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On the Effect of the Film Hydrogen Content and Deposition Type on the Grain Nucleation and Grain Growth During Crystallization of a-Si:H Films

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ON THE EFFECT OF THE FILM HYDROGEN CONTENT AND DEPOSITION TYPE ON THE GRAIN NUCLEATION AND GRAIN GROWTH DURING CRYSTALLIZATION OF A-SI:H FILMS*

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ABSTRACT

We report the effect of the initial film hydrogen content (C_H) on the crystallization kinetics, crystallite nucleation rate and grain growth rate when HWCVD and PECVD a-Si:H films are crystallized by annealing at 600°C. For the HWCVD films, both the incubation time and crystallization time decrease, and the full width at half maximum (FWHM) of the XRD (111) peak decreases with decreasing film C_H. However, other sources of XRD line broadening exist in such materials in addition to crystallite size, including the density of crystallite defects. To address these issues, TEM measurements have also been performed on a-Si:H films deposited directly onto TEM grids. Following the procedure of Iverson and Reif (J. Appl. Phys. 62 (1987) 1675), an examination of films with low grain density enables a determination of the crystallite nucleation rate as well as grain growth rate. We compare the results for HWCVD films of different film C_H, and also for HWCVD and PECVD a-Si:H films containing the same initial film C_H. We also perform Raman measurements on fully crystallized HWCVD films to explore whether film disorder plays a role in the different XRD FWHMs when different amounts of film hydrogen are evolved.

INTRODUCTION

The crystallization of as deposited a-Si:H thin films is becoming increasingly important because of its potential use to produce higher mobility polycrystalline materials for use in solar cells and high performance thin film transistors. This process is believed, at relatively low temperatures (<1000C), to follow a classical model of nucleation and grain growth [1], where an amorphous incubation time, a steady state nucleation rate, grain growth of these nuclei, and a characteristic time of crystallization can be identified. In limited previous studies at an anneal temperature of 600C, all of these process steps were seen to depend on the film substrate temperature (T_S) [2,3]. While there was agreement in these studies that lower T_S films exhibited longer amorphous incubation times and larger grain sizes, the latter due primarily to the smaller nucleation rate, there was no general consensus as to why this occurred. One approach linked the trends in grain size with T_S to differences in the Raman signatures of the as grown films, which were then related to differences in short range structural order [2,3]. However, these Raman analyses were either not rigorous [2] or were done with an interpretation no longer considered appropriate [3]. Further, recent results have shown that the crystallization time, for a given film C_H, can depend upon the a-Si:H deposition method [4]. The present work thus re-examines a-Si:H crystallization [5], with an attempt to determine not only what factors limit grain size, but also to understand how H influences nucleation.

EXPERIMENTAL

A-Si:H films were deposited using the HWCVD and PECVD techniques, using deposition conditions described previously [6,7]. Two different thickness films were then analyzed. First, ~1 μm thick a-Si:H films were deposited on glass, and XRD and reflectivity were used to probe film crystallinity. Second, thinner (~0.1 μm) films were also grown directly on C-coated, 200 mesh Mo TEM grids which were mounted on the glass using colloidal graphite paste. The latter thicknesses were chosen because no sample thinning was required. TEM analysis was performed on a CM200 Scanning TEM using a Phillips single-slit holder and a Gatan Model 652 double-slit heating holder for in-situ annealing. TEM images were acquired in the conical dark-field mode with a 12-bit digital camera from Soft Imaging System, with the direct beam tilted by 0.70° and dynamically pressed about the optic axis of the microscope. To determine the crystalline volume fraction Xc from TEM images, we assume grain growth is two dimensional and use the 'magic wand' tool in Photoshop for boundary recognition to binarize the images, converting crystalline (amorphous) regions to black (gray) respectively. Histograms of the one-bit images were then computed in Digital Micrograph to

