한국표면공학회지
Journal of the Korean Institute of Surface Engineering
Vol. 34, No. 5, Oct. 2001
<연구논문>

Growth and Characterization of a-Si :H and a-SiC:H Thin Films Grown by RF-PECVD

Y. T. Kim[a], S. J. Suh[a], D. H. Yoon[a]*, M. G. Park[b], W. S. Choi[b], M. C. Kim[b], J.-H. Boo[b], B. Hong[b]*, G. E. Jang[c], and M. H. Oh[d]

[a] *School of Metallurgical & Materials Engineering, Sungkyunkwan University, Suwon 440-746, Korea*
[b] *Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon 440-746, Korea*
[c] *Department of Materials Science & Engineering, Chungbuk University, Cheongju 361-763, Korea*
[d] *Neosemitech, Inchon, 404-310, Korea*

Abstract

Thin films of hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous silicon carbide (a-SiC:H) of different compositions were deposited on Si (100) wafer and glass by RF plasma-enhanced chemical vapor deposition (RF-PECVD). In the present work, we have investigated the effects of the RF power on the properties, such as optical band gap, transmittance and crystallinity. The Raman data show that the a-Si:H material consists of an amorphous and crystalline phase for the co-presence of two peaks centered at 480 and 520 cm^{-1}. The UV-VIS data suggested that the the optical energy band gap (E_g) is not changed effectively with RF power and the obtained E_g (1.80 eV) of the μc-Si:H thin film has almost the same value of a-Si:H thin film (1.75 eV), indicating that the crystallity of hydrogenated amorphous silicon thin film can mainly not affected to their optical properties. However, the experimental results have shown that E_g of the a-SiC:H thin films changed little on the annealing temperature while E_g increased with the RF power. The Raman spectrum of the a-SiC:H thin films annealed at high temperatures showed that graphitization of carbon clusters and microcıystalline silicon occurs.

1. Introduction

After LeComber et al. reported the first amorphous hydrogenated silicon (a-Si:H) TET[1], many laboratories started the development of an active matrix LCDs (AMLCDs) using a-Si:H TETs formed on glass substrate. Since a-Si:H has inherently low mobility (0.3-0.7 area/voltage seconds), usually a capacitor must added at each pixel. With increasing the display area and pixel density of TFT-LCD, however, high mobility TFTs are required for pixel driver of TFT-LCD in order to shorten the charging time of pixel electrodes. The most important of these drawbacks is a-Si:H's electron mobility, which is the speed at which electrons can move through each transistor. The problem of low carrier mobility for the a-Si:H TFTs can thus be overcome easily by introducing polycrystalline silicon (p-Si) or hydrogenated amorphous silicon carbide (a-SiC:H) thin

films instead of a-Si:H as a semiconductor layer of TFTs[2, 3].

Recently, a-SiC:H thin films have attracted much attention because they are not only a promising material for making efficient solar cells[4] but are also an interesting system for the study of amorphous materials[5-11]. The physics of these alloys is more complex due to the presence of carbon: the atomic ratio of C to (C + Si) can be varied from 0 to 1. Consequently, the optical gap can be tailored over a wide range of values. Furthermore, there are different possible carbon configurations. For this reason a detailed understanding of the parameters that determines the growth mechanisms is essential for the optimization of the optoelectronic properties.

The most conventional methods to fabricate p-Si and a-SiC:H thin films were low pressure chemical vapor deposition (LPCVD) as well as solid phase crystallization (SPC), pulsed rapid thermal annealing (PRTA), and eximer laser annealing (ELA)[12-14]. However, these methods have some disadvantages such as high deposition temperature over 600 ℃, small grain size (< 50 nm), poor crystallinity, and high grain boundary states. So that the low temperature and large area processes using a cheap glass substrate are impossible because of high temperature process. To enhance crystal properties, SPC is more useful method to increase the grain size than the as-deposited p-Si thin film by LPCVD[14]. But it needs a long time annealing at high temperature over 600 ℃. On the other hand, even though up to now LPCVD and PECVD always produced poor crystallinity and relatively small grain, these methods can be utilized at below 600 ℃. Among them the RF-PECVD method was our focus to improve the crystallinity and grain size of a-SiC:H thin film grown at low temperature of below 600 ℃.

