Annealing Effect on the Optical Properties of a-SiC:H Films Deposited by PECVD *¹

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Effects of annealing temperature (T_a) on the structure of hydrogenated amorphous silicon carbide (a-SiC:H) films prepared by RF plasma chemical vapor deposition (CVD) method are investigated by using Fourier Transform-Infrared Spectrometry (FT-IR), X-ray Photoelectron Spectroscopy (XPS) and UV-VIS spectrophotometer techniques. It is found that an annealing process results in structural rearrangement and evacuation of hydrogen atoms from CH_n and SiH_n bonds. The emission of hydrogen bonded to silicon and carbon responsible for the decrease of optical band gap (E_{opt}) by 0.70 eV in the range of T_a from 573 to 873 K. This hydrogen loss is interpreted in terms of hydrogen molecule formation and outerdiffusion. In addition, the surface morphology of films was investigated by atomic force microscopy (AFM).

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1. Introduction

Hydrogenated amorphous silicon carbide (a-SiC:H) films are of great interest owing to their structural electronic, optical and mechanical properties. Indeed, a-SiC:H films are extensively studied both as typical materials of an amorphous system with variable disorder and microstructures,¹⁻³ and for potential applications such as optoelectronic devices,⁴ solar cells,⁵ high temperature coatings⁶ and X-ray masks.⁷ The main reason for its success in device applications is that by incorporating hydrogen during plasma deposition, the paramagnetic dangling bonds are saturated,⁸ which reduces the gap state density significantly and makes the n- and p-type doping possible.⁹ Since the deposition of a-SiC:H does not require high temperature it is essential to examine the thermal stability of the material, which is essentially determined by the bonding states of hydrogen.¹⁰ Many phenomena can occur during thermal annealing of a-SiC:H, such as hydrogen emission and structure rearrangement that affect the properties of the amorphous material and its applications, the study of thermal treatment of a-SiC:H is of great importance.

In this paper, a-SiC:H films are prepared by an RF plasma CVD technique. X-ray photoelectron spectroscopy (XPS) and fourier transform-infrared spectroscopy (FT-IR) technique were used in order to characterize the annealed films qualitatively and quantitatively. The influence of T_a on the optical gap, the bonding state and the amorphous network is investigated by absorption measurements in the ultraviolet to visible (UV-VIS) range, fourier transform-infrared spectroscopy (FT-IR) and atomic force microscopy (AFM), respectively. The T_a range (573–873 K) has been chosen to scan the hydrogen effusion.

2. Experiment

The a-SiC:H films were deposited onto crystalline silicon and glass substrates using a capacitively coupled RF plasma CVD reactor. The reaction system is of the parallel planar discharge type using a rectangular RF electrode (lower) and substrate electrode (upper). The substrate is set on the tray with the surface to be coated facing downward, so that deposition of dust particles and flakes can be minimized. Hydrogen plasma cleaning at 200 W for 10 min was followed directly by the deposition process. The flow rate of hydrogen was 90 sccm. All deposition times presented here were 30 min. The full range of process parameters for the system is shown in Table 1.

Annealing of a-SiC:H films is performed in a furnace of Ar atmosphere for 3 h at temperatures ranging from 573 to 873 K. After each annealing step, the XPS measurement was run on a Perkin-Elmer PHI 5700 surface analysis instrument using Mg K α X-rays (1253.6 eV) as the photoexcitation source with an electron take-off angle of 45° from the surface. UV-VIS and FT-IR absorption measurements were conducted. Then the Si–C, Si–H and C–H absorption bands were analyzed by plotting the absorption coefficient as a function of radiation frequency using the Lambert-Beer law without any corrections for multiple reflections. The E_{opt} of the a-SiC:H films was de-

Table 1 Range of deposition parameter for investigation of process parameter effects.

Parameters	Range
Base pressure	$<4 \times 10^{-3}$ Pa
RF power (13.56 MHz)	100 W
Substrate temperature	523 K
Working pressure	360 Pa
Excitation gas	H ₂ (50–100 sccm)
Reaction gas	SiH ₄ : CH ₄ = 1 : 1

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posited on a glass substrate using a UV-VIS (Perkin-Elmer) spectrometer in the range of 300–1200 nm. IR vibrational spectra were taken employing fourier transform infrared, (FT-IR, Perkin-Elmer 1700) spectrometer. The morphology of film surface was examined by using the contact mode AFM (Multimode SPM Nanoscope III A).

