

Optical properties of amorphous $\text{Si}_x\text{C}_y\text{N}_z$ ternary thin films prepared by plasma enhanced chemical vapor deposition

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Amorphous ternary $\text{Si}_x\text{C}_y\text{N}_z$ thin films were obtained by plasma enhanced chemical vapor deposition (PECVD) using N_2 , SiH_4 and C_2H_4 as the reaction sources. The chemical state were characterized by x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). The optical properties of the thin films were investigated by UV-visible spectrophotometer and ellipsometer, and the optical band gaps of thin films were determined from corresponding transmittance spectra following Tauc equation.

1. Introduction

In recent years a great deal of attention has been devoted to growth of amorphous silicon based alloys because of their potential applications in electronic devices. Thin films, with band gaps variable over a wide range of energy, are of particular interest in amorphous semiconductor technology. Both $\text{a-Si}_x\text{C}_y$ and $\text{a-Si}_x\text{N}_y$ are attractive materials with many attractive properties, such as high hardness, chemical stability and large band gap, and consequently have been expected to offer great potential for mechanical, optical, electronics and other application. There are a large amount works dedicated to $\text{a-Si}_x\text{C}_y$ and $\text{a-Si}_x\text{N}_y$ on studying their optical, electrical, optoelectronic and chemical state properties [1-9], but there are few work on the Si-C-N ternary system. The Si-C-N ternary system may be very interesting because it maybe includes SiC , Si_3N_4 and C_3N_4 three phases, and in this system we may find the new phase, ultrahard carbon nitride predicted by M. L. Cohen et al [10], so the phases of the ternary system are worthy to study. Also the properties of Si-C-N ternary system may be preferred and could exhibit all the useful characteristics of SiC , Si_3N_4 and C_3N_4 compounds. And there are few literatures on the optical property of the Si-C-N ternary system. In this paper, we present the optical characteristics of PECVD Si-C-N thin films, and the chemical states of the films are also investigated.

2. Experiments

The $\text{Si}_x\text{C}_y\text{N}_z$ thin films were fabricated by PECVD using C_2H_4 (>99.9%) + SiH_4 (5% diluted by hydrogen) + N_2 (99.999%) mixture with different $\text{C}_2\text{H}_4/\text{SiH}_4$ flow ratios on SiO_2 , KBr and NaCl. The RF power is about 760 W, and the substrates temperatures are controlled at 420°C.

The composition and binding energies spectra of the films are obtained on KARATO XSAM-800 x-ray photoelectron spectrometer (XPS). The chemical bonding states are characterized by Fourier transform infrared spectrometer (Nicolet 170x model).

Optical transmission spectra of $\text{Si}_x\text{C}_y\text{N}_z$ thin films are measured on a double beam spectrophotometer (Shimadzu, UV-240 model) in wavelength from 190nm to 900nm. The measurement of static refractive index and extinction coefficient at the wavelength of 6328Å and thickness were carried out by ellipsometer. Values of absorption coefficient, α were calculated from transmission spectra in 190nm-900nm wavelength range. Fitting of absorption spectra $\alpha h\nu$ to Tauc plots

$$(\alpha h\nu)^{1/2} = B(h\nu - E_{\text{opt}})$$

yielded values of the optical gap E_{opt} .

3. Results and Discussions

3.1 X-ray photoelectron spectroscopy (XPS)

Basic deposition parameters, binding energies of Si 2p, C 1s and N 1s lines and atomic concentrations of nitrogen, silicon and carbon are shown in Table I, and the typical Si 2p, C 1s and N 1s binding energies spectra are shown in Fig. 1. The N1s binding energies of all samples are centered at about 397.9eV, the corresponding Si 2p binding energies are centered at about 102.0eV. And A. Fejfar et al[4] have studied laser-ablation silicon nitride thin films and found that when N/Si atom ratio approximated the stoichiometry of Si_3N_4 , the Si 2p and N 1s binding energies were observed at 102.0eV, 397.9eV respectively. The data are similar to our results. In the Si-C-N ternary system, the C 1s and Si 2p binding energies all upshifted those in silicon carbide whose Si 2p and C 1s peaks were observed at binding energies of 100.8eV and 283.3eV respectively[10]. So we can conclude that there are no Si-C bond in our Si-C-N ternary system, and Si and N bonded in Si_3N_4 phase. Deducting the N concentrations in Si_3N_4 , the surplus nitrogen can bond with carbon and form carbon nitride. So we think that the as-deposited Si-C-N system includes silicon nitride, carbon nitride and carbon three

phases.

