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Structural changes in a-Si:H film crystallinity with high H dilution

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Using infrared absorption (ir) spectroscopy, H evolution, and x-ray diffraction (XRD), the structure of high-H-dilution, plasma-enhanced chemical vapor deposition a-Si:H films ''on the edge of crystallinity'' is examined. From the ir Si-H wag mode peak frequency and the XRD results, we postulate the existence of very small Si crystallites contained within the as-grown amorphous matrix with the majority of the bonded H located on these crystallite surfaces. Upon annealing, a low-temperature H-evolution peak appears, and film crystallization is observed at temperatures as low as 500 °C, which is far below that observed for a-Si:H films grown without H dilution. While the crystallite sizes and volume fraction are too small to be detected by XRD in the as-grown films, these crystallites catalyze the crystallization of the remainder of the amorphous matrix upon annealing, enabling the evolution of H at low temperatures. The large spatial inhomogeneity in the H bonding thus produced throughout the film is suggested to be one of the reasons for the reduced Staebler-Wronski effect observed in solar cells utilizing these films.

Hydrogenated amorphous silicon (a-Si:H), deposited by plasma-enhanced chemical vapor deposition (PECVD) using high H dilution, has become increasingly important from a technological as well as scientific point of view.[1] It is well established that the improved stability of a-Si:H films and solar cells, deposited using H dilution, has been obtained using films deposited ''on the edge of crystallinity.''[2,3] In spite of several experimental factors[4,5] and the narrowness in deposition space needed for film deposition, new information is starting to emerge on the structure and electronic properties of such films.[3,6–9]

In this paper we report the results of infrared (ir), x-ray diffraction (XRD), H evolution, and (partial) annealing measurements on a series of a-Si:H films deposited with increasing H dilution. We find that, although the XRD shows no evidence of crystallinity, the ir peak frequency of the Si-H wag mode shifts downward to 620 cm^{-1} with increasing H dilution; this frequency is identified as due to H bonded on crystalline Si surfaces.[10] By considering the inclusion of crystallites of various sizes and shapes into the predominantly amorphous matrix, we show that the only way to simultaneously satisfy the XRD and ir results is for the crystallites to be very small and randomly oriented. We confirm their presence by annealing experiments, and relate their existence to recent structural and electronic film property observations.

A series of intrinsic films was deposited by PECVD onto ⟨100⟩-oriented c-Si substrates, at varying levels of H dilution and film thicknesses (0.5–1.05 μm), at a deposition temperature of 300 °C. ir measurements were performed using a dual-beam Perkin-Elmer 580-B spectrometer, with an instrumental resolution of 2.3 cm^{-1}. Transmission data, after appropriate baseline substraction, were transformed into absorption peak profiles.[8] H evolution was performed using final anneal temperatures of 400, 500, and 700 °C, with the ramp rate adjusted such that all films were in the evolution furnace for the same time (1 h). When the ramp temperature reached the desired value, the films were promptly removed from the furnace, and all measurements were done at ambient temperatures. No uptake of oxygen was observed upon annealing. The XRD measurements were carried out with a Siemens D-500 diffractometer operating with Cu $K\alpha$ radiation in the Bragg-Brentano geometry. Long counting times enabled good signal-to-noise ratios.

Figure 1 shows ir absorption curves for the Si-H wag modes versus H dilution. These films were deposited on the rough side of the c-Si substrates, with thicknesses ~0.9–1.05 μm. Both H dilution samples were seen by scanning electron microscopy (SEM) to lift off from their substrates while remaining intact structurally. As can be seen, the film H content (C_H) is changed only slightly with increasing dilution, and the full width at half maxima (FWHM's) are typical of device-quality a-Si:H films containing 8–10 at. % H.[11] The stretch mode frequencies for all films (not shown) are centered around 2000 cm^{-1},[8] indicating predominantly monohydride (Si-H) bonding. Of interest is the wag mode peak frequency. This shifts from 635–640 cm^{-1} to ~620 cm^{-1} for the ''high-dilution'' sample. While the former peak frequencies are typical for ''standard'' a-Si:H,[12] the latter lies distinctly outside this frequency range and is consistent with monohydride (Si-H) bonding on c-Si(100) surfaces.[10] While H bonded in other [SiH_2,$(SiH_2)_n$] configurations on c-Si can show a wide variety of peak frequencies,[13] for pure monohydride bonding only one peak frequency is observed. We thus assert that the frequency shift for the high-dilution