3. Results and Discussion

The optical band gap (E_{opt}) is estimated from a plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$, where α is the optical absorption coefficient, h is Planck's constant and ν is the radiation frequency. The optical absorption coefficient, α , was calculated from transmittance using the Lambert-Beer law

$$I = I_0 e^{-\alpha d}, \quad (1)$$

Where d is the film thickness and I , I_0 the film, and the substrate transmittance, respectively.

Figure 1 shows the relationship between E_{opt} and T_a . E_{opt} decreases slightly for low temperature (<673 K) annealing as the structure of an amorphous network undergoes relaxation and reordering without any change in the composition or bonding of the atoms. At annealing temperature above 673 K, E_{opt} decreases significantly indicating the creation of new defect gap states most likely due to the effusion of hydrogen or other species. At temperature above 773 K, E_{opt} reaches a saturation value of about 2.1 eV. The dependence of E_{opt} on T_a taking into account that a-SiC:H films do not crystallize in this range of T_a .

Figure 2 shows the transmittance as a function of wavelength for as-deposited and 873 K annealed films, respectively. The annealed film becomes more transparent than as-deposited film. It has been shown that the absorption is due to transitions from the top of the valence band to the bottom of the conduction band. Increase in density of state in the valence band with increasing in annealing temperatures shifts the absorption edge to lower energies.

Figures 3 and 4 show the FT-IR spectra of a-SiC:H films for investigating the bonding configuration, in the range 400–4000 cm^{-1} for various annealed and as-deposited films. It is reported that upon annealing, hydrogen evolves in a two-step process. Which is firstly the breaking of Si–H bonds, and then C–H bonds, which is justified by the higher C–H single bond energy (98.8 kcal/mol) compared to that of Si–H (70.4 kcal/mol).¹¹⁾ It can be clearly seen that the results shown in Fig. 3 are in good agreement. Intensity of the peaks from 2100 to 2150 cm^{-1} decrease with increasing annealing temperature, which is due to the break of Si–H bonds.

In the Fig. 4, the peaks of about 2900 cm^{-1} weaken slightly when the temperature is higher than 773 K, which indicates the break of C–H bonds in CH_n . As discussed before, the emission of hydrogen bonded to silicon and carbon responsible for the decrease of E_{opt} by 0.70 eV in the range of T_a from 573 to 873 K. The emission of hydrogen bonded to silicon and carbon causes void formation in the a-SiC:H films.

Figure 5 presents the results for the bonding densities of the hydrogen-related modes for different T_a . The Si–H and C–H bonding densities could be estimated from the SiH_n and CH_n stretching mode bonds using the formula

Fig. 1 Relationship between the optical band gap and annealing temperature.

Fig. 2 Optical transmittance of as-deposited and 873 K annealed film.

Fig. 3 FT-IR Si–H spectra of the as-deposited and annealed films at various temperature ranging from 573 to 873 K.

Fig. 4 FT-IR C-H spectra of the as-deposited and annealed films at various temperature ranging from 573 to 873 K.

Fig. 6 Wide scan XPS spectra of as-deposited and 873 K annealed film.

Fig. 5 Bonding density and peak height of Si-H and C-H vs. T_a for an a-SiC:H films.

$$N(\text{bonding density}) = A_s \int \frac{\alpha(\nu)}{\nu} d\nu \cong \frac{A_s}{\nu_0} \int \alpha(\nu) d\nu, \quad (2)$$

where A_s is the reciprocal cross section of a given vibration mode, ν_0 is the center band wave number, α is the absorption coefficient and ν is the radiation frequency. The A_s values have been taken from the literature:

$$A_s(\text{Si-H}) = 1.4 \times 10^{20} \text{ cm}^{-2}, \quad (11)$$

$$A_s(\text{C-H}) = 1.35 \times 10^{21} \text{ cm}^{-2}, \quad (11,12)$$

The density of Si-H bonds decreases from $2.67 \times 10^{21} \text{ cm}^{-3}$ for the as-deposited film to $0.303 \times 10^{21} \text{ cm}^{-3}$ for 873 K annealed film. The density of C-H bonds similarly decreases from $3.608 \times 10^{21} \text{ cm}^{-3}$ for the as-deposited film to $0.537 \times 10^{21} \text{ cm}^{-3}$ for 873 K annealed film. The bonding density for CH_n is an order of magnitude higher than for SiH_n indicating that a high concentration of hydrocarbons are incorporated into the film. This seems to suggest that hydrogen may have an affinity for carbon over silicon, as suggested by Gat *et al.*⁽³⁾ When the T_a is increases, the hydrogen atoms resulting from

