Study of Amorphous to Microcrystalline Silicon Transition from Argon Diluted Silane

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ABSTRACT

We have studied the structural evolution in amorphous and microcrystalline silicon deposited from silane-argon mixture by radio frequency plasma enhanced chemical vapour deposition (PECVD) method. Sharp increase in small angle x-ray scattering (SAXS) intensity, in accordance with tilt measurements, indicates columnar morphology in the sample deposited in the amorphous-microcrystalline transition region. The variation of SAXS measured heterogeneity and a gradual shift of Si-H stretching vibrational frequency at 2000 cm⁻¹ towards higher wave number with increase of power density indicate structural modifications in the films. Observation of sharp increase in the ratio of the intensity of Ar⁺ to SiH⁺ in the transition region may explain the surface modification assisted by Ar⁺ and hence the structural changes in the material.

INTRODUCTION

Growth of microcrystalline silicon (µc-Si:H) by PECVD of silane has been extensively studied in recent years. The importance of H in µc-Si:H nucleation is well established. Several models have been proposed regarding the role of H (reacts at the growing film surface and/or sub-surface) in µc-Si:H nucleation. The existing µc-Si:H growth models include chemical equilibrium between deposition and etching [1], preferential etching of disordered phase [2], enhanced surface diffusion of the precursors due to adequate H coverage of the surface [3], indiffusion of H into the sub-surface growth zone causing elimination of strained Si-Si bonds and structural relaxation via chemical annealing [4]. Insertion of H into strained Si-Si bonds may cause structural relaxation in the immediate vicinity leading to the formation of µc-Si:H nuclei [5]. All the above processes indicate the necessity of a H rich atmosphere for µc-Si:H formation. However, doped and undoped µc-Si:H has also been deposited from Ar diluted SiH₄ [6,7,8]. The question then arises as to which of the above processes plays the major role in case of Ar dilution.

We have studied the structural properties of a series of samples prepared by RF PECVD of SiH₄ and Ar mixture using HRTEM, FTIR, and SAXS. A wide range of film structures from totally amorphous to totally microcrystalline passing over the transition region was achieved by simply varying the RF power. We concentrate here on the mechanism of µc-Si:H formation and the contribution of Ar⁺ on the process. Various plasma species were monitored by Optical Emission Spectroscopy (OES) to understand their role in µc-Si:H formation.
EXPERIMENTAL DETAILS

A set of samples were deposited by 13.56 MHz PECVD from SiH₄-Ar mixture in the ratio 5:95 at 0.2 Torr deposition pressure and substrate temperature of 200°C. The radio frequency power density was varied in the range of 20 - 285 mW/cm². The samples in the thickness range of 1.5 - 3 µm were deposited on c-Si and on high purity (99.99%) Al-foils for FTIR and SAXS measurements respectively. For HRTEM about 0.07 µm thick samples were deposited on carbon coated copper grids. The crystalline fraction (fₓ) was estimated from the measurement of the relative area occupied by the crystallites in the HRTEM images at 490 K magnification, with the help of the software Digital Micrograph. An OES setup was used to monitor the emission lines at 750.4 nm and 414.2 nm corresponding to the excited species, Ar⁺ and SiH⁺ respectively in the plasma [9]. The FTIR spectra were recorded from 400 to 4000 cm⁻¹ at a resolution of 1 cm⁻¹. The bonded hydrogen content was calculated from the Si-H wagging mode at 640 cm⁻¹. The microstructure parameter

\[ R = \frac{I_{2090}}{I_{2000} + I_{2090}} \]  

was calculated from the intensity of the absorption peaks at 2000 and 2090 cm⁻¹[10].

RESULTS AND DISCUSSION

Figure 1 shows HRTEM micrographs with the corresponding diffraction patterns for two films deposited at 163 mW/cm² and 285 mW/cm². The sample deposited at 285 mW/cm² has a large crystalline fraction (fₓ), estimated to be ~ 40%. Whereas the film deposited at 163 mW/cm² presents a more diffused diffraction pattern and fₓ is estimated to be of the order of 15%. The films deposited at lower power densities (<163 mW/cm²) appear amorphous from electron microscopic studies.

