

Crystallization of a-Si:H and a-SiC:H thin films deposited by PECVD

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Hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous silicon carbide (a-SiC:H) films of different compositions were deposited by plasma enhanced chemical vapor deposition (PECVD). For a-Si:H thin films, we have investigated the effect of the rf power on the microstructural properties, such as crystal structure and crystallinity. A diffraction peak (Si (111)) positioned at about $2\theta = 28^\circ$ appeared from a thin film grown on a Si (100) substrate at rf power of 300 W, suggesting a local crystallization of the film. For a-SiC:H thin films, the predominant peak is ascribed to (200) of β -SiC structure, which confirms the formation of β -SiC upon 900 annealing. No peak corresponding to the (111) or (220) planes of β -SiC is detected, suggesting that the films might exist in a single crystalline state.

Key words: Plasma enhanced chemical vapor deposition, Amorphous silicon, Amorphous silicon carbide, Crystallinity.

Introduction

Although the plasma enhanced chemical vapor deposition (PECVD) technique for the deposition of amorphous silicon based films (a-Si:H and a-SiC:H) is a well established technology for industrial applications, recently there is a renewed interest for the growth of micro-crystalline silicon (μ c-Si:H) which has been demonstrated to have excellent properties suitable for applications in both passive and active electronic and optoelectronic devices [1, 2]. Among many technological requirements, the growth of microcrystalline silicon at lower than 300 °C is needed although the crystallization is hindered at low temperatures by the poor migration of the precursors on the growth surface. In order to overcome this drawback, a silane plasma highly diluted with H₂ and operating at 13.56 MHz has been used for μ c-Si:H deposition at low substrate temperatures (200-300 °C) and high power densities [3].

The conventional methods used to synthesize a-Si:H and a-SiC:H thin films are low pressure chemical vapor deposition (LPCVD) as well as solid phase crystallization (SPC), pulsed rapid thermal annealing (PRTA), and eximer laser annealing (ELA) [4-6]. However, these methods have some disadvantages such as high deposition temperature over 600 °C, small grain size, poor crystallinity, and high grain boundary states. On the other hand, although LPCVD and PECVD always result in poor crystallinity and relatively small grains,

these methods can be utilized at below 600 °C. Therefore, we have deposited the hydrogenated amorphous silicon (a-Si:H) and the hydrogenated amorphous silicon carbide (a-SiC:H) thin films by rf PECVD.

In the present study, the effects of the rf power for a-Si:H films and annealing for a-SiC:H films on the properties, such as surface roughness, structure, and crystallinity, were mainly studied.

Experimental Procedures

The a-Si:H and a-SiC:H films were deposited on silicon substrates using a capacitively coupled rf PECVD system (ULVAC, CPD-6108) as described in Fig. 1. The reaction system is of the parallel planar discharge type using a rectangular rf electrode (lower) and substrate electrode (upper). The substrate is placed on a tray with the surface to be coated facing downward, so that the deposition of dust particles and flakes can be minimized. Hydrogen plasma pre-treatment was performed at 200 W for 10 minute before the film deposition process.

For a-Si:H films, the substrate temperature (T_s) was kept at 150 °C and the rf power was varied from 50 to 400 W. The working pressure was fixed at approximately 319.97 Pa flowing silane(SiH₄) as a-Si:H source. For a-SiC:H films, SiH₄ and CH₄ gas mixture was utilized as a-SiC:H source. In this case, the T_s was kept at 150 °C and the rf power was fixed at 200 W. The working pressure was identical with the deposition conditions of a-Si:H films.

Annealing of a-SiC:H films was performed in a furnace of Ar atmosphere for 3 h at temperatures ranging from 400 to 900 °C. The effects of rf power for a-Si:H films and annealing temperature for a-SiC:H

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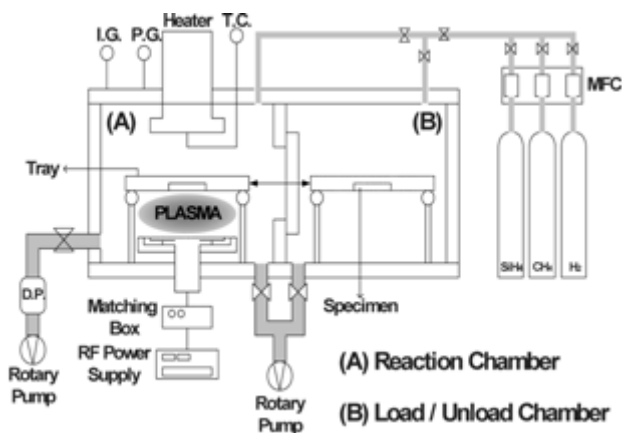


Fig. 1. Schematic diagram of rf PECVD system.

films on the crystallinity, structure, and surface roughness were investigated by a X-ray diffractometer, Raman spectroscopy, Fourier transform-infrared spectroscopy (FT-IR) and atomic force microscopy (AFM).