In this paper, therefore, we have deposited the hydrogenated amorphous silicon (a-Si:H) and the hydrogenated amorphous silicon carbide (a-SiC:H) thin films on Si(100) wafer and glass by RF plasma-enhanced chemical vapor deposition (PECVD). In the present work, the effect of the RF power on the properties, such as optical band gap, transmittance and crystallinity, was mainly studied.

2. Experimental

The a-Si:H and a-SiC:H thin films were deposited by a radio frequency (13.56 MHz) plasma enhanced chemical vapor deposition (RF-PECVD) system with various RF powers and annealed at different temperatures. Figure 1 shows a schematic illustration of the RF-PECVD system (ULVAC, CPD-6108) used for film deposition.

The system employs the load-lock system comprising a reaction chamber and a loading/unloading chamber. The substrate is set on the tray with the surface to be coated facing down, so that deposition of dust particles and flakes can be

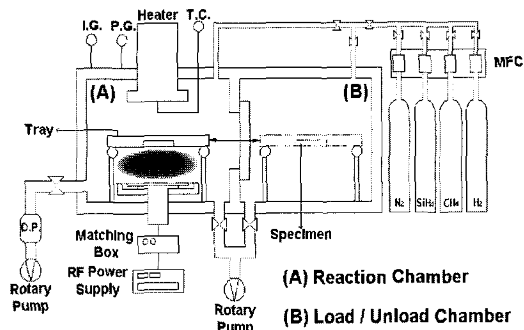

Fig. 1 Schematic diagram of RF-PECVD system used in this work.

minimized. In addition, before thin film deposition, all substrates were pre-treated by hydrogen plasma for 60 min. to enhance nucleation rate and film adhesion. The substrate temperature, T_s was kept between 150-400 ℃, the RF power was varied from 30 W to 400 W. The working pressure was fixed in the range of 1.6 to 2.4 Torr. Silane (SiH_4) gas was used as a-Si:H source, and SiH_4 and CH_4 gas mixture was utilized as a-SiC:H source, respectively. The flow rate ratios $r_Q = Q(CH_4) / [Q(SiH_4) + Q(CH_4)]$, where Q represents the flow of the respective gas, was fixed at 0.5. The annealing temperature was varied from 400℃ to 600 ℃. The as-deposited films were annealed for 90 mins in a quartz tube under nitrogen (N_2) atmosphere, respectively. The films were deposited on glass substrates for the measurements of the optical properties.

We measured the optical properties, such as band gap energy, transmittance, and absorption coefficient. UV-Vis spectrophotometer (Shindoricoh, UVS-1100) was used to determine the transmittance. The Tauc's plot was used to determine the optical bandgap energy (E_g) using the thickness measured by spectroscopic ellipsometry (SE) and a-step profiler, respectively, and then the results from Tauc's plot were compared with $E0_4$. The Raman spectrophotometer was also used for structural analysis.

3. Results and Discussion

3. 1 a-Si:H thin films

Figure 2 shows the typical X-ray diffraction patterns of a-Si:H (a) and μc-Si:H thin films grown on Si(100) substrates at 150 ℃ with different RF powers without hydrogen pre-treatment. In the case of a-Si:H thin film growth, no diffraction peaks due to thin film was observed through the whole RF powers. However, a broad diffraction peak at about $2\theta = 28°$ was appeared from a thin film grown on Si(100) substrate at 150 ℃, 300 W of RF power with hydrogen pre-treatment. The obtained peak was attributed to Si(111) diffraction, suggesting formation of a microcrystalline hydrogenated silicon (μc-Si:H) thin film on Si(100) substrate. This indicates that the hydrogen plasma can makes an important role of enhancing nucleation sites and of crystallization of a-Si:H.