Table I Preparation conditions of samples and XPS results

sample	flow rate(L/min)			N 1s	Si 2p	C 1s	Si _x C _y N _z		
	C ₂ H ₄	SiH ₄	N ₂	(eV)	(eV)	(eV)	x	y	z
1	0.1	1.0	3.0	397.97	102.14	285.31	0.14	0.44	0.42
2	0.3	1.0	3.0	398.07	102.03	285.20	0.15	0.42	0.43
3	0.5	1.0	3.0	397.87	101.85	285.07	0.12	0.57	0.31
4	0.5	0.5	3.0	397.99	101.94	285.20	0.19	0.41	0.40

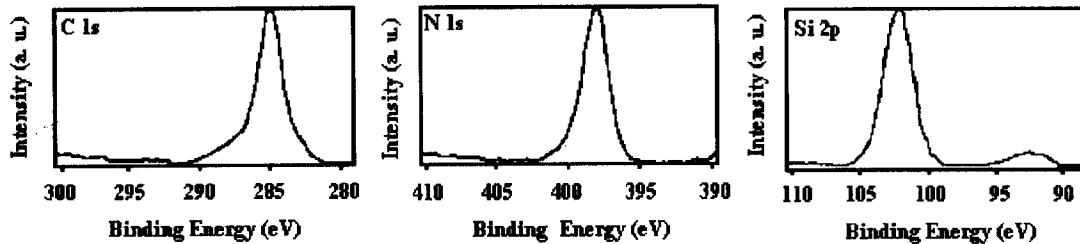


Fig. 1 The typical C 1s , N 1s, Si 2p binding energy spectra of Si-C-N ternary system films

3.2 FTIR spectra

The typical FTIR spectra of the Si-C-N samples are shown in Fig 2 and Fig 3. Because NaCl substrate has strong absorption below the wavenumbers of 600cm^{-1} , so we can not observe the features of the films below 600cm^{-1} . The Si-N stretching mode will appear at wavenumbers between 820 and 870cm^{-1} [6]. So the peaks at 865cm^{-1} in Fig. 2 and 836cm^{-1} in Fig. 3 can be assigned to Si-N stretching vibration. The peak at 477cm^{-1} is caused by Si-N "breathing" mode, and the very weak peak at 3344cm^{-1} and 1590cm^{-1} can be assigned to N-H stretching and N-H₂ scissors vibration respectively[6]. The absorption peak centered at $\sim 2168\text{cm}^{-1}$ is due to the stretching mode of C \equiv N bands[11](carbon in sp state). When the symmetry of sp² carbon rings has been broken by the incorporation of nitrogen atoms in the films, the broad absorption peak from 1200 to 1700cm^{-1} will be active in FTIR spectra[11]. In the above discussion, we note that nitrogen has incorporated with carbon, but in all FTIR spectra, we can not observe the broad absorption peak from 1200 to 1700cm^{-1} , so there are no graphite phase (carbon in sp² state) formed in the ternary films. And diamond is inactive in FTIR spectra, so carbon exists in sp and sp³ states in these films

The frequency value of Si-N stretching mode is sensitive to the hydrogen content, and the less hydrogen content can lead the Si-N stretching peak shifted to lower wavenumbers[12]. In Fig. 2 there appear

N-H stretching and N-H₂ scissors modes, the corresponding Si-N stretching vibration peak is at 865 cm⁻¹, but in Fig. 3 the N-H stretching and N-H₂ stretching modes disappear, the corresponding Si-N stretching vibration is downshifted to 836 cm⁻¹. This result is in agreement with the data of the reference [6]. The C-N stretching vibration, which can appear from 1200 to 900 cm⁻¹ wavenumbers[13], is difficult to be observed due to the existing of the strong broad Si-N stretching mode between 1200 and 600 cm⁻¹. From FTIR discussion, we can know that the ternary films include silicon nitride, carbon nitride and diamond three phases, which agrees the results of XPS data.

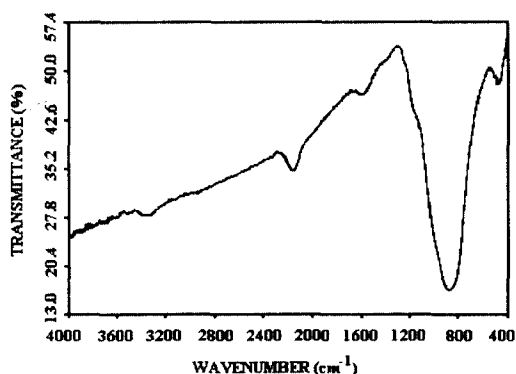


Fig. 2 The FTIR spectrum of sample 3 deposited on KBr

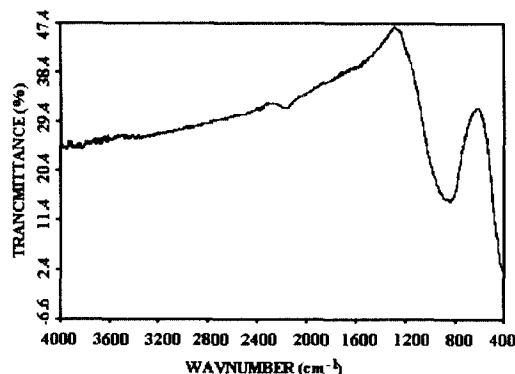


Fig. 3 The FTIR spectrum of sample 2 deposited on NaCl

3.3 Optical properties

Fig. 4 shows the dependence of absorption coefficient α on incident the photon wavelength λ plots of the four samples. All four samples have strong absorption in ultraviolet and violet regions. The maximum absorption peaks are different. Sample 1 has maximum absorption at 206nm(6.06eV photon energy). The maximum absorption peaks for the sample 2, 3, 4 are at 210nm(5.91eV photon energy), 230nm(5.40eV photon energy), 195nm(6.37eV photon energy), respectively. The band gap of diamond is 5.5eV, and a-Si₃N₄ can reach energy gaps up to 5.2eV[5], and β -C₃N₄ also has 6.40eV band gap predicted by J. L. Corkill and M. L. Cohen[14]. So the absorption peaks of the four samples may be caused by common effects of the three phases in the Si-C-N ternary system.