Results and Discussions

a-Si:H thin films

Figure 2 shows the X-ray diffraction patterns of *a*-Si:H thin films grown on Si (100) substrates at 150 °C with different rf powers. From the films grown above an rf power of 300 W, a diffraction peak located at about $2\theta = 28^\circ$ was obtained. The obtained peak was attributed to Si (111) diffraction, suggesting the formation of μ c-Si:H thin film on Si (100) substrates.

Figure 3 shows the Raman spectrum of the films grown using an rf power of 300 W. Raman data show that the *a*-Si:H thin film consists of an amorphous and crystalline phase due to the co-presence of two peaks centered at 480 and 520 cm^{-1} . Takenaka et al. [7] and van Cleef et al. [8] reported that if the film does not have any crystalline structure, only one Raman peak is observed at 480 cm^{-1} . In our case, the reason for having an additional shoulder peak (480 cm^{-1}) besides

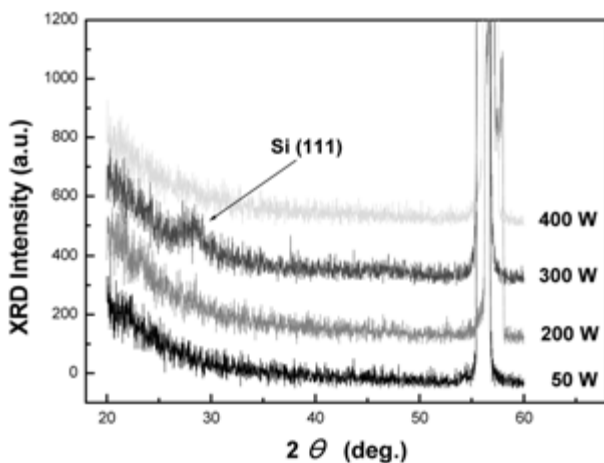


Fig. 2. XRD pattern of *a*-Si:H thin films as a function of rf power.

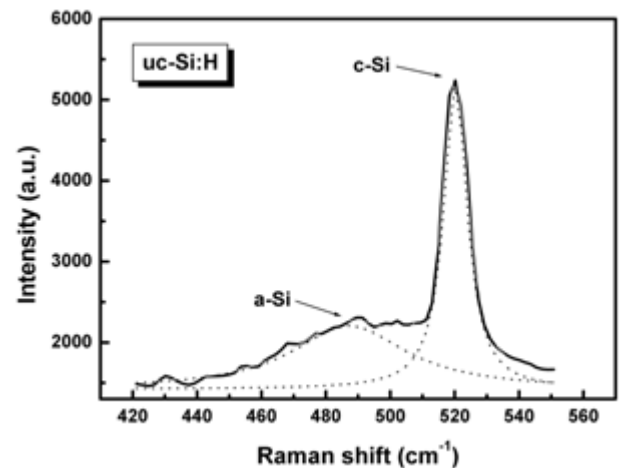


Fig. 3. Raman spectra of μ c-Si:H thin film grown using an rf power of 300 W.

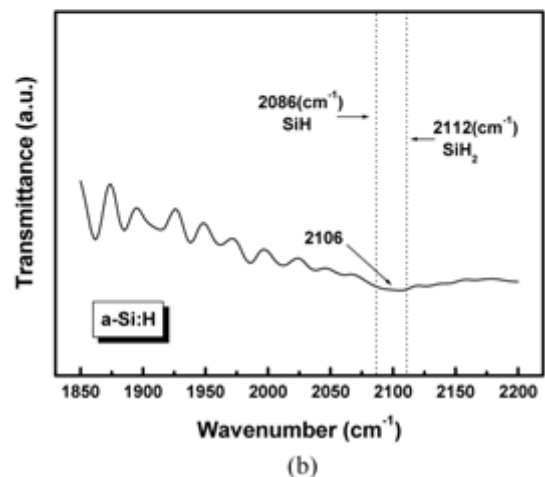
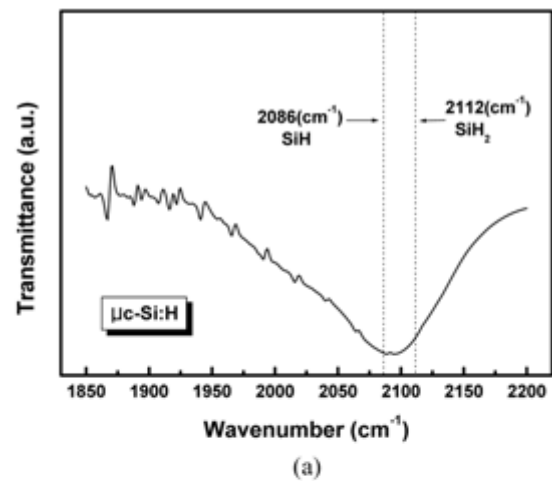