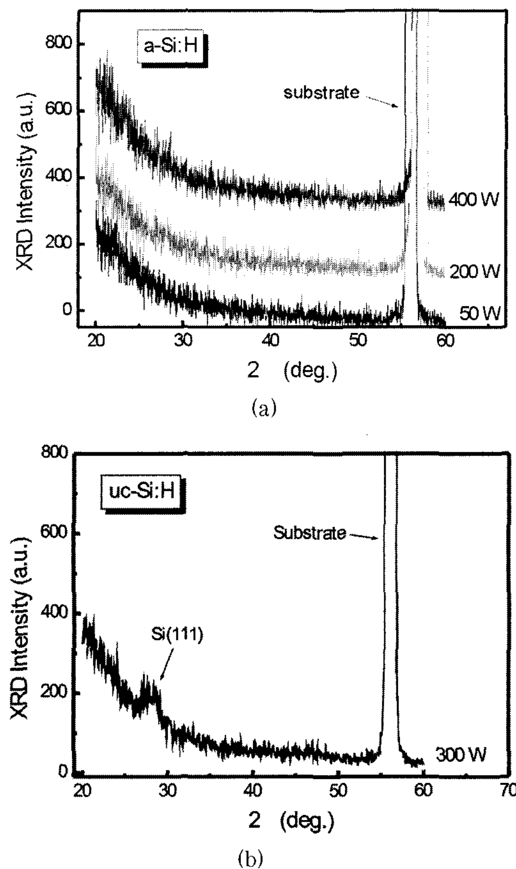

Fig. 2 XRD peaks of (a) a-Si:H and (b) μc-Si:H thin films.

Figure 3 shows the Raman spectrum of a thin film grown on Si(100) at 150 ℃, SiH_4:H_2=1:10, 300 W of RF power. Raman data show that the a-Si:H thin film consists of an amorphous and crystalline phase for the co-presence of two peaks centered at 480 and 520 cm^{-1}. S. Takenaka et. al.[15] reported that if the film have no crystalline structure, the Raman vibrational peak will be observed at 480 cm^{-1}.

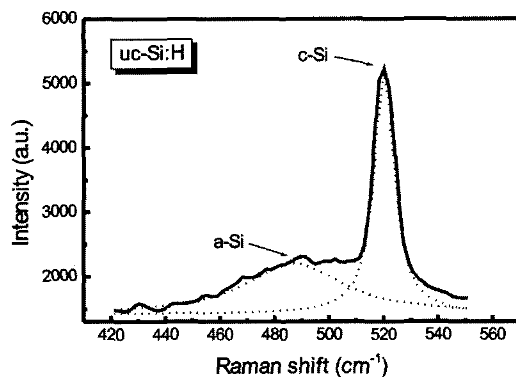

Fig. 3 Changes of the optical energy band gap of a-Si:H and μc-Si:H thin films with RF powers.

In our case, the reason of arising the peak at 480 cm^{-1} as a shoulder peak of the major Raman vibrational peak (520 cm^{-1}) is attributed to the contents of amorphous phases in the μc-Si:H thin film. This is well agreement with the XRD result that showed a broad diffraction peak with weak intensity. Conclusively the as-grown μc-Si:H thin film has a locally crystallized structure with a network of amorphous silicon. From our FT-IR measurements (not shown), we confirmed the detailed structure of the μc-Si:H thin film. For μc-Si:H thin film, a lot of SiH_2 bonding species were observed compared with a-Si:H. This can be explained that since the silicon atoms in the μc-Si:H thin film have a random network, that can makes many dangling bonds. Thus, many hydrogen atoms will be bonded with the silicon atoms in the dangling bonds, resulting in SiHx species formation.

In order to obtain the energy band gap, E_g of the μc-Si:H thin film, we carried out the transmittance measurements using UV-VIS spectrometer after the μc-Si : H thin films growth on glass substrates. The E_g of films was evaluated from the Tauc's plot. An alternative method, in which the bandgap energy is defined as the energy (E_{04}) at which the absorption coefficient equals 10^4 cm^{-1}, was also used. Figure 4 shows the variation of E_g as a function of RF power.