![HRTEM micrographs with corresponding diffraction patterns](image)

Figure 1. High resolution transmission electron micrographs and diffraction patterns of samples deposited from SiH₄-Ar mixture at (a) 163 mW/cm² and (b) 285 mW/cm²

The IR spectra have revealed some interesting features. Usually IR spectra are analysed by decomposing the stretching mode of the Si-H related bonds in two bands [10]. The one at 2000 cm⁻¹ is assigned for isolated monohydrides and 2090 cm⁻¹ for dihydrides and/or monohydrides.
decorating the surface of microvoids. However these frequencies could shift due to changes in the local bonding environment. Figure 2 shows the peak frequency of the low frequency part of the stretch band versus the power density.

![Figure 2](image)

**Figure 2.** Variation of monohydride stretching mode with increasing power density.

A continuous increase is depicted until the power density of 163 mW/cm² is reached and then a slight decrease is observed. A similar behaviour has been observed for the high frequency part (2090 cm⁻¹) of the stretch band. This indicates a gradual change of the Si-H neighbourhood in the films when going from amorphous towards microcrystalline. Indeed at low power densities the films, which appear amorphous, are compact with negligible void fraction (0.06 %) as measured by SAXS (see Table1) and the low frequency part of the stretch band appears at nearly 2000 cm⁻¹ indicating that monohydrides are mostly isolated. Increasing the power density increases the void fraction to a maximum of 3.8% at 163 mW/cm² and the shift of the low frequency peak to higher frequencies (Figure 2). SAXS scattering intensity Q_N which indicates heterogeneity in the

**Table 1.** Variation of SAXS intensity (Q_N) and volume of void fraction (V_f) (measured from SAXS), and microstructure factor (R) and bonded hydrogen content (C_H) (measured from FTIR) with power density

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Power density (mW/cm²)</th>
<th>Q_N (10^{23} eu/cm³)</th>
<th>V_f (%)</th>
<th>R</th>
<th>C_H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA80</td>
<td>20</td>
<td>1.1</td>
<td>.064</td>
<td>.21</td>
<td>10.8</td>
</tr>
<tr>
<td>PLA81</td>
<td>41</td>
<td>1.01</td>
<td>.060</td>
<td>.21</td>
<td>11.4</td>
</tr>
<tr>
<td>PLA70</td>
<td>82</td>
<td>13.1</td>
<td>.77</td>
<td>.25</td>
<td>9.8</td>
</tr>
<tr>
<td>PLA72</td>
<td>109</td>
<td>22.2</td>
<td>1.3</td>
<td>.27</td>
<td>7.5</td>
</tr>
<tr>
<td>PLA71</td>
<td>163</td>
<td>62.3</td>
<td>3.8</td>
<td>.4</td>
<td>5.4</td>
</tr>
<tr>
<td>PLA73</td>
<td>285</td>
<td>20.4</td>
<td>1.2</td>
<td>.36</td>
<td>9.1</td>
</tr>
</tbody>
</table>

A20.7.3
sample, increases sharply from $1.01 \times 10^{23}$ eu/cm$^3$ to $62.3 \times 10^{23}$ eu/cm$^3$ during transition from amorphous to microcrystalline regime. The increase in heterogeneity in the films in this power density range has also been corroborated by the increase in the microstructure factor $R$ (from 0.21 to 0.4). Moreover SAXS measurements in normal and tilt modes, presented in Figure 3, show that the film deposited at the onset of microcrystalline growth has a columnar structure. The SAXS signal becomes much less intense when the incident beam is tilted at 45° indicating a preferential orientation of the voids in a direction normal to the plane of growth. Presence of columnar structure in samples deposited from argon diluted silane was also observed by Knights et al [11].

