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STRUCTURAL CHANGES IN a-Si:H FILMS DEPOSITED ON THE EDGE OF CRYSTALLINITY

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ABSTRACT

Using infrared, H evolution and x-ray diffraction (XRD), the structure of high H dilution, glow discharge deposited a-Si:H films "on the edge of crystallinity" is examined. From the Si-H wag mode peak frequency and the XRD results, we postulate the existence of very small Si crystallites contained within the amorphous matrix, with the vast majority of the bonded H located on these crystallite surfaces. Upon annealing at ramp rates of 8-15°C/min, a H evolution peak at ~400°C appears, and film crystallization is observed at temperatures as low as 500°C, both of which are far below those observed for a-Si:H films grown without H dilution using similar ramp rates. While the crystallite volume fraction is 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 moderate annealing, thus explaining the existence of the low temperature H evolution peak.

INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) films, deposited by the glow discharge (GD) process using silane highly diluted in hydrogen, have become increasingly important both from a technological as well as a scientific point of view. Since the first observation that H dilution led to an improved stability (1), this process has been used extensively in the production of a-Si:H films and solar cells. It has been well established not only (a) that increasing H dilution leads eventually to the deposition of microcrystalline silicon (μc-Si) (2), but also (b) that the improved stability of the a-Si:H films as well as solar cells, deposited using H dilution, has been obtained using films deposited "on the edge of crystallinity" (3,4). However, several experimental factors such as film thickness and substrate effects (5,6) suggest that it is not easy to identify and investigate this material in a cohesive (consistent) fashion.

Nevertheless, new information is starting to emerge regarding the properties of these "on the edge" materials. A succession of papers has examined properties of "on the edge" a-Si:H films deposited by the same group using high H dilution. Xu et al. (7) first reported the existence of a low temperature H evolution peak and an anisotropic (columnar-like) structure effect as measured by SAXS. Tsu et al. (4) then reported, as seen by TEM, the existence of large linear-like objects; these were interpreted, with the help of a shifted Raman peak, to be intermediate in order between the continuous random network (amorphous) and crystalline phases. These (randomly oriented) objects appeared even for films deposited using undiluted disilane, and the number of these objects increased at high H dilution. Finally, Guha et al. (8) showed that the width of the first x-ray diffraction (XRD) peak narrowed at high H dilution, and that this narrowing was suggestive of an improvement in medium range order.

In this work we examine, from a different perspective, "on the edge" films deposited by the same group using infrared (IR) spectroscopy, XRD, H evolution, and (partial) annealing. We find that, even though the XRD shows no evidence of crystallinity and the peak frequency of the IR active stretch mode remains at ~2000 cm-1, indicating monohydride bonding associated with device quality a-Si:H, the peak frequency of the Si-H wag mode shifts downward from ~640 cm-1 to 620 cm-1 at high H dilution. This latter frequency is identified as being due to H bonded on crystalline Si surfaces (9). This shift in peak position suggests that, even though the matrix is still almost completely amorphous, the vast majority of the H is bonded on the surfaces of Si

crystallites. We show that the only way to simultaneously satisfy the IR (H content) and XRD (sensitivity) results is for these crystallites to be very small and to be randomly oriented. Under these conditions, we estimate that the crystallite volume fraction (vf) can be ~ 5-10%. Although this vf is still too small for the grain boundary precursors to serve as H percolation (evolution) pathways, thus explaining the existence of the low temperature H evolution peak, the crystallites serve as nucleation sites for further crystallization after sample annealing. That is, as there is no nucleation barrier to overcome upon sample heating, such samples can be expected to crystallize at annealing temperatures far lower than samples which are entirely amorphous (10). Indeed, crystallinity is detected some 200°C lower in "on the edge" samples as compared to fully amorphous samples comparably annealed (11), thus (indirectly) confirming the existence of these small Si crystallites.