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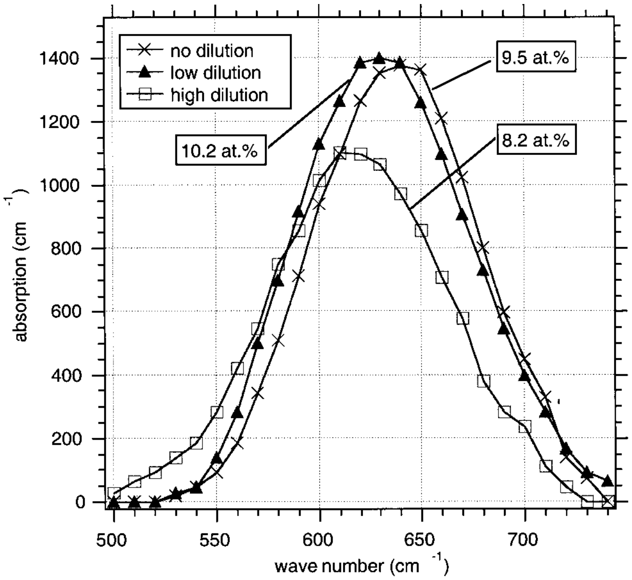

FIG. 1. ir wag mode absorption spectra (cm^{-1}) for three a-Si:H samples grown using different H-dilution conditions.

sample indicates the presence of crystallites contained within the amorphous matrix, with the majority of the H bonded on these crystallite surfaces.

These results are contrasted with XRD results on the same samples, seen in Fig. 2. Also noted are the angular positions where the first three peaks in powdered (randomly oriented) c-Si [the (111), (220), and (311) crystal orientations] would occur. The only features observed for all films are the strong (first amorphous) peak occurring at roughly 28.5°, and a less intense (second amorphous) peak occurring at ~51°. The substrate reference is included for comparison. The only noticeable change with increasing H dilution is the slight narrowing of the first XRD FWHM.[7] From XRD, all samples appear to be fully amorphous.

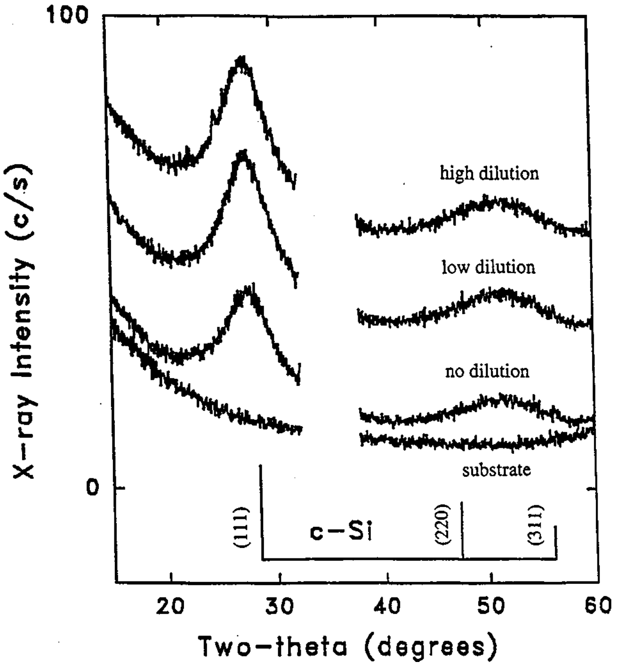

FIG. 2. XRD patterns for the identical samples whose ir spectra are shown in Fig. 1.

To reconcile these results, we must understand, for the high-dilution film, how to incorporate enough crystallinity into the film to enable enough H bonding on the crystallite surfaces to account for the majority (>5 at. %) of the bonded H (thus satisfying the wag mode peak frequency shift), while at the same time not generating any detectable crystalline features in the XRD pattern. We address this by considering crystallite size. We estimate from the Scherrer formula[14] that large c-Si crystallites, with a grain size >50 Å, will yield relatively sharp diffraction peaks and can thus be distinguished from any (broad) amorphous diffraction signal with a sensitivity of 1–2 % in crystallite volume fraction (VF). Looking first in the scattering region $2\theta=25°–35°$, we note that the first XRD peak FWHM for the high-dilution film is ~5°.[7] Thus, if the dimension of any crystallites contained within the film were hypothetically reduced to ~15–20 Å, the FWHM of any [(111)-oriented] c-Si crystallites observed in this region now becomes comparable to that of the amorphous signal.[14] As a result, crystallite detection is now more difficult than before, enabling an upper ''adjustment'' in the VF detection limit. We assume that similar arguments hold for other scattering regions where the c-Si (220) and (311) crystallographic peaks would appear. Going further with this argument, the existence of very small crystallites, on the order of ~10 Å in diameter, which produce even broader XRD features, would be even more difficult to detect. Thus, size arguments alone can enable the existence of a considerably larger real crystallite volume fraction than that given by our initial estimate (1–2 %).

In Table I we summarize these arguments. In these calculations we assume an upward sliding scale in VF versus decreasing crystallite size, with a VF sensitivity limit ranging from 2% for crystallite sizes of >50 Å to 8% for crystallite sizes of 10–15 Å. The XRD FWHM's are noted in Table I.[14] Assuming a H coverage density of $1\times10^{15}\,\mathrm{cm}^{-2}$ on c-Si surfaces,[15] we estimate the total amount of H on these crystallites versus the number of Si atoms/crystallite. We consider three different crystallite shapes (disks, spheres, cylinders), with representative dimensions (length, diameter) noted in Å. For crystallites with a large eccentricity, we assume a random orientation[3] and take the average of the three dimensions to be the size detected by XRD. The scatter in the data reflects different surface area/volume ratios for crystallites of different shapes, yielding different H coverages. However, the overall trend is easily seen. For large crystallites we are unable to put enough bonded H on the surfaces to satisfy the ir results, while for small crystallites containing <100 Si atoms, we exceed our 5-at. % H limit for all three shapes. We note that long and very thin cylinders, similar to the ''linear objects'' observed previously by transmission electron microscopy[3] but on a much smaller scale, also satisfy this additional ir requirement.

We (indirectly) confirm the existence of these crystallites by annealing and XRD experiments. If small crystallites already exist in an as grown film, there is no nucleation barrier to overcome upon annealing,[16] and crystallization can be expected to occur at lower temperatures. The results are seen in Table II, using the annealing procedure previously described on thinner (~0.5 μm), identically prepared films. While the

TABLE I. Estimation of total amount of H on crystallite surfaces versus number of Si atoms per crystallite. The XRD FWHM is calculated from the Scherrer formula, and the upward sliding scale in VF reflects the reduced XRD sensitivity to broadened crystalline features in relation to the amorphous features.

Crystallite type (length, diameter)	No. Si atoms/ crystallite	XRD FWHM (deg)	VF limit (%)	C_H (at. %)
Disk (20 Å, 80 Å)	5000	1.25	2	0.6
Sphere (50 Å)	3262	1.4	2	0.4
Cylinder (200 Å, 20 Å)	3140	1.0	2	0.8
Disk (20 Å, 40 Å)	1250	2.5	2	0.8
Sphere (30 Å)	675	2.7	2	0.8
Disk (2.5 Å, 80 Å)	628	1.5	2	3.4
Disk (5 Å, 40 Å)	314	3	2	2.0
Cylinder (20 Å, 20 Å)	314	4	4	2.4
Disk (10 Å, 20 Å)	157	5	5	4.8
Cylinder (50 Å, 8 Å)	125	4	4	4.4
Sphere (15 Å)	85	5	5	4.0
Cylinder (50 Å, 6.5 Å)	83	4	4	4.9
Cylinder (20 Å, 10 Å)	79	6.5	6	6.0
Disk (4 Å, 20 Å)	63	5	5	7.5
Disk (2.5 Å, 20 Å)	40	5	5	10
Cylinder (50 Å, 4 Å)	31	4	4	8
Cylinder (30 Å, 5 Å)	30	7	6	9.6
Sphere (10 Å)	25	8.5	7	8.4
Cylinder (20 Å, 5Å)	20	8.5	7	12.6
Sphere (7.5 Å)	11	10	8	19.6

high-dilution film remains amorphous after the 400 °C anneal, crystallinity is already observed at 500 °C, and after the 700 °C anneal the film appears to be almost fully crystallized. From the ir results, 40% (75%) of the bonded H is lost after the 400 °C (500 °C) anneal, and no bonded H remains after annealing at 700 °C. This is contrasted with results for standard no-dilution films, which lose almost no bonded H at 400 °C and crystallize only at very high temperatures (>750 °C).[17] In addition, low-C_H films deposited by the hot-wire (HW) technique, which exhibit a similar narrowing of the first XRD peak,[7,18] also show no crystallinity when examined in a similar fashion.

We now comment on how the existence of small crystallites in an amorphous matrix relates to several recent observations. First, they provide an explanation for the existence of the low-temperature H evolution peak.[6] For such a peak to occur, some sort of connective path to the surface (microvoids, grain boundaries) is needed. In the as-grown high-dilution films, the crystallite VF is too small to provide such a path unless the crystallites are highly oriented; however, this is not seen to occur.[3] A more likely explanation is the rapid growth of the crystallites with moderate annealing, and the evolution of the H along the suddenly accentuated grain boundaries, either directly to the surface or to a columnarlike microstructure, as detected by small-angle x-ray scattering,[19] and then to the surface. However, these are not grain boundaries in the traditional sense, as they exhibit only one of the two ir signatures (the wag mode shift). We note, however, no contradiction to the existing literature, as Rath, Barbon, and Schropp[20] have shown that grain boundaries with the stretch mode peak position at 2000 cm^{-1} can occur in microcrystalline Si.

Secondly, they provide a plausible mechanism to enable a large H spatial inhomogeneity within the present films. We emphasize again its magnitude—that the crystallite VF is certainly <10%, and yet the majority of the bonded H is located on these crystallite surfaces. Before discussing the present data, and its effect upon film properties, we review another case where such an H inhomogeneity has been definitively observed. In low C_H (1–2 at. %) films deposited by the HW technique,[18] NMR measurements revealed that H clustering in these films was so enhanced, and the C_H so

TABLE II. Crystallinity observed, by XRD, versus sample type after ramp anneal in evolution furnace to indicated final temperatures.

Sample type	400 °C	500 °C	700 °C
High-dilution PECVD *a*-Si:H	None	Some	Almost complete
Standard PECVD *a*-Si:H (no dilution)	None	None	None
Low-C_H HW *a*-Si:H	None	None	None

low, that there existed large spatial regions without appreciable H.[21] The consequences of the generation of such H deficient regions are twofold. First, the film exhibits better lattice ordering. XRD measurements have shown that these low C_{H} HW films were better ordered compared either to 'standard' *a*-Si:H films deposited by the PECVD process (containing ~10 at. % H) or to HW films containing similar (high) C_{H}.[18] Since the low C_{H} HW films are composed largely of spatial regions without appreciable H, it is reasonable to assert that these H deficient regions, as probed by XRD, are better ordered, since XRD is a volume measurement. Thus, the generation of these (better ordered) H deficient regions results in a narrower XRD FWHM. The second consequence of this H inhomogeneity relates to the reduced Staebler-Wronski Effect (SWE) observed in such low C_{H} HW films.[22] It has been suggested that better ordered (more crystalline like) spatial regions can tolerate recombination events without damage (i.e., defect creation) more easily than regions which are less well ordered, and thus may be less susceptible to SWE degradation.[23] In the HW case, therefore, these better ordered regions may be those containing minimal H.

We propose that the same thing is happening in the present 'high dilution' films, but for a different reason. Certainly better lattice ordering (again compared to 'standard', higher C_{H} *a*-Si:H films) has been demonstrated. This was first postulated to occur by Tsu *et al.*[3] and has been recently confirmed, using XRD, by Guha *et al.*[7] In particular, the (narrow) XRD FWHM for the present 'high dilution' PECVD films is identical to that for the low C_{H} HW films.[7] In addition, as mentioned earlier, solar cells deposited using the 'high dilution' films have also demonstrated a significantly improved stability (reduced SWE). Therefore, these H deficient regions may play a role similar to that of crystallites in μc-Si[24] in reducing the magnitude of the SWE. While we do not know the precise extent of the H inhomogeneity in the present 'high dilution' films, we argue that the presence of the crystallites enables a plausible mechanism for such an inhomogeneity to occur. Furthermore, the identical XRD FWHM as well as the reduced SWE for the two cases suggests that better ordered, H deficient spatial regions, may exist in these 'high dilution' films as well.

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