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Optical and electrical properties of carbon nitride films deposited by cathode electrodeposition

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Carbon nitride (CN_x) films were prepared on silicon (100) wafers and ITO conductive glasses by cathode electrodeposition, using dicyandiamide ($C_2H_4N_4$) in acetone as precursors. The composition ratios (N/C) were approximated to or larger than 1 from XPS. The optical properties and electrical resistivities of the films were investigated. Intense PL with two bands in the range 2.5–3.5 eV was observed on the CN_x films. The band gaps (E_{opt}) deduced from measurements of the optical absorption coefficients in the UV-VIS spectra were found to be in the range of 1.1–1.6 eV. From the PL and UV-VIS spectra, the nitrogen content has a large effect on the PL band gap and E_{opt}. The electrical resistivities of the films on Si wafers are in the 10^9–10^{10} $\Omega \cdot$cm range.

1. Introduction

The current interest for the preparation of carbon nitride materials comes from the theoretical work of Liu and Cohen [1]. Up to now, the experimental work on this new material has not shown clearly its existence. Most of the deposited films are amorphous with the atomic ratio of $N/C < 1$ [2]. But many researches of recent years have got interesting properties such as high thermal stability, high electrical resistivity, and good optical characterization comparable to those of amorphous carbon films. All these properties make amorphous CN_x films attractive for applications in optics, electronics etc. [3, 4]. In this paper, we report on the electrical resistivity, optical properties of carbon nitride films deposited by electrodeposition using Si (100) wafers and ITO conductive glasses as substrates. This preparation method only needs simple apparatus and conditions are easy to control. This can provide good foundation for carbon nitride film applications.

2. Experimental

The apparatus used in our experiment is the same as described in [5]. The silicon wafers and ITO conductive glasses with the size of $10 \times 20 \times 0.3$ mm^3 are used as cathode. The anode was a graphite plate with the same size as the cathode. Before deposition, the substrates were cleaned by ultrasonic treatment in methanol and acetone. The distance between the two electrodes was set to 7 mm. We used modulation power source (voltage range: 1000–2000 V, frequency: 7 kHz, duty cycle: 0.8) and direct current power source with the voltage range of 1000–2000 V as energy source. The composition and structure of the films were characterized using XSAM800 X-ray photoelectron spectroscopy (XPS) using an Al K_α 1486.6 eV X-ray source and system 2000 Fourier-transform infrared (FT-IR) spectroscopy. Optical characteristics of the films were investigated by the UV3101 UV-VIS spectrum and photoluminescence (PL) system. The PL system was excited with radiation from a He-Cd laser operating at 325 nm (3.8 eV), and the measurements were carried out at room temperature. The resistivities of CN_x films were determined by ZC43 super high resistance testing apparatus (Shanghai, China).

3. Results and discussion

The N/C ratio of the carbon nitride films was determined based on the area ratio of the N1s (A_N) to Cls peaks (A_C) in XPS spectra of the samples using $N/C = A_N/0.41 : A_C/0.24$ (1), where the constants of 0.41 and 0.24 are the atomic sensitivity factors of nitrogen and carbon respectively. XPS analysis showed that the CN_x film contain N, C, and O. The typical N/C ratio of the films deposited on Si (100) wafer can get to 0.95, while for the sample deposited on glasses the N/C ratio reaches the maximum of 1.08. And most of the N/C ratios of films on ITO glasses are higher than those of films on Si substrates. The O contents of both are about 6–7% owing to the surface absorption. Fig. 1a shows the Cls deconvoluted XPS spectra to the sample deposited on silicon substrate with the N/C ratio of 0.95. By using a mixture of Gaussian and Lorentzian profiles, it can be fitted well with four components at approximately 284.6, 286.5, 287.7, and 288.5 eV. The Cls spectra of film on ITO glass shown in Fig. 1b can be decomposed with three components at approximately 284.6,

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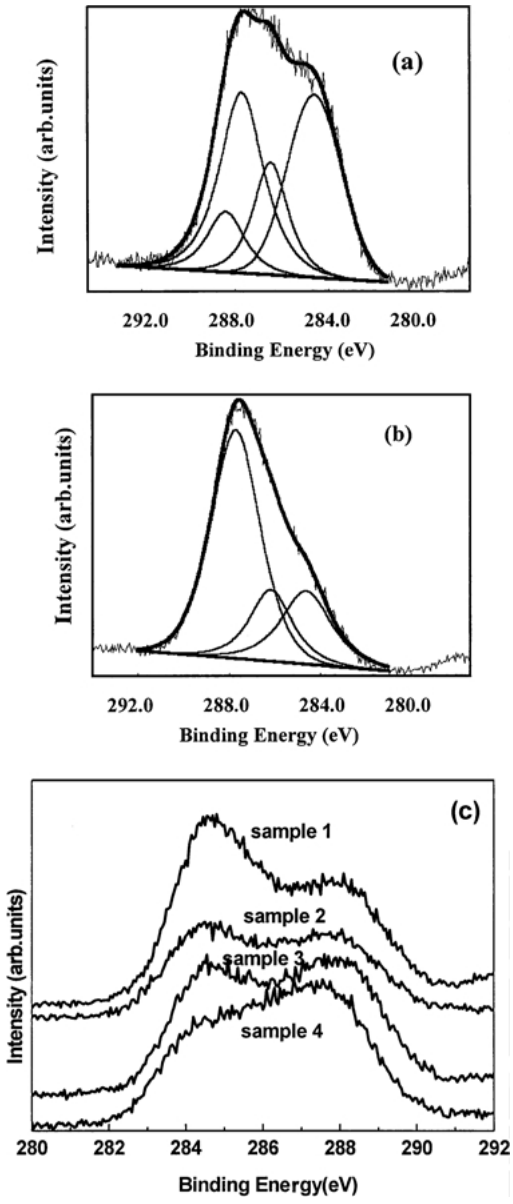