EXPERIMENT

An extensive series of intrinsic films were deposited by the glow discharge (GD) process at varying levels of H dilution, all at a deposition temperature of 300°C, onto c-Si substrates. Three different H dilutions were used; "no dilution", "low dilution", and "high dilution". The "high dilution" films used in solar cells demonstrate high efficiency and improved stability (3). Sample thicknesses ranged from 0.5-1.05 μm. 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 subtraction, were transformed into absorption peak profiles using the analysis of Brodsky et al. (12). H evolution was performed using ramp rates between ~6-14°C/min, with the rates adjusted such that the total time in the H evolution furnace for each (piece of) film was ~ 1 hr. For step-wise evolution experiments on films which were later examined for crystallinity, the samples were promptly removed from the H evolution apparatus when the ramp temperature reached the appropriate value; these temperatures were 400°, 500°, and 700°C respectively.. The XRD measurements were carried out with a Siemens D-500 Diffractometer operating with Cu-Kα radiation in the Bragg-Brentano geometry. Long counting times were used to achieve good signal-to-noise ratios.

RESULTS

Figure 1 shows IR spectra for (a) the Si-H stretch and (b) wag modes for the "no dilution" and "high dilution" films; both film thicknesses were ~1.0 μm. The "high dilution" film was seen by SEM to lift off from its substrate while remaining intact structurally. Although there exists some difference in the stretch mode shape, the peak frequencies are both centered around 2000 cm-1, indicating predominantly monohydride (Si-H) bonding, and thus state-of-the-art device quality. From Figure 1b, the film H contents (CH) do not change appreciably with dilution; that is, the CH is 9.6 and 8.2 at.% respectively for the "no dilution" and "high dilution" films. The wag mode full width at half maximum (FWHM) for the films are also almost identical (100 cm-1), a value typical of device quality a-Si:H films containing similar CH. On the other hand, the wag mode peak frequency is seen to shift from 635-640 cm-1 for the "no dilution" film to ~ 620 cm-1 for the "high dilution" film. Although the former peak frequency is typical for "standard" a-Si:H (13), the latter lies distinctly outside this frequency range.

We consider it significant that the wag frequency of H bonded in the monohydride (Si-H) configuration on both the c-Si (100) and (111) surfaces is identically at ~ 620 cm-1 (9). Although H bonded in other (SiH2, (SiH2)n) configurations on c-Si can show a wide variety of peak frequencies (from 620 cm-1 to as high as 675 cm-1) (14), for purely Si-H monohydride bonding only one wag mode frequency is observed. Hence, combining these observations with the present measurements, we assert that the IR frequency shift for the "high dilution" film indicates the presence of crystallites contained within the amorphous matrix, with the large majority of the H bonded on these crystallite surfaces.

This is to be contrasted with XRD data. This is seen in Figure 2, where the XRD intensity for the "no dilution" and "high dilution" sample is plotted vs. the scattering angle 2θ