Fig. 4. FT-IR spectra of a (a) μ c-Si:H (b) *a*-Si:H thin film grown using an rf power of 300 W.

the major Raman peak (520 cm^{-1}) is attributed to the existence of an amorphous phase in the μ c-Si:H matrix. This is in good agreement with the previous XRD results that showed a corresponding diffraction peak with a weak intensity. In summary, the μ c-Si:H thin

film grown at high rf power has a locally crystallized structure with a network of amorphous silicon.

Figure 4 shows the infrared spectra of the thin films which were deposited under the identical deposition conditions of Fig. 3. The infrared spectra revealing the information on structural and compositional properties, exhibit absorption peaks centered at 2000–2100 cm^{-1} (Si-H stretching mode) [9]. Also, the stretching mode peak shifts at higher wavenumber (to 2100 cm^{-1}) and this is related to a more abundant presence of SiH_2 (2100 cm^{-1}) than SiH (2000 cm^{-1}) which is a typical characteristic of a higher crystallinity material. From our FT-IR measurements, we identified the detailed structure of the $\mu\text{c-Si:H}$ thin film. For $\mu\text{c-Si:H}$ thin film, many SiH_2 bonding species were observed compared to a-Si:H film. This can be explained by the fact that the silicon atoms in the $\mu\text{c-Si:H}$ thin film have a random network, which can make many dangling bonds.

a-SiC:H thin films

Figure 5 shows XRD patterns of a-SiC:H films with and without annealing (900 °C) deposited using rf power and a methane flow rate of 150 W and 20 sccm,

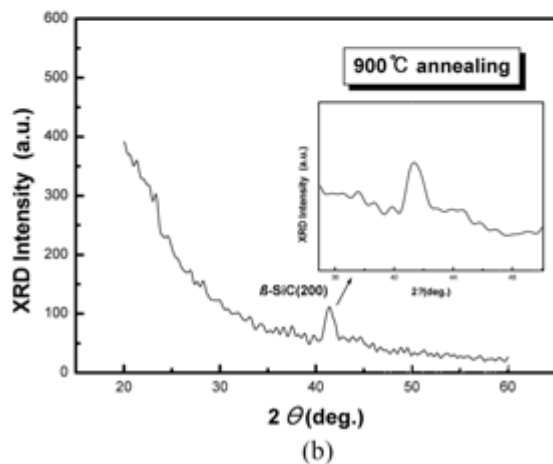
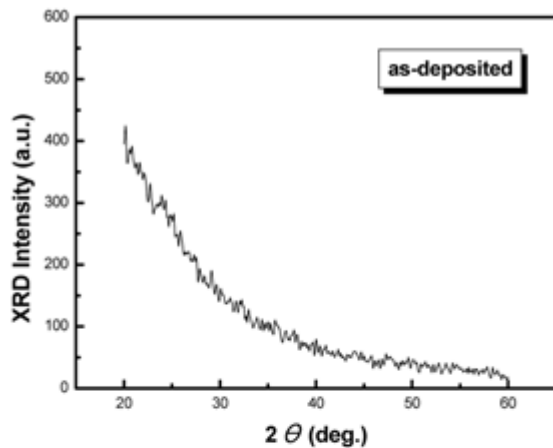


Fig. 5. XRD spectra of a (a) as-deposited and (b) annealed a-SiC:H films at 900 °C.

respectively. The predominant peaks in Fig. 5(b) are ascribed to (200) of the $\beta\text{-SiC}$ structure, which confirms the formation of $\beta\text{-SiC}$ upon 900 °C annealing, and full width at half maximum (FWHM) is about 1.26° . From the FWHM of the (200) peak, a mean grain size of 83.5 Å was calculated using the Scherrer formula [10]. No peaks, corresponding to the (111) or (220) planes of $\beta\text{-SiC}$ was detected, suggesting that the films might be single crystalline.