The optical gap is a very useful parameter for characterization of amorphous semiconducting films. Fig. 5 shows a Tauc plot ($(\alpha hv)^{1/2}$ vs. hv) for all samples. The optical band gap is defined as the energy at which the straight line extrapolated from the straight part of the plot intersects the horizontal(energy) axis. The obtained optical band gaps of

the sample 1, 2, 3, 4 are about 3.55eV, 2.80eV, 2.58eV, 3.96eV, respectively, which are lower than the corresponding maximum absorption photon energy. The values are higher than those of a-CN_x[15,16], which almost have zero gap and show that there are large sp² carbon in the a-CN_x films. And these wide optical band gaps can be comparable to those of a-SiN_x and a-SiC_x[6]. The values of the optical band gaps of the Si-C-N ternary systems suggest that there are few sp² carbon in the films, and carbon is in sp³ state in the films.

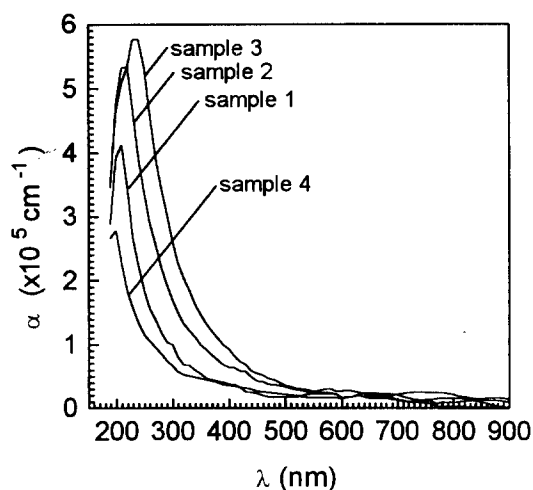


Fig. 4 Dependence of absorption coefficient α on the incident wavelength λ

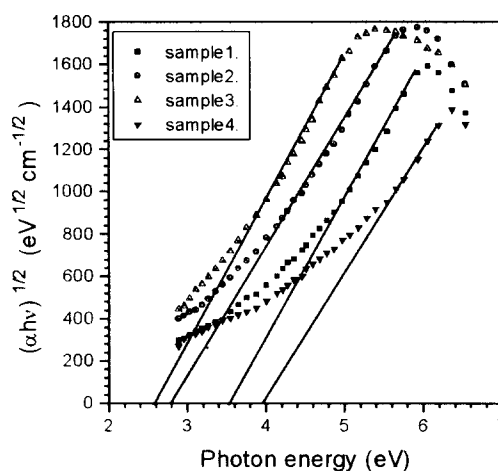


Fig. 5 Results from Fig. 4 replotted to determine optical band gap

The N₂ flow rate is the same in depositing the four samples, so we listed the refractive index n and extinction coefficient k at the wavelength of 6328Å, optical band gaps and the SiH₄/C₂H₄ flow ratios of the four samples in table II. It is seen that n decreases with increasing SiH₄/C₂H₄ flow ratio, whereas k increases with increasing SiH₄/C₂H₄ flow ratio, when the values of SiH₄/C₂H₄ flow ratio are below 3.3. The values of n of the four samples are between 1.90 and 2.45, and those of k are between 0.12 and 0.35.

Table II The refractive index n , extinction coefficient k , the corresponding SiH₄/C₂H₄ flow ratio, and the optical band gaps of the four samples.

sample	SiH ₄ /C ₂ H ₄ flow ratio	n	k	E _{opt} (eV)
1	10	2.36	0.12	3.55
2	3.3	1.90	0.35	2.80
3	2	2.21	0.25	2.58
4	1	2.45	0.20	3.96

4. Conclusions

In summary, we have obtained Si-C-N ternary thin films by PECVD. The chemical state of the films were investigated by XPS and FTIR, and carbon (in sp^3 state), silicon nitride and carbon nitride three phases have formed in the films. The all obtained films have strong absorption in the ultraviolet and violet regions, and also have wide optical band gaps between 2.58eV and 3.96eV, which suggests that few sp^2 carbons are in the films. The optical constants depended on SiH_4/C_2H_4 flow ratio were also discussed. It is found that n decreases as SiH_4/C_2H_4 flow ratio increases to 3.3, whereas k exhibits an opposite trend.

Acknowledgement

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