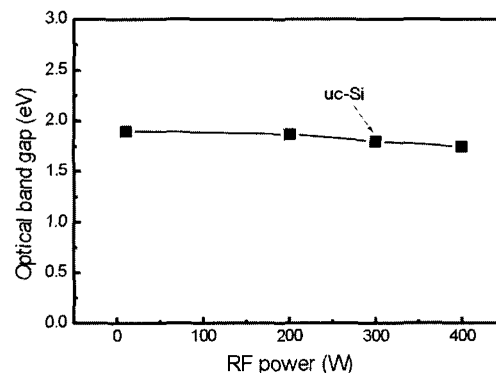

Fig. 4 Raman spectra of a μc-Si:H thin film.

The data suggested that the E_g is not changed effectively with RF power and the obtained E_g (1.80 eV) of the μc-Si:H thin film has almost the same value of a-Si:H thin film (i.e. 1.75 eV). This indicates that the crystallity of hydrogenated amorphous silicon thin film can mainly not affected to their optical properties, signifying that more systematic studies on the relationship between crystallity and optical energy band gap are still necessary.

3. 2 a-SiC:H thin films

Figure 5 shows the variation of E_g values obtained from a-SiC:H thin films that grew at 250 with different RF powers.

In Figure 5, for the same changes in the RF power, the E_g varied between 3.68 eV and 4.09 eV, while the E_{04} values which were evaluated by using the thickness of films measured from SE and a-step varied between 3.55 eV and 4.1 eV. This indicates that to enhance sp^3 bond the radicals are increased with the RF power and the band gaps. After annealing, we observed no change in the E_g and E_{04}. Because the quantity is little changed, it is sure that the thermal stability is superior than that of a-Si:H thin films.

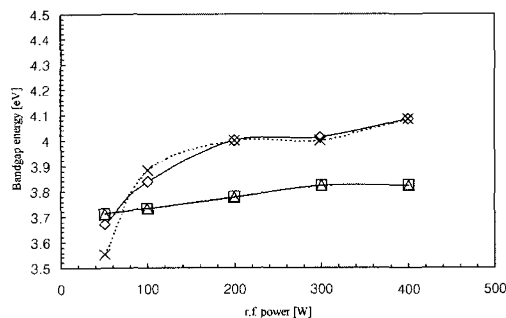

Fig. 5 Variation of optical energy band gap of a-SiC:H thin films with RF powers, compared E_{04} with E_g.

The annealing effect has been investigated using a Raman spectrophotometer. The Raman scattering results (Fig. 6) showed that the microcrystalline phase in the films was rapidly enhanced as the annealing temperature increased, indicating coexistence of crystalline Si and graphite in the films. In the low wavenumber region shown in figure 6, as annealing temperature is increased, one can observe that the band centered around 520 cm^{-1} resembles the Raman peak of c-Si and

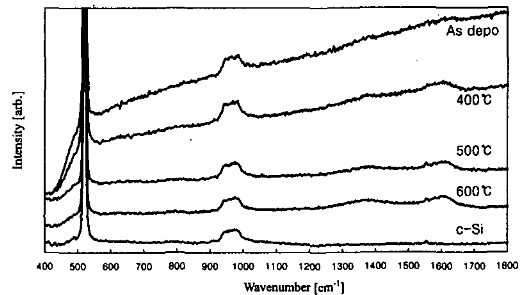

Fig. 6 Raman spectra of a-SiC:H thin films as a function of annealing temperature

becomes much narrower. This is the evidence of silicon crystallization after annealing at higher temperature, however X-ray diffraction measurements did not show any indication of silicon crystals in the films. In the case of a-SiC:H film which was annealed at higher temperature, two asymmetrical peaks in the high wavenumber are observed, which are centered at 1355 cm^{-1} (D band) and 1580 cm^{-1} (G band), respectively and it is generally known that D band peak indicates disordered microcrystalline graphite and G band peak indicates sp^2 graphite[16]. However, for the as-deposited a-SiC:H film before annealing, D band peak is rarely observed. Therefore, it means that a-SiC:H films before annealing is mostly consisted of sp^2 bond and sp^3 bond increase with increasing of annealing temperature. And this is consistent with the result of FTIR which shows that C-H bond and Si-H bond break and C-C bond is generated. And also it agrees with Dischler et al.[17] who showed that the graphitic component is increased when H is eliminated from the amorphous network. This occurs upon sample annealing. However, Si-C bond peak was not observed in this work and the absence of SiC crystalline clusters suggests that the silicon microcrystallines are likely to be embedded within the amorphous

matrix. Further evidence for this argument is the large value of the optical gap obtained from the annealing samples (~ 3.9 eV).