Figure 1 The typical decomposed Cls XPS spectra of CN_x films on silicon wafer (a) and ITO glass (b) substrates; the comparison of Cls spectra of four samples with different nitrogen contents on silicon substrates (c).

286.5, and 287.7 eV. The peak at the binding energy of 284.6 eV represents an amorphous carbon structure including the C═C bonds. The peaks at 286.5, 287.7 eV are attributed to sp^2 C, sp^3 C atoms bonded to nitrogen atoms, respectively [6–8]. The peak at 288.5 eV in Fig. 1a should be attributed to C≡N bond. There is no component to C≡N signal in the XPS spectra of film on glass, which agrees with the IR analysis in Fig. 2b. The Cls XPS spectra of samples 1–4 are shown in Fig. 1c. Using calculation method of formula (1), The N/C atomic ratios of samples 1–4 are 0.62, 0.72, 0.76, and 0.95 respectively, which were deposited under 1400 V, 1600 V, 1800 V, and 2000 V respectively for 2 h. From Fig. 1c, we can see that with the increment of nitrogen content the peaks at 284.6 eV become smaller which means the sp^2 hybridized graphite decreases while the proportion of sp^3 C─N bond (287.7 eV) become relatively larger. The states of carbon and nitrogen also can be characterized by the FT-IR spectra (Fig. 2). They

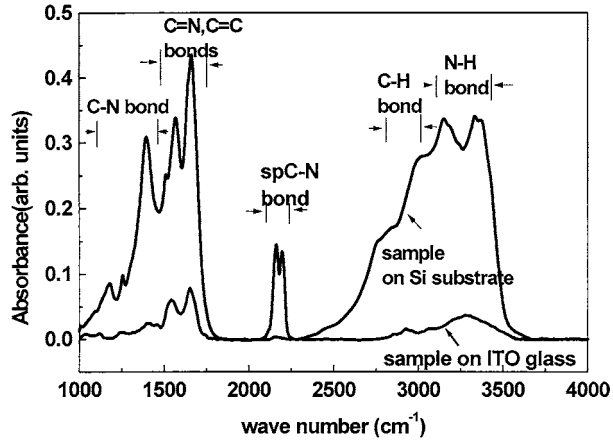

Figure 2 The comparison about FT-IR spectra of CN_x films on silicon (100) and ITO conductive glass substrates.

show the comparison of film on Si and glass substrates. The absorption bands at about 3300 cm^{-1}, 2920 cm^{-1}, 2200 cm^{-1}, 1650 cm^{-1}, 1550 cm^{-1}, and 1350 cm^{-1} are associated with the existence of N─H, C─H, C≡N, C═C, C═N, and C─N bonds respectively [9]. But the evident difference of them is there is no C≡N bond in the film on ITO glass.

Fig. 3 shows the photoluminescence (PL) spectra of the films deposited on both Si (100) and ITO glass. As shown in Fig. 3a, both spectra on the above substrates consist of the same broad bands with their maximum

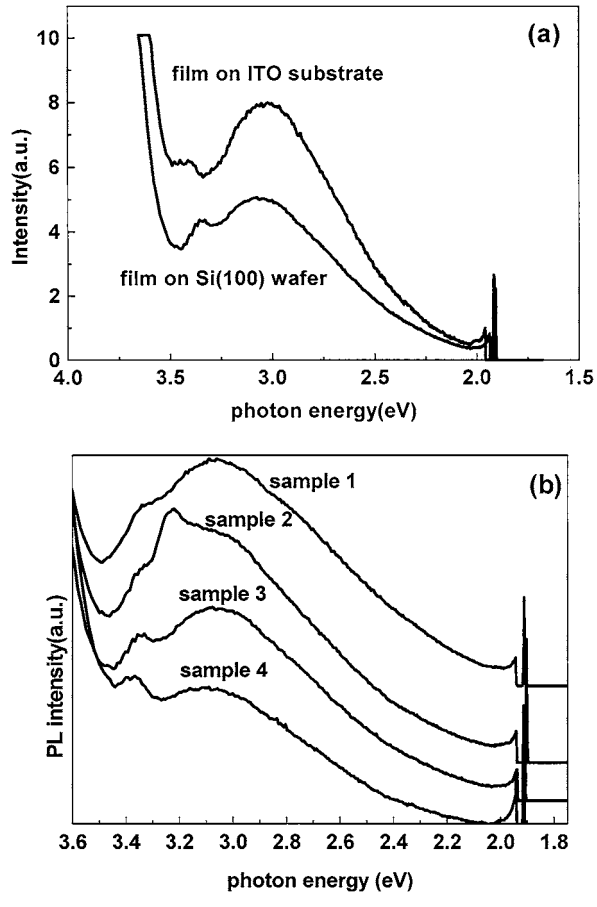

Figure 3 The Photoluminescence (PL) spectra of the deposited CN_x films: (a) the comparison of PL spectra of films on different substrates and (b) The comparison of PL spectra deposited on silicon wafers with different N contents.

around 3.058 eV and 3.35 eV, and which belong to the blue-violet light band. Fig. 3b presents the different PL spectra of sample 1–4 deposited on Si wafers with different N contents. We can see that the band at around 3.35 eV becomes more and more clearer and sharper with the increment of N content, while the intensity of the band at about 3.05 eV becomes weaker and weaker. It has been reported that the PL of the a-C: H arises from the recombination of optically excited carriers in π and π^* states of sp^2-bonded clusters [10]. PL of CN_x films can be explained by this theory. Both sp^2 C─N and sp^3 C─N bonds exist in our deposited films and sp^2 sites are segregated into clusters embedded in the sp^3 bonded sites. PL arises by the geminate radioactive recombination of the electron hole pairs within the sp^2-bonded clusters [11, 12]. So the two bands at about 3.05 and 3.45 eV observed are thought to be due to a distribution of luminescence centers with different energy gaps, and the relative contents of different luminescence centers are different with the increase of nitrogen content.

The optical absorbance of the CN_x films deposited on Si (100) substrates with different nitrogen contents was measured with an UV-VIS spectrometer, as shown in Fig. 4a. From these measurements the absorption coefficients were calculated and the optical band gap (E_{opt}) of CN_x films was obtained through the "Tauc plot" [13], written as $(\alpha E)^{1/2} = B(E - E_{opt})$, where α is the absorption coefficient in cm^{-1}. The corresponding $(\alpha h\nu)^{1/2}$ vs $h\nu$ curves are shown in Fig. 4b. The band gaps of these samples are about 1.1, 1.5, and 1.6 eV but the corresponding N/C atomic ratios decrease. This result agrees with many reports [14, 15]. From the PL and absorbance spectra we can see that the optical gap of the film is smaller than the emission energy of PL. Perhaps because the optical gap represents an average result of the distribution of cluster sizes and shapes, and luminescence centers which can be identified as the undistorted sp^2 clusters having energy gaps lower than the excitation energy [16].

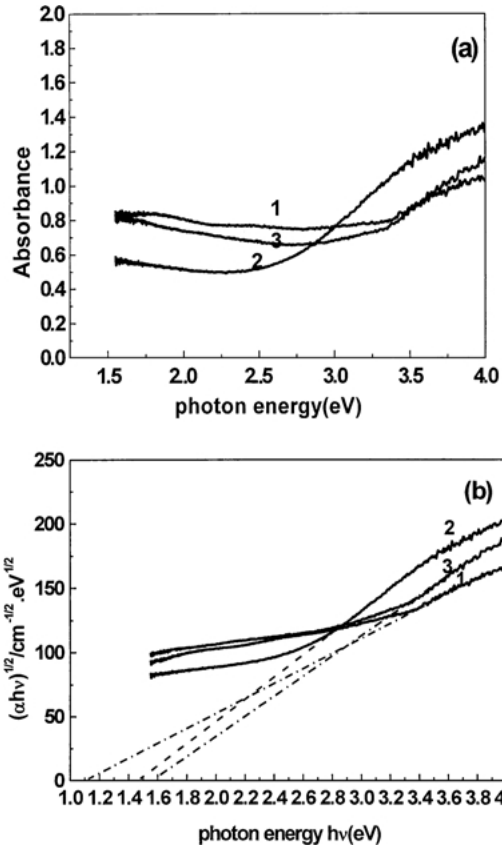

Figure 4 Absorption spectra (a) and $(\alpha h\nu)^{1/2} \sim h\nu$ curves (b) of CN_x films deposited on Si (100) wafers with different nitrogen contents.

We have determined the electrical resistivities of CN_x films by super high electrical resistance apparatus. The result shows that the films have high resistance. The value of the films on Si (100) wafers is about 10^9–10^{11} $\Omega \cdot cm$, and those on ