1 of 1

ELECTRON MICROSCOPY STUDIES OF UNDOPED AND PHOSPHORUS DOPED Si:H AND Si,C:H FILMS

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ABSTRACT

The microstructure of undoped and phosphorus doped Si:H and Si,C:H films was analyzed by selected-area diffraction, conical dark-field imaging, energy-dispersive x-ray spectroscopy and electron energy-loss spectroscopy in transmission electron microscopes. Thin films were synthesized by remote plasma-enhanced chemical vapor deposition and characterized in terms of degree of crystallinity. The distribution of phosphorus in the Si:H and Si,C:H films, and carbon in the Si,C:H films was evaluated. The results indicate that i) the microstructure of a film may be two phase, consisting of silicon microcrystallites in an amorphous matrix, ii) phosphorus doping as well as the presence of carbon influences the degree of crystallinity by reducing the average size and volume fraction of microcrystallites, iii) the presence of carbon and phosphorus doping completely suppresses the crystalline phase, iv) phosphorus is distributed at approximately the same concentration in both the crystalline and amorphous phases of diphasic films, and v) carbon is detected in the amorphous phase of the Si,C:H films.

INTRODUCTION

Thin films of microcrystalline Si:H ($\mu\text{c-Si}$) and microcrystalline Si,C:H ($\mu\text{c-Si,C}$ alloys) and their phosphorus and boron doped counterparts have been synthesized by remote plasma enhanced chemical vapor deposition (RPECVD),^{1,2} reactive magnetron sputtering,^{3,4} and glow discharge.⁵⁻⁷ This class of thin films shows interesting electrical and optical properties.^{8,9} For example, the dark conductivity of a film can be high depending on the microstructure and doping level. Because of these electrical and optical properties, the films are candidates for i) stacked gate electrodes and source/drain contacts in the context of module cluster processing as well as ii) photovoltaic structures and solar cell devices.¹⁰⁻¹⁴

Previous studies which combined transmission electron microscopy (including diffraction contrast imaging, selected-area diffraction and high-resolution imaging) and vibrational spectroscopies (including infrared and Raman scattering)^{4,15} have shown that i) the microstructure of Si:H and Si,C:H films may be two phase, consisting of microcrystallites in an amorphous matrix; ii) the crystalline phase is silicon which has a columnar-like grain structure - the major axes of these grains have preferred orientations predominantly along the direction of deposition (i.e. [001]) and the average diameter of columnar-like grains is about 10 nm; iii) the columnar grains are embedded in a matrix of a-Si:H for $\mu\text{c-Si}$ films and a-Si,C:H for the $\mu\text{c-Si,C}$ alloys; iv) the degree of crystallinity depends on both the doping level and the presence of carbon - for the boron case, a high doping level inhibits crystallinity completely, independent of the presence of carbon, whereas for the phosphorus case, doping without carbon does not appear to influence the degree of crystallinity and the presence of carbon completely suppresses the crystalline phase at the highest level of phosphorus doping investigated; and v) the necessary conditions for high dark conductivity of the films are a two phase microstructure, doping, and the absence of carbon. In this paper, results of transmission electron microscopy studies which are based on selected-area diffraction, conical dark-field (DF) imaging and high-spatial resolution analytical electron microscopy are reported.

EXPERIMENTAL DETAILS

Undoped and phosphorus doped films of Si:H and Si,C:H alloys were prepared by RPECVD. For these depositions, chemically active species extracted from a remote He plasma

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(primary electrons, He^+ ions and He metastables) are mixed downstream from the plasma with the Si-atom or Si-atom plus C-atom source gases (SiH_4 or SiH_4 plus CH_4 , respectively), H_2 and the dopant atom source gas (PH_3). The films of concern in this study are defined in the included Table along with the corresponding downstream gas ratio (PH_3/SiH_4). There is about 7 at % [H] in these films and the hydrogen is bonded mainly in a monohydride configuration.^{1,2} For the carbon alloy films, the carbon levels are typically in the range 5 to 10 at %. Depositions are done onto thermally grown SiO_2 layers of thickness ~ 100 nm on Si (001) substrates. The substrate temperature is $\sim 250^\circ\text{C}$ for all depositions and the deposited films are typically 150 to 200 nm in thickness.^{1,2}