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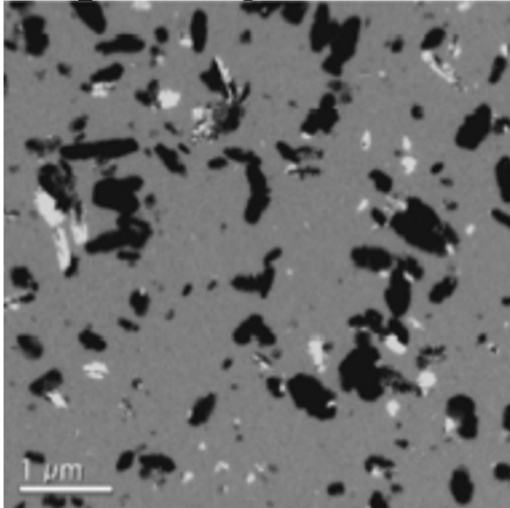
determine Xc. Direct grain counting was used to determine the areal grain number densities. Each image series was analyzed incrementally, starting at the early stages of crystallization, and keeping a running total while counting emerging nuclei in subsequent images.

RESULTS AND DISCUSSION

Figure I shows TEM images of partially crystallized HWCVD and PECVD a-Si:H films annealed at 600°C, with the annealing times indicated in the figures. Based upon infrared measurements of the Si-H wag mode, the film H contents (C_Hs) are 2.7, 12.5, and 11.5 at.% respectively for the low H HWCVD, high H HWCVD, and PECVD films. The Xc's of these images are roughly similar. These images, and those taken in the respective image series, show clearly that crystallization occurs via grain

H2511_LH4: 67 min. @ 600°C



L1596_P3:657 min. @ 600°C

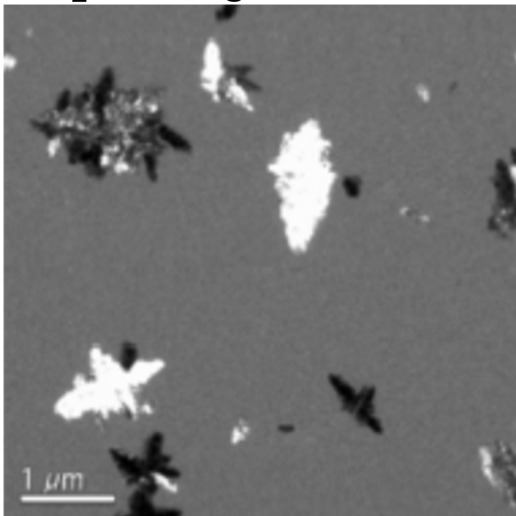


Figure 1. TEM images of the partially crystallized 2.5 at. % HWCVD film (top) and the 11.5 at.% PECVD film (bottom).

nucleation, which occurs at random in the amorphous matrix, and grain growth into the surrounding amorphous material. From Figure 1, clear differences are seen not only in grain density but also in grain morphology between the different films. While a somewhat less distinct difference is seen between HWCVD films of different C_H, the PECVD films by contrast show much lower grain densities and larger grains overall. These differences are tabulated in Table 1, which gives the measured crystallization parameters for the HWCVD and PECVD films annealed at 600°C. These include the crystallite nucleation rate (r_n), the grain growth rate (s_g), and the extrapolated final grain size (d_g), the latter calculated following the methodology of Iverson and Reif [1].