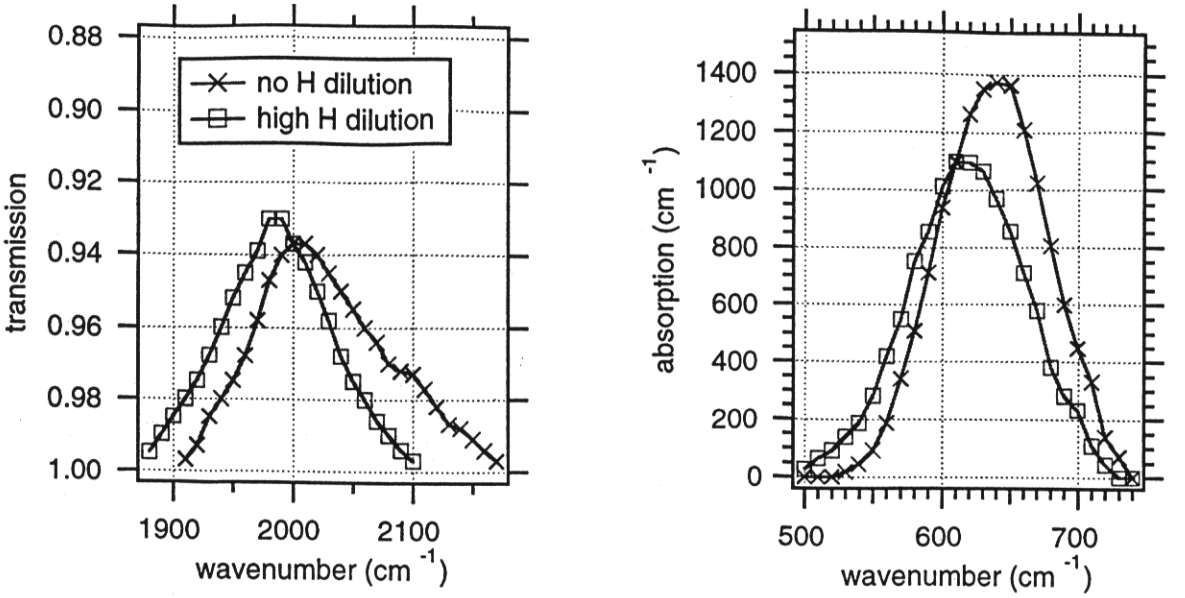

Figure 1. (a) IR stretch mode peak position (b) and wag mode absorption spectra for the "no dilution" and the "high dilution" a-Si:H samples.

from 15°- 60°. 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 breaks in the curves correspond to second order diffraction effects from the c-Si substrate, which are omitted. As can be seen, the only features observed in the spectrum 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. Based on these results, both films appear to be fully amorphous.

The problem, then, is to reconcile these two sets of measurements. That is, we must, for the "high dilution" film, understand how to incorporate enough crystallinity into the sample to enable enough H bonding on the surfaces of these crystallites 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 spectrum. We address this by considering crystallite size. From the Scherrer formula and the XRD sensitivity, we estimate that large c-Si crystallites (>50Å), yielding sharp diffraction peaks, can easily be distinguished from any (broad) amorphous diffraction signal with a sensitivity of 1-2% in vf. On the other hand, the first XRD peak FWHM of the 'high dilution' a-Si:H film is ~5° (8), so if the dimension of any crystallites contained within the film were reduced from the >50Å size previously discussed to ~15-20Å, the XRD FWHM of these crystallites now becomes comparable to the width of the amorphous XRD signal. The only method of distinguishing these (smaller) crystallites from the (first XRD peak) amorphous feature now becomes the very small difference in peak positions, and crystallite detection is becomes more difficult than before, enabling an upper "adjustment" in the vf limit. Going further with this argument, the existence of even smaller crystallites, on the order of ~10Å in

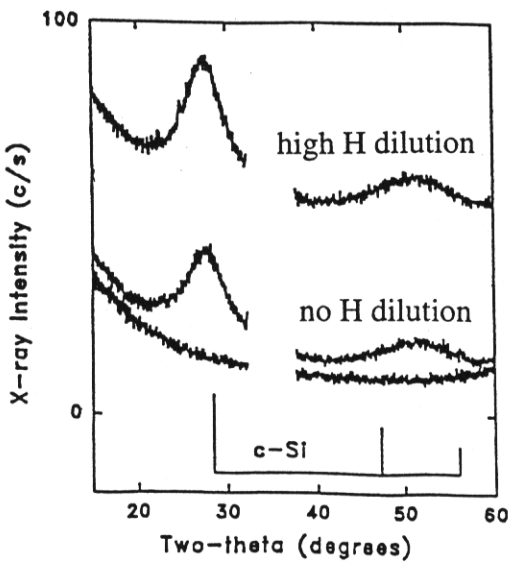

Figure 2. X-ray intensity vs. 2θ (°)