The present transmission electron microscopy results include analyses from both plan-view and cross-sectional specimens. These specimens were thinned to electron transparency using conventional mechanical and argon ion-beam milling techniques. Because of the preferred orientation of the columnar-like grains, the plan-view mode is most appropriate when estimating the size and volume fraction of the microcrystallites. In this mode, the microcrystallites are observed 'end-on'. Selected-area diffraction data and conical DF images were recorded using a Philips CM12 electron microscope, operated at 120 kV. The reason for choosing conical DF over conventional DF imaging to evaluate the degree of crystallinity can be understood from a consideration of a typical selected-area diffraction pattern (SADP) from a diphasic Si:H film. As can be seen in Fig. 1a, such a diffraction pattern exhibits an intensity distribution which is typical of a material consisting of small crystallites - several sharp but discontinuous rings and an amorphous phase - several diffuse rings. Each sharp ring is formed by electrons that are scattered/diffracted into the same Bragg angle (i.e. $2\theta_B$) but in different directions (i.e. 360°). Typically, the first ring which is closest to the central spot and corresponds to silicon d_{111} exhibits the maximum diffracted intensities. In conventional dark-field imaging, only a small fraction (i.e. $\sim 1/60$) of the diffracted intensity from a ring passes through the objective aperture, as is shown schematically in Fig. 1a. Therefore, when the volume fraction of crystallites is estimated from conventional DF images, the estimates are less than the actual values. This problem can be minimized by conical DF imaging. In this mode, it is possible to obtain images which are formed by the integration of the entire ring (e.g. the first diffracted ring from a microcrystalline specimen, as is shown in Fig. 1b). This result is achieved by conically scanning a tilted incident beam of electrons about a fixed point on the specimen. In this way, the diffracted electrons corresponding to $2\theta_B$ are sequentially brought onto the optical axis of the image forming system and these electrons then pass through an 'on-axis' objective aperture.

Phosphorus and carbon were localized relative to the microstructure of the appropriate films using x-ray and energy-loss spectroscopies, respectively. Spatially resolved spectral data were obtained in the context of a Philips EM-400T microscope equipped with a field-emission gun, an energy-dispersive x-ray spectrometer (EDXS) fronted by a conventional beryllium window, and a parallel-detection electron energy-loss spectrometer (PEELS). The microscope was operated at 100 kV and a probe diameter of ~ 3 nm was achieved with the field-emission electron source. A low drift-rate, liquid-nitrogen cooled, double-tilting specimen holder was used for these experiments in order to minimize specimen contamination and local specimen heating. The x-ray technique was used to study phosphorus and the K-shell x-ray emission at ~ 2.02 KeV was monitored. An approximate estimate of the relative concentration of phosphorus with respect to silicon (K-shell x-ray emission at ~ 1.74 KeV) was obtained directly from the ratio of the net integrated intensities in their respective K_α peaks. This result follows from the thin-film approximation (i.e. absorption and fluorescence effects are negligible) and from the fact that the proportionality factor (i.e. the so-called K ratio¹⁶) between the ratio of measured (net) intensities and the desired atomic ratio is ~ 1 for the K_α peaks of phosphorus and silicon.¹⁷ The energy-loss technique was used to study carbon and the K-shell loss which has an onset at ~ 284 eV was monitored. Less than 1 eV resolution was reached with the PEELS system and only energy-loss spectra which were acquired from thin specimen regions for which the intensity ratio of the first-plasmon loss to the zero loss was less than 0.2 were analyzed. In this way, multiple scattering effects were minimized. Since the apparent level of carbon was very close to the detectable limit, spectra were acquired in both the conventional mode and the second difference mode to reveal very weak edges. This latter approach to the detection of inner-shell losses utilizes a digital filter routine (similar to a negative second derivative) which averages over certain contiguous channels and subtracts half the averages in two adjacent 'wings' of a definable width.¹⁸

Figure 1. a) SADP from a diphase film of Si:H. The sharp, discontinuous rings correspond to silicon (111), (220), and (311) reflections. Two weak diffuse rings are also present. The schematic representation of an objective aperture illustrates the position in reciprocal space where diffracted intensity must occur to produce bright image features from crystallites in a conventional DF image. b) Conical DF diffraction pattern of the first ring in a).

Figure 2. Plan view conical DF images generated from (111) diffracted intensities: a) Si:H, b) Si:H:P, c) Si:C:H:P, and d) Si:C:H:P. Bright image features correspond to crystallites.

RESULTS

Microstructure of the films

In agreement with previous studies,¹⁵ selected-area diffraction data from the two-phase films which are the focus of the present work exhibit sharp rings whose relative spacings are consistent with a diamond cubic structure having a lattice parameter of 0.543 nm, as expected for elemental silicon (e.g. Fig. 1a). In the present work, the microstructure of Si:H and Si,C:H diphasic films is described quantitatively in terms of the degree of crystallinity, which includes the average size and volume fraction of the crystallites. Four plan-view conical DF images from films of the type listed in the included Table are shown in Fig. 2 and the bright image features correspond to crystallites. The influence of phosphorus and carbon on the degree of crystallinity is clearly visualized from these data. The results of quantitative image analyses are summarized in the Table. The tabulated results indicate that the microstructure, average size of crystallites, and volume fraction of crystallites depend on both the presence of phosphorus and carbon in such a way that i) phosphorus doping without carbon reduces the average crystallite size as well as the volume fraction of the crystallites, ii) the presence of carbon without phosphorus doping reduces the average size and the volume fraction of the crystallites, and iii) the presence of both carbon and phosphorus at the level investigated completely suppresses the crystalline phase. Results ii) and iii) agree with previous studies,¹⁵ however, result i) differs from previous studies which were interpreted as indicating that phosphorus doping without carbon does not appear to influence the degree of crystallinity.

Table Gas ratio, microstructure, average size of crystallites, and volume fraction of crystallites

Films	Gas ratio PH ₃ /SiH ₄	Microstructure	Average size of crystallites (nm)	Volume fraction of crystallites (%)
Si:H	0	two phase	25 ± 1	50 ± 5
Si:H:P	1/100	two phase	5 ± 1	5 ± 0.5
Si,C:H	0	two phase	10 ± 1	20 ± 2
Si,C:H:P	1/100	amorphous	NA	NA

Distribution of phosphorus and carbon

The concentration of phosphorus in the doped films is very close to the detectable limit of the Si(Li) detector used in the present experiments. Both the spatial distribution and the relative level of phosphorus with respect to the microstructure of the films was assessed by monitoring the K-shell x-ray emission at ~2.02 KeV. The situation is made difficult by the fact that this peak intensity is on the high-energy side of the silicon K-shell x-ray peak at ~1.74 KeV and therefore peak overlap occurs. Nevertheless, the spectral data are consistent in that doped films exhibit excess and statistically reproducible counts above the high-energy tail of the silicon K_α signal and the appropriate background intensity. The situation is illustrated by the spectra which are given in Figs. 3a - 3d. For the control film (i.e. an undoped two-phase film (Si,C:H)), no statistically reproducible intensity is measured above the decay of the silicon K_α signal, as is expected. Whereas spectra from the phosphorus-doped amorphous films (e.g. Fig. 3b) and from both the amorphous and crystalline phases (Figs. 3c and 3d, respectively) of the phosphorus-doped diphasic films (Si:H:P) contain measurable intensity above the tail of the silicon K_α signal and the corresponding background intensity. Estimates of the relative atomic fraction of phosphorus within the two phases indicate that the doping level is ~1 at % and is approximately the same for both the amorphous and crystalline phases.

Selected-area diffraction patterns from the diphasic Si,C:H films contain no intensity maxima that would indicate that carbon is bonded to silicon in a crystalline structure, suggesting that carbon resides in the amorphous phase. Preliminary electron energy-loss data from which the spatial distribution of carbon is determined from the characteristic K-shell loss at ~284 eV show that the carbon level is detectable by the second difference mode. Typical spectral results from a single-phase amorphous Si,C:H:P film are shown in Fig. 4. Spectral studies of the two-phase, undoped carbon films will be the subject of a future study.

Figure 3 X-ray spectra from: a) an undoped diphasic film (Si,C:H), b) a phosphorus-doped amorphous film (Si,C:H:P), c) the amorphous phase of a phosphorus-doped diphasic film (Si,H:P), and d) the crystalline phase of a phosphorus-doped diphasic film (Si,H:P). A phosphorus K-shell signal is identified at ~ 2.02 KeV in b), c) and d), but this signal is not present in a) which is from the control film (i.e. no phosphorus doping). The peaks at ~ 2.3 KeV are from contamination which occurs during the ion-beam thinning and these peaks correspond to L-shell x-rays from molybdenum.

Figure 4 Electron energy-loss data from a phosphorus-doped amorphous film (Si,C:H:P): a) is a portion of a conventional spectrum showing the silicon $L_{2,3}$ edge which has an onset at ~ 100 eV, and b) is the second difference profile from the same area of the film - the presence of a carbon K-shell loss is identified at ~ 284 eV in the amplified portion of the profile.

SUMMARY

Electron diffraction, conical DF imaging, and spatially resolved inner-shell spectroscopies have been used to characterize the microstructure of undoped and phosphorus doped Si:H and Si₃C:H films which are synthesized by RPECVD. It has been shown that: i) phosphorus doping in the absence of carbon as well as the reverse situation controls the degree of crystallinity by decreasing the average size and volume fraction of microcrystallites, ii) the presence of carbon and phosphorus doping completely suppresses the crystalline phase, iii) phosphorus is distributed at ~ 1 at % in both the amorphous and crystalline phases of the doped diphasic films, and iv) carbon is detected in the amorphous phase of Si₃C:H films.

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