COMPOSITIONAL ANISOTROPY AND MICROSTRUCTURE OF a-Si:H

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Electron microscopy is combined with Raman and ir spectroscopy to relate microstructure to atomic bonding configurations. *In situ* TEM measurements made on a-Si with columnar structure showed an increase in electron transparency of material between the islands relative to the islands themselves when samples were annealed to ~350°C. Partial etching of the samples with a diluted HF:4(HNO₃) solution caused "spaghetti" like structures in the SEM micrographs, and Raman and ir measurements showed decreases in lines associated with polysilane structures. A hydrogen-rich intercolumnar phase is thus demonstrated.

The hydrogen environments in a-Si produced by glow discharge decomposition of silane have been the subject of many recent studies. These studies have been motivated by the fact that a-Si has been produced with low quantities of electrically active defects. In addition it has also been shown that under certain deposition conditions, samples exhibit sub-micron scale structures.[1] This is most evident in material which exhibits a morphology in which columnar structures run parallel to the growth direction. In addition it has been proposed that the material between the columns is a hydrogen-rich phase.[2] In this paper we describe several measurements in which we attempt to relate the sub-micron scale structure to the atomic scale hydrogen-silicon environments in the films.

The material used in this study was prepared in a rf diode configuration reactor which has been described in detail elsewhere.[3] Deposition conditions were chosen to obtain material which exhibited columnar morphology. In particular samples were deposited on RT or 230 °C substrates on the anode with 5% silane in Ar and 18W of RF power. These samples are known to exhibit ir and Raman active lines at 2000 and 2090 cm⁻¹ which have been associated with \equiv Si-H and =Si-H₂ environments respectively.[4]

The smallest scale micro-structure or morphology is characterized by ~200Å island like structures in thin films (<500Å). These islands apparently evolve into the columnar structures in thicker films. An example of the island structure is displayed in the TEM micrograph shown in Figure 1. It has been suggested that the island structures may be characterized as a continuous random network of Si with monohydride inclusions while the region between the islands is a lower density material including polysilane structures. In order to examine this proposal, the films were heated to 350°C in the TEM and micrographs were taken before and after. Previous ir measurements have shown that annealing at this temperature causes a large decrease in the lines associated with = Si-H₂ polysilane structures.[5] Our micrographs visually show an increase in contrast of the islands. In order to quantify this effect, densitometer traces from the plates were obtained. This was achieved by measuring the transmission of a focused laser scanned across the photographic plates. Here 0.5 mW of 5145Å Ar ion laser radiation was focused to



Figure 1 TEM micrograph,(a), and densitometer traces, (b) and (c), of a-Si:H. Trace (b) was obtained from a virgin film while (c) was obtained after annealing at \sim 350°C.

~30 μ m spot on the plates. This dimension is smaller than the features on the photographic plates. The data was stored digitally. Examples of the traces are also shown in Fig. (1). The TEM micrographs were made with the instrument in focus and at a preset underfocus ($\Delta f = 1680$ Å). This degree of underfocus is several times larger than possible focussing errors. Several densitometer traces were made from each plate. For each trace, the normalized mean square deviation was calculated and the results are shown in Table (1). Clearly the mean square deviation increased upon annealing. We note the same trend in both the focused and under-focused conditions. The difference in mean square deviation in the focus and under focussed condition demonstratively eliminates the possibility that small focus changes are responsible for the observed effects.

Another way to explore the compositional anisotropies of this material is to use an etch which affects one composition more than the other. We found that $HF:4(HNO_3)$ diluted 50/50 in water caused a velvet black surface on the samples which exhibited columnar morphology. In contrast samples which did not show columnar structures etched smoothly. The effects of etching are displayed in the series of SEM micrographs shown in Fig. (2). We emphasize that the columnar structure in the virgin material shown in Fig. (2a) is on a different scale than that shown in the TEM. The etching process first causes cracks to form apparently along columnar boundaries. It then penetrates to leave "spaghetti like" structures. We suggest that the etch primarily affects regions which contain high concentrations of H and "polysilane" structures and that these atomic scale configurations occur primarily between the columnar structures. To demonstrate

Table 1 The normalized mean square deviation of the transmission through TEM plates: The normalization was determined by averaging the transmission of the nearest 100 data points

Focus	Scan	Mean Square	Deviation
∆f		Virgin	Annealed (350°C)
0	1	.195	.333
0	2	.156	.317
-1680Å	1	.277	.401



Figure 2 SEM micrographs of as-deposited a-Si:H, (a), preliminary etching effects, (b), and well etched sample, (c)

this Raman and ir measurements have been carried out on the etched samples. Of particular interest is the dependence of the 840cm⁻¹ ir active mode assigned to polysilane and the 2090cm⁻¹ ir and Raman active mode assigned to = Si-H₂ structures.

The ir spectra were carried out in transmission with the films deposited on crystalline Si substrates. The resultant spectra of the virgin film and an identical film etched for approximately 10 sec is shown in Fig. (3). There are several notable differences in the spectra. The strong ~860 cm⁻¹ line is dramatically reduced and a strong broad mode appears at ~1100 cm⁻¹. In addition the high frequency spectra is dominated by a mode at ~2110 cm⁻¹ while for the virgin film the strongest high frequency mode is observed at ~2090 cm⁻¹. We attribute the strong decrease of the 860 cm⁻¹ line to preferential etching of the polysilane structures which reside predominantly between the columnar structures. The mode at ~1100 cm⁻¹ and most likely the mode at 2110 cm⁻¹ are associated with oxygen incorporated in the film after etching. We found that the amount of oxygen [6] incorporated in the film varied from sample to sample and as yet we have not been able to correlate this effect with the film properties.

One particular set of samples that apparently did not oxidize rapidly when etched was studied by Raman spectroscopy. The Raman experiments were carried out in a near backscatter geometry using less than 100mW of 5145Å Ar ion laser excitation. The results for the high frequency region are shown in Fig. (4). For the normal backscatter configuration little difference was observed in the spectra obtained before and after etching the samples. However, when the sample was tilted to ~45° from normal so that only the upper extremities of the "spaghetti like" structures were exposed, a marked decrease in the 2090cm⁻¹ line was observed. This experiment was repeated with the sample at ~10K to exclude effects due to laser heating of the sample, and similar results were obtained. Thus the decrease in intensity of the ~2090 cm⁻¹ Raman line indicates that the etching causes a relative decrease in Si-H₂ configurations.





Figure 3 The ir transmission of a-Si:H films before, (a), and after etching(b)

Figure 4 The room temperature high frequency Raman spectra of a-Si:H films before, (a), and after etching, (b) Spectra (a) and (b) were and (c): obtained in a normal backscatter configuration while spectrum c) was obtained with the sample tilted to ~45° from normal

Thus the etching and annealing experiments described here yield consistent results. From the inhomogeneous thermal evolution (TEM) we find that hydrogen is more readily evolved from the inter island regions. The differential etching corroborates this result by simultaneously removing inter columnar material along with spectroscopic features associated with polysilane structures.

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