The annealing effect has been investigated in detail using a Raman spectrophotometer. The Raman scattering results (Fig. 6) showed that the content of microcrystalline phase in the films rapidly increased as the annealing temperature increased, indicating the coexistence of crystalline Si and graphite in the films. In the low wavenumber region as shown in Fig. 6, with the increase of the annealing temperature, one can observe that the band centered around 520 cm^{-1} resembles the Raman peak of c-Si and becomes much narrower. This is evidence of silicon crystallization after annealing at higher temperature. In the case of a-SiC:H film which was annealed at higher temperature, two asymmetrical peaks in the high wavenumber region are observed, which are centered at 1360 cm^{-1} (D band) and 1530 cm^{-1} (G band), respectively. It is well known that a D band peak indicates disordered microcrystalline graphite and a G band peak indicates sp^2 graphite [11]. However, for the as-deposited a-SiC:H films before annealing, the D band peak is rarely observed. Therefore, it can be concluded that a-SiC:H films before annealing is mostly composed of sp^2 bonds and sp^3 bonds increase with an increase of annealing temperature.

Figure 7 shows the rms surface roughness values of a-SiC:H film annealed at 900 °C obtained from AFM measurements. It was found that the surface morphology of the sample is strongly affected by the annealing temperatures. The as-deposited sample surface was relatively smooth but typical protrusions were observed

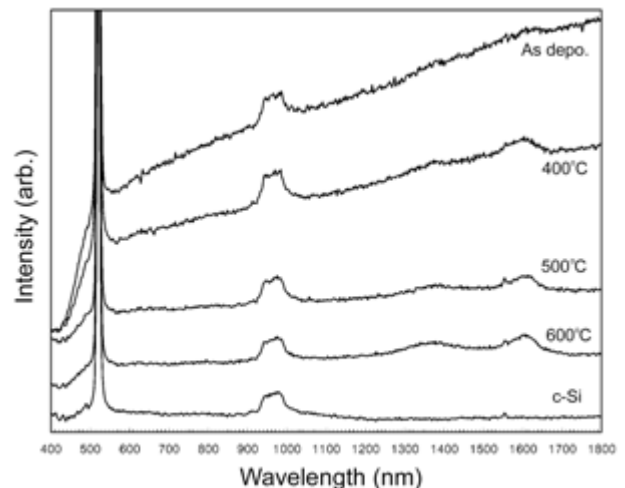


Fig. 6. Raman spectra of a-SiC:H thin film as a function of annealing temperatures.

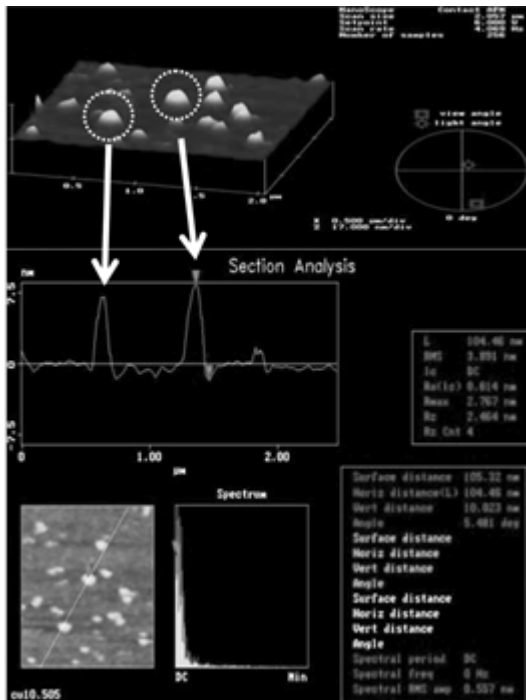


Fig. 7. Rms surface roughness of the a-SiC:H samples after 900 °C annealing.

after annealing at 900 °C for 3 hrs, For temperatures lower than 600 °C, surface roughness was approximately the same with that of the as-deposited sample surface. However, at higher annealing temperatures, an increase of surface roughness (both in the vertical and lateral directions) was observed. Above 900 °C this trend was found to be more obvious. In comparison with the as-deposited sample, the rms value increased from 0.36 to 2.37 nm.

The formation of protrusions with an increase of annealing temperature can be explained by the phase transition from the amorphous to the crystalline state. It was shown in the previous experimental results (XRD and Raman) that the crystallinity of the β -SiC phase increased dramatically above a critical annealing temperature of 900 °C.

Conclusions

We have deposited hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous silicon carbide (a-SiC:H) thin films by a rf PECVD method. For a-Si:H thin films, a diffraction peak (Si (111)) positioned at about $2\theta = 28^\circ$ appeared from a thin film grown on a Si (100) substrate at rf power of 300 W. Raman data show that the a-Si:H thin film consists of an amorphous and crystalline phases exhibiting the co-presence of two peaks centered at 480 and 520 cm^{-1} . For a-SiC:H thin films, the predominant peak is ascribed to (200) of β -SiC structure, which further confirms the formation of the β -SiC upon 900 annealing. No peaks, corresponding to the (111) or (220) planes of β -SiC are identified, suggesting that the films might be single crystalline.

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