H contents of the SERI films from infrared spectroscopy to be 8–9 at.%, or $(4.0\text{–}4.5)\times 10^{21}$ H/cm^3. The data analysis followed that of Brodsky, Cardona, and Cuomo[29] with the proportionality constant[30] of the Si-H 630 cm^{-1} bending mode, $A_W = 1.6 \times 10^{-19}$ cm^{-2}. Previous measurements of $I(2070)$ indicated microvoids,[3,5,12,15–18] but did not quantify how much H was bonded in this stretch mode. We now quantify the number of H atoms bonded in the Si-H 2070 cm^{-1} (H_{2070}) shifted stretch mode, and assume that they are bonded on the surfaces of the presently discussed microvoids because of the linear relationship between H_{2070} and v_f presented elsewhere.[13,31] Figure 2 shows a deconvolution which is typical of all our samples, where the complete SiH stretch mode is deconvoluted into two Gaussians of variable peak position and intensity but of equal full width at half maximum (FWHM); the best fit (χ^2 indicator) was obtained with the frequency of the small peak at $\sim$2070–2080 cm^{-1}. This peak position is consistent with the fact that the complete infrared scans of these samples showed a very small absorption peak in the 845–890 cm^{-1} range, suggesting that $I(2070)$ may be due at least in part to the SiH_2 [or $(SiH_2)_n$] bonding configuration.[32] Since neither the FWHM nor the proportionality constant A_s for $I(2070)$ have been firmly established,[30,33] assumptions are made to obtain H_{2070}. We estimate H_{2070} by three methods. In the first, we assume equal FWHM's and identical proportionality constants A_s for the two peaks shown in Fig. 2. For this method, $H_{2070} = H_{630} \times I(2070)/[I(2070)+I(2000)]$. The second method is

TABLE I. SAXS results.

Film	R_g	v_f	Total No. missing atoms/cm^3	No. missing atoms/void	Microvoid No. density (cm^{-3})
SERI No. 1	3.30	0.015	7.3×10^{20}	16 (12)	4.5×10^{19} (6.1×10^{19})
SERI No. 2	3.41	0.012	6.0×10^{20}	18 (14)	3.3×10^{19} (4.3×10^{19})
SERI No. 3	3.53	0.014	7.0×10^{20}	20 (16)	3.5×10^{19} (4.4×10^{19})
ECD No. 1	3.89	0.010	5.0×10^{20}	26 (20)	1.9×10^{19} (2.5×10^{19})

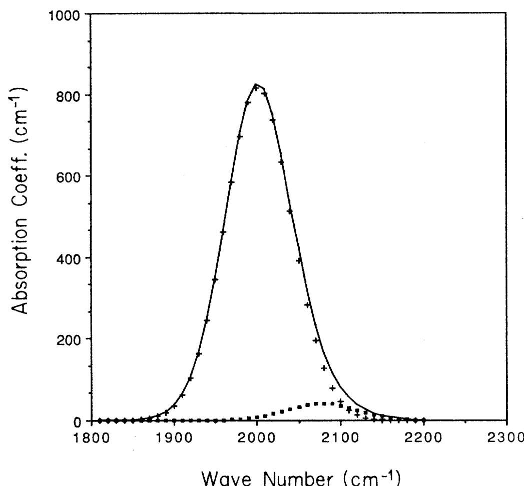

FIG. 2. Typical infrared deconvolution of the Si-H stretch mode (solid line) into components centered at 2000 cm^{-1} (+) and ~2070 cm^{-1} (■) wave numbers, respectively. Equal FWHM's were assumed for the two peaks.

identical to the first, except that we allow the FWHM of the 2070 cm^{-1} mode to be narrowed from ~85 cm^{-1} to ~70 cm^{-1}, consistent with the narrowing of this mode observed[34] in lower substrate temperature deposited *a*-Si:H. Finally, for the third method we calculate $H_{2070} = I(2070)A_s$, where $A_s = 1.4\times10^{20}$ cm^{-2} is the *average* proportionality constant for the Si-H 2070 cm^{-1} mode.[30,33,35] We thus obtain H_{2070} in the range $(1.5-3.5)\times10^{20}$ cm^{-3} for the three SERI samples, or < 0.7 at.% H. When we now divide these numbers by the respective microvoid number densities for each film, and average the results of the three methods, the number of bonded H atoms per microvoid becomes *5 to 9* if spherical microvoids are assumed, and *4 to 7* if (unoriented) ellipsoidal ($a = 2b$) microvoids are assumed. These numbers are in excellent agreement with the number of clustered H atoms found using the multiple-quantum NMR technique,[1] and support the correlation found[4] between clustered H and $I(2070)$. Therefore, we suggest that one source of 5-8 clustered H atoms detected by multiple-quantum NMR are those bonded on the surfaces of microvoids of $R_g \sim 3.4$ Å, as detected here by SAXS.

Second, we constructed a ball and stick model of a microvoid of ~20 missing atoms, and estimated that the number of surface atoms having bonds which protrude into the microvoid is ~1.25 times the number of atoms missing in a microvoid. Therefore, within the framework of this model, the number of surface sites on a microvoid available for H bonding (15-25) in *a*-Si:H is significantly larger than the number of bonded H atoms estimated to sit on a typical microvoid surface (5-9). This shows that these microvoid surfaces are not heavily hydrogenated. Note that since at least some of H_{2070} is due to dihydride bonding, the fraction of the surface bonds that are hydrogenated is even smaller than would be indicated by a simple ratio of the above numbers.

Third, measurements of the number of midgap states in these samples by PDS give $< 5\times10^{15}$ cm^{-3} midgap states. Based on published correlations between PDS and electron spin resonance data, we deduce that our samples contain $\sim 10^{-4}$ dangling bonds per microvoid. It is thus not clear whether the dangling bonds observed in device-quality *a*-Si:H are even associated with these microvoids. In any case, these results clearly show that bonds on the microvoid surfaces that are unhydrogenated must reconstruct to reduce the number of dangling bonds to the levels observed here. Dangling bonds have been postulated to reconstruct during H_2 evolution experiments.[16]

Finally, we comment that the H bonded in the 2000 cm^{-1} mode cannot all be bonded on the microvoid surfaces. From the previous discussion, $H_{2000} = H_{630} - H_{2070} \sim 3.8\times10^{21}$ cm^{-3}. This means that, on the average, 60-100 of these H atoms must be bonded on each microvoid surface. This is unreasonable not only because of the lack of surface sites needed to accommodate these H atoms, but also because the multiple-quantum NMR technique observed clusters of at most 5-8 H atoms in device quality *a*-Si:H. In addition, calculations[36] predict that these microvoids are too large to produce enough screening to shift the Si-H frequency from ~2080 cm^{-1}, observed for both SiH and SiH_2 bonds on crystalline Si surfaces,[3] down to 2000 cm^{-1} observed in device-quality *a*-Si:H. On the other hand, part of H_{2000} may contribute to the proton NMR clustered phase (5-8 atoms),[37] but be bonded in microvoids smaller than the ones reported here. Such small microvoids (i.e., multivacancies) would be small enough such that the electrostatic screening would be effective, and at the same time, from scattering-angle limitations of the SAXS apparatus, produce a negligibly small SAXS signal. We estimate that the integrated SAXS signal due to multivacancies would be at most 10% of the total SAXS signals we observe.

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[27]We could equally well have chosen for normalization purposes the a-$Si_{0.7}C_{0.3}$:H sample used for normalization in the a-SiC:H study of Refs. 12 and 13; were we to do this, there would be minimal change (± 0.001 in v_f) in the present results.

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