Three comments can be made from these data. First, since the grain growth rates are roughly similar for all three films, the final extrapolated grain size is seen, to a first approximation, to be inversely proportional to the nucleation rate. Second, the film C_H, for a particular film deposition type (i.e., HWCVD), does affect the crystallization kinetics, in that the high C_H HWCVD film has a lower nucleation rate and a larger extrapolated final grain size than the low C_H HWCVD film [8]. This trend is similar to that observed for PECVD films versus film C_H [2], but the magnitudes of the crystallization parameters are different. Finally, these results show that deposition type also has a major influence on crystallization, in that HWCVD and PECVD films containing approximately the same film C_H have strikingly different crystallization

Film Type	HWCVD (low H)	HWCVD (high H)	PECVD (high H)
r_n $(\text{min.}\mu m^3)^{-1}$	2.3	0.16	0.027
s_g (nm/min)	4.1	3.1	2.7
d_g (x) (μm)	0.31	0.66	1.20

Table 1. Measured crystallization parameters for HWCVD and PECVD films annealed at 600°C.

parameters. Significant differences in film incubation periods have been previously observed for HWCVD versus PECVD films [4,9]. A tentative model has been proposed to explain the very short incubation times for the HWCVD films [9].

Table 2 shows values of the apparent final grain size as determined from the XRD peak broadening using the Scherrer formula [5]. As can be seen, while the absolute magnitudes of the sizes for the HWCVD films are in general agreement with XRD literature values [10] for a-Si:H, the trends are in the opposite direction compared to the d_g values seen in Table 1 when film C_H is considered [2]. However, other sources of XRD line broadening exist in such materials in addition to the crystallite size, such as the density of crystallite defects, in particular stacking faults and twins [5]. It is interesting to consider if the evolution of H, and the changes in structural ordering so produced when this H evolves, has any correlation to the XRD line broadening. Accordingly, Raman transverse optical mode half with at half maxima (HWHMs), which are traditionally used as a measure of short range order in a-Si:H [11], are also presented in Table 2 for the HWCVD

films, both in the as-grown state and which are also annealed long enough to evolve the vast majority of the film H but still remain amorphous. For the latter, the anneal times are still within the film 'incubation periods'.

Film Type	HWCVD (low H)	HWCVD (high H)	PECVD (high H)
XRD 'grain size' (fully crystallized)	0.08 μm	0.052 μm	0.045 μm
Raman HWHM (as grown)	28 cm^{-1}	28 cm^{-1}	
Raman HWHM (at end of incu-bation period, but still amprphous)	28 cm^{-1}	33 cm^{-1}	

Table 2. XRD grain size and Raman TO HWHM for HWCVD and PECVD films as grown and annealed at 600°C for indicated times.

As can be seen, while the Raman HWHMs are similar for the as grown low and high C_H HWCVD films, the film that evolves the largest amount of H (the high C_H HWCVD film) exhibits Raman line broadening (a wider HWHM), indicating more film disorder, and this film also exhibits the smallest (largest) XRD (TEM) grain size. The present results for the HWCVD films therefore suggest that significant H evolution may translate into increased XRD line broadening, which may be an indication of i.e. an increased density of crystalline defects. In any case, the present results show that the XRD line broadening cannot be attributed to grain-size effects alone, but may be some signature of structural disorder due to inhomogeneous strain or intergranular defects, perhaps caused by the evolution of (significant) film H. Experiments are in progress to measure the Raman HWHMs for the as grown and annealed PECVD films, as well as determine the relative strains existing in the fully crystallized HWCVD and PECVD films [12]. Regarding the former, an increased Raman HWHM upon sample annealing was previously observed by Lee et al. in PECVD films containing varying hydrogen contents, with the broadening appearing larger for the film initially containing more bonded hydrogen [2], but this broadening was not quantified.

CONCLUSIONS

The crystallization parameters for HWCVD and PECVD films containing different initial film hydrogen contents have been determined. The film hydrogen content (C_H) was found to affect grain growth for HWCVD films, with films containing more initial film hydrogen exhibiting lower film nucleation rates and larger extrapolated final grain sizes. In addition, the deposition type also was shown to play a major role in the crystallization process, in that a PECVD film exhibiting a film C_H similar to that of a HWCVD film showed a much lower film nucleation rate and a larger extrapolated final grain size. The increased Raman short range disorder, occurring for the high C_H HWCVD film, was suggested to play a role in the crystallization process.

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