Conclusions

We have deposited hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous silicon carbide (a-SiC:H) thin films on Si(100) wafer and glass substrates by RF plasma-enhanced chemical vapor deposition (RF-PECVD). With X-ray diffraction, Raman spectroscopy, UV-VIS spectroscopy, spectroscopic ellipsometry, and a-step profiler, the effects of the RF power and annealing on the properties, such as optical energy band gap (E_g), transmittance, and crystallinity, were mainly studied in this work. XRD and Raman data show that the μc-Si:H thin film consists of the co-presence of an amorphous and crystalline phases with (111) orientation. The UV-VIS data suggested that the E_g is not changed effectively with RF power and the obtained E_g (1.80 eV) of the μc-Si:H thin film has almost the same value of a-Si:H thin film (i.e. 1.75 eV), indicating that the crystallity of hydrogenated amorphous silicon thin film can mainly not affected to their optical properties.

On the other hand, the optical energy band gap of a-SiC:H films was drastically changed with the RF power and the annealing temperature. Both the E_g and the E_{04} followed a specific trend of variation with an increase in the RF power. The E_g values increased from 3.68 eV to 4.09 eV, while the E_{04} values increased from 3.55 eV to 4.1 eV for the same increase in the RF power. After annealing, we observed no change in the E_g and E_{04}. The Raman scattering results showed that the microcrystalline phase in the films was rapidly enhanced as the annealing temperature increased.

In conclusion, we proved that the a-SiC:H thin films were more stable than a-Si:H thin films in optical characteristics, as well as being more thermally stable. Therefore, it is expected that the a-SiC:H thin film may be effectively used for the window layer in high efficiency solar cells.

References

1. P. G. LeComber, W. E. Spear, and A. Ghaith, Electron Lett. 15 (1979) 179.
2. T. Sameshima, S. Usui, and M. Sekiya, IEEE Electron Dev. Lett. EDL-7 (1986) 276.
3. K. Sera, F. Okumura, H. Uchida, S. Itoh, S. Kaneko, and K. Hotta, IEEE Trans. Electron Dev. 36 (1989) 2868.
4. Y. Tawada, H. Okamoto, and Y. Hamakawa, Appl. Phys. Lett. 39 (1981) 237.
5. D. A. Anderson and W. E. Spear, Philo. Mag. 35 (1977) 1.
6. Y. Catherine and G. Turban, Thin Solid Films 60 (1979) 193.
7. H. Munekata, S. Murasato, and H. Kukimoto, Appl. Phys. Lett. 37 (1980) 536.
8. Y. Katayama, K. Usami, and T. Shimada, Philo. Mag. B 43 (1981) 283.
9. R. S. Sussmann and R. Ogden, Philo. Mag. B 44 (1981) 137.
10. H. Weider, M. Cardona, and C. R. Guarnieri, Phys. Status Solid b 92 (1979) 99.
11. T. Takubo, M. Takeda, T. Tamura, H. Iwai, K. Ukita, Y. Bessho, and I. Yamashita, Proc. of Japan Display 89 (1989) 584.
12. M. Schadt and W. Helfrich, Appl. Phys. Lett. 184 (1971) 127.

13. A. Chiang, I. W. Wu, M. Hack, A. G. Lewis, T. Y. Huang, and C. C. Tsai, Extended Abstract of SSDM 91 (1991) 586.
14. M. Yuki, K. Masmo, and M. Kunigita, Tech. Digest of SID 89 (1989) 143.
15. S. Takenaka, M. Kinil, H. Oka, and H. Kurihara, Jpn. J. Appl. Phys. 29 (1990) L2380.
16. Y. Inoue, S. Nakashima, A. Mitsuishi, S. Tabata, and S. Tsuboi, Solid State Commun. 48 (1983) 1071.
17. S. F. Yoon, Int. J. Electronics, 85 (1998) 723.