Thus the morphology of the films changes as the deposition conditions lead to the transition from amorphous to microcrystalline phase. A decrease of the hydrogen content together with an increase of the void fraction are observed as the amorphous to microcrystalline transition approaches (Table I), as was also reported in literature [12]. A concurrent stretching mode peak shift of the Si-H bonds, observed in our present study, essentially suggests that their local bonding environments change during the amorphous to microcrystalline transition. The maximum shift has been observed for the film deposited at 163 mW/cm$^2$. Increasing power density further leads to an increase of the crystalline fraction as depicted by HRTEM together with a more compact material, which consists of less voids, higher bonded hydrogen (Table-I) and a smaller peak shift (Fig.2).

Lucovsky [13] has shown that silicon-hydrogen vibrational frequency, $\omega$, is directly proportional to the average electronegativity of the neighbouring environment, i.e

$$\omega = \omega_0 + b \sum_j \chi_{Aj},$$

(2)
where the constants, $\omega_0$ and $b$, are determined empirically, $\chi_{Aj}$ is the stability electronegativity (as defined by Sanderson [14]) of a group and the sum is over three neighbouring groups of the silicon-hydrogen bond. Considering the above model Sidhu et al [15] explained the shift of the low frequency part of Si-H stretch band by the presence of monohydride clusters in one or two dimensional chains. The shift of Si-H stretch band with the power density in our films, along with the increase in film heterogeneity and void fraction, may therefore arise due to the formation of monohydride clusters in the film in the amorphous to microcrystalline transition region.

We now discuss how morphological changes occur in our material during amorphous to microcrystalline transition. We have seen that in this region the film morphology as well as the distribution of the hydrogen in the films becomes more inhomogeneous. The observed increase in heterogeneity may be due to the presence of voids and/or hydrogen clusters. Increase in the microstructure factor $R$ during transition indicates a decrease in the isolated monohydride bonding in the film. In addition to isolated SiH bonds, which predominate in the amorphous regime, the monohydride bonds now tend to exist in clustered form. Increase of these regions during amorphous to microcrystalline transition suggests that the clusters are linked to microcrystalline nucleation. On H elimination from SiH bonds, these clusters may collapse to form strong Si-Si bonds. A similar mechanism for Si-Si bond formation from H platelets had been proposed by Jackson and Tsai [16]. The platelets may thus act as precursor state for nucleation centre of microcrystalline grains [17]. The break of Si-H bonds, however, is unlikely unless aided by some external agent. In case of $H_2$ dilution, increased flux of atomic H from the plasma is the likely agent to promote H abstraction. Bombardment of Ar*, in case of Ar dilution, can be an alternative way of providing the energy necessary for hydrogen elimination from Si-H bonds leading to the formation of microcrystalline nucleation centres. In the post transition region, the decrease in heterogeneity and void fraction, and an increase in the crystalline fraction from 15% to 40% as observed from HRTEM images indicate that Si-Si bonds may coalesce together at the expense of intercolumnar voids to form large microcrystalline grains.

Figure 4 shows the variation of the ratio of the intensity of the Ar* ($I_{Ar^*}$) to that of SiH* ($I_{SiH^*}$) with rf power density.

![Figure 4](https://doi.org/10.1557/PROC-715-A20.7)

**Figure 4.** The ratio of the intensity of the Ar* ($I_{Ar^*}$) to that of SiH* ($I_{SiH^*}$) with rf power density.
(I_{\text{SiH}}) with rf power density. The ratio shows a sharp increase above the power density identified as the threshold at which microcrystallisation onsets. Neutral Ar* species reach the film surface with thermal energies. Subsequent de-excitation of these species imparts the energy necessary for the breaking of loose Si-H bonds in the H cluster regions of the growth zone. H rich regions collapse and subsequently form stronger Si-Si bonds. These locally ordered regions may serve as nucleation sites for \(\mu\text{c-Si:H}\) films.

CONCLUSION

Amorphous to microcrystalline transition was studied for Ar diluted samples by increasing the power density. During transition, a definite change in the structural morphology and hydrogen distribution of the film was observed which has been suggested to be linked with microcrystalline nucleation. Bombardment of the film surface during growth by Ar* has been proposed as an alternative way to provide sufficient energy for bond rearrangement which in turn paves the way for microcrystalline formation.

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REFERENCES