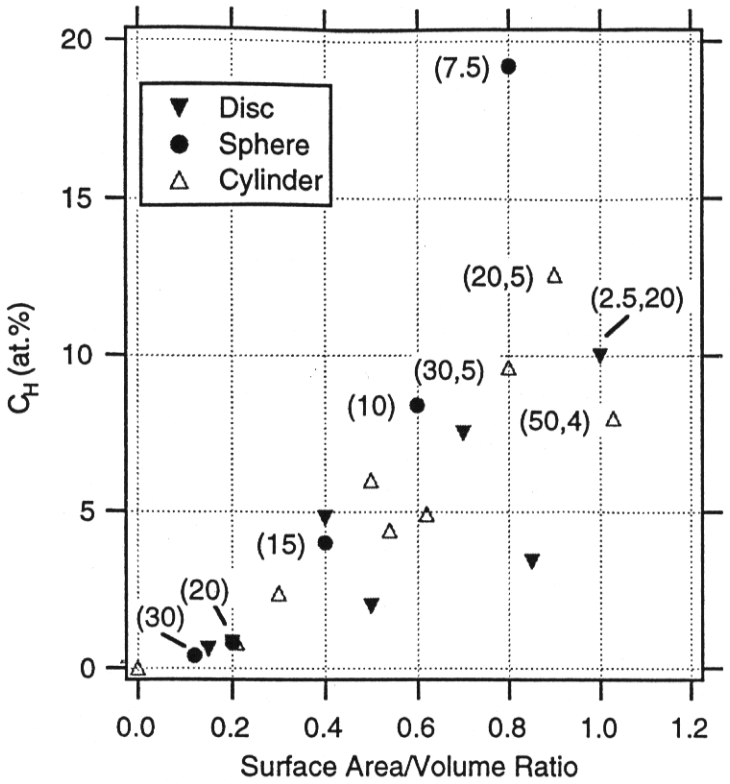

Figure 3. CH vs. crystallite surface area/volume ratio.

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 Figure 3 we summarize numerically the arguments made in the preceding paragraph. In making this figure, we have assumed an upward sliding scale in vf vs. decreasing crystallite size, with a sensitivity limit of 5% for crystallite sizes of 15-20Å (yielding XRD FWHM's of ~ 5°), and a limit of 8% for even smaller crystallites having sizes of 10 - 15Å (yielding XRD FWHM's of > 9°). Using Aw = 2.3e19/cm3 (15) and assuming a H coverage density of 1e15/cm2 on c-Si surfaces (16), we plot the total amount of H on these crystallites vs. the crystallite surface area/volume ratio. We consider spheres, discs, and cylinders, with representative dimensions in Å (length, diameter) noted in the figure; for crystallites with a large eccentricity, we assume a random orientation in the film (7) and take the average of the three dimensions to be the size detected by XRD (17). We note some scatter in the data. This is ascribed to different surface area/volume ratios for crystallites of different shapes as well as the fact that crystallites having one large dimension weight the averaged dimension as seen by XRD to larger values; hence, in our model, a lower CH is thus observed for these crystallites due to the higher XRD sensitivity. However, the overall trend is easily seen. That is, large crystallites have small surface area/volume ratios, and we are unable to put enough bonded H on the surfaces to satisfy the IR results, while for small crystallites with large surface area/volume ratios, we exceed our 5 at.% H limit for all three shapes. Thus, we are able to satisfy the XRD and the IR results simultaneously by considering the inclusion of small crystallites within an amorphous matrix

Finally, given the presence of small crystallites in our "high dilution" a-Si:H film (up to a vf = 5-10%), we now examine in this context the H evolution results (6). That is, we need to explain the existence of a H evolution peak that occurs at a temperature ~100°C lower than observed in "standard" a-Si:H films of similar thickness (18). To do this, we partially anneal pieces of our films up to 400°, 500°, and 700°C, respectively, in our H evolution furnace, and then examine them for crystallinity. While the "high dilution" film remains amorphous after the 400°C anneal, crystallinity is observed after the 500°C anneal, and after the 700°C anneal the

film appears to be almost fully crystallized. From the IR, 40% (75%) of the bonded H is lost after the 400°C (500°C) anneal, while no bonded H remains after the 700°C anneal. This is to be contrasted with results for 'standard' a-Si:H, which lose almost no bonded H at low (400°C) anneal temperatures and crystallize only at very high temperatures (>750°C) (11). In addition, low CH films deposited by the hot wire (HW) technique, which exhibit as similar narrowing of the first XRD peak (19), also show no crystallinity when annealed in a similar fashion.

DISCUSSION

While acknowledging the strong substrate dependence on film structural properties, as well as the sensitivity of film structure to small changes in film deposition conditions for films in this "on the edge" region, we nevertheless comment on how the present results add to the structural picture emerging for these films. In particular, they add to and extend the results of Tsu et al. (7). In that publication, TEM and Raman measurements showed the existence of "somewhat ordered linear-like objects", which were randomly oriented, and which made up from Raman about 10-15% of the total Raman signal. Assuming that this percentage relates to volume fraction, the similarity of those results to that of the present work, particularly the magnitude of the vf, is highly suggestive. In particular, we suggest that the "objects" discussed by Tsu et al. (7) may in fact be crystallites, that those objects observed by TEM must be those at the very extreme (upper) end of a Gaussian size distribution, and that most of these crystallites must be very small in size. Further, we show how the presence of crystallites in an a-Si:H matrix explains the existence of the low temperature H evolution peak seen by Xu et al. (6). It is well known, for a low temperature H evolution peak to occur, that some sort of connective path to the surface (microvoids, grain boundaries) is needed. By both accounts (Mahan, Tsu), the vf of the present as grown films (5-10%, 10-15%) is not large enough for percolation to occur unless these objects are highly oriented; yet, in both cases this preferential orientation is not seen to occur. On the other hand, if small crystallites already exist in the as grown material, there is no nucleation barrier to overcome upon low temperature sample annealing (10). Therefore, the existing crystallites can grow rapidly in size with moderate annealing, enabling H to effuse out of the film along the suddenly accentuated grain boundaries, and thus contribute to the low temperature H evolution peak. However, these are not grain boundaries in the traditional sense, as they exhibit only one of the two IR signatures commonly observed (the wag mode shift). That is, traditional grain boundaries in μc-Si show a shift in both the stretch and wag mode peak frequencies (2); as mentioned previously, the peak frequency of the stretch mode of the present "high dilution" sample remains at 2000 cm-1, which is not indicative of H bonded on c-Si surfaces. We note, however, that the present results are in fact not in contradiction to the existing literature, as Rath et al. (20) have shown that very compact grain boundaries (compact in the sense that the stretch mode peak position is still at 2000 cm-1) can in fact occur in μc-Si.

Finally, we comment on the better lattice ordering, postulated to occur by Tsu et al. (7) and recently observed by XRD by Guha et al. (8) for the "high dilution" films. Both publications agree that a more ordered structure is produced using high H dilution. We note, however, that a more ordered structure has been previously been obtained, as observed by XRD, with low CH films deposited by the HW technique (19). In those films, NMR measurements (21) showed that H clustering in the HW films was so enhanced, and the CH so low, that there existed large spatial regions without appreciable H; from XRD, these regions were observed to be better ordered. We postulate that the same thing is happening in these high H dilution GD films, but for a different reason. What may be needed deposition-wise to produce the narrower XRD FWHM is a method to produce a H spatial inhomogeneity throughout an a-Si:H film; what results are regions containing minimal H with better ordering. In the HW films, on the one hand, higher H clustering and lower CH produced these better ordered (devoid of H) regions, while for the present high H dilution films, H preferentially bonded on the surfaces of the small crystallites serves the same function.

CONCLUSIONS

We have examined GD a-Si:H films, deposited "on the edge of crystallinity" using high H dilution, by IR, H evolution and XRD. The Si-H wag mode peak position, along with the XRD results, are interpreted as evidence for the existence of very small Si crystallites contained within the as-grown amorphous matrix, with the vast 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 deposited without H dilution. While the crystallite vf is too small to be detected by XRD in the as-grown films, the crystallites catalyze the crystallization of the remainder of the amorphous lattice after annealing, thus providing a connectivity path to the surface and explaining the existence of the low temperature H evolution peak.

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