this breaking of hydrogenated bonds can either combine to form hydrogen molecules which are expected to diffuse towards the interfaces during the annealing, or be trapped in the Si or C dangling bonds to form new hydrogenated bonds. These observations clearly point out that when the temperature is increased from 573–873 K, both a breaking of hydrogenated bonds resulting in a decrease of hydrogenated bond areas and peak height.

Figure 6 shows the XPS wide scans of the as-deposited and the 873 K annealed film. Both scans show the silicon (Si_{2p}), carbon (C_{1s}), nitrogen (N_{1s}) and oxygen (O_{1s}) peaks. After the Ar sputter cleaning treatment, oxygen was found to be still present in films. The oxygen peak was due to absorbed oxygen and surface oxidation of the films. The Si_{2p} component, with binding energy of $(101.8 \pm 0.2) \text{ eV}$, was attributed to Si atoms bonded to oxygen in agreement with Si oxide contamination in a-SiC:H films.⁽¹³⁾ The C_{1s} line peak at $(284.6 \pm 0.2) \text{ eV}$ binding energy was attributed to adventitious carbon originating from the residual gas contamination. The carbon contamination peak shifted to about 285 eV for 873 K annealed film. This is due to additional oxygen contamination.⁽¹⁴⁾

The AFM images were acquired by using the contact mode AFM system at room temperature. Figure 7 shows AFM images ($4 \mu\text{m} \times 4 \mu\text{m}$) of the surface morphology of the as-deposited and annealed films at various temperatures, ranging from 573 to 873 K. It is found that the surface morphology of the films is strongly affected by the annealing temperature. The as-deposited film surface was comparatively smooth and the roughness over an area of $4 \mu\text{m} \times 4 \mu\text{m}$ was less than 0.5 nm. After annealing at 873 K for 3 h, typical protrusions were seen. Root-mean-square (rms) roughness is usually used to evaluate surface morphology because it is the least affected by tip induced distortion of all the roughness parameters. Figure 8 shows the rms-roughness values obtained from AFM images ($4 \mu\text{m} \times 4 \mu\text{m}$). For temperature lower than 573 K, surface roughness is approximately the same as that of the as-deposited film surface. At higher annealing temperature, an increase in roughness (both in the vertical and lateral direction) took place. Above 873 K, this tendency is found to be more obvious. In comparison with the as-deposited film,

Fig. 7 AFM images of the as-deposited and annealed films at various temperature. (a) as-deposited, (b) 573 K, (c) 773 K, (d) 873 K.

Fig. 8 Rms roughness of the a-SiC:H films as a function of T_a .

the rms value increases six times from 0.38 to 2.37 nm. This increase of rms-roughness value is interpreted in terms of hydrogen molecule formation and outdiffusion. The increasing phenomenon of the rms-roughness value is called “kinetic roughening”,¹⁵⁾ and is an important parameter for structural and optoelectronic properties.

4. Conclusion

The a-SiC:H films deposited by PECVD technique are studied as a function of the T_a in the range from 573 to 873 K.

Using the FT-IR technique, we find a strong correlation between the bonding state of the a-SiC:H film formed and annealing conditions. The annealing indicates the breaking of Si–H bonds at first, and then C–H bonds at higher temperature. This hydrogen loss is interpreted in terms of hydrogen molecule formation and outdiffusion. But, hydrogen molecules were not completely outdiffused and a part of free hydrogen remains trapped in the film. At T_a above 673 K, E_{opt} decreases significantly indicating the creation of new defect gap states most likely due to the effusion of hydrogen or other species. At T_a above 773 K, E_{opt} reaches a saturation value of about 2.1 eV. We note a decrease in the E_{opt} at temperature above 773 K which indicates an irreversible process and may be mainly attributed to the loss of hydrogen. At higher T_a , an increase in roughness took place. Above 873 K, this tendency is found to be more obvious. In comparison with the as-deposited film, the rms value increases six times from 0.38 to 2.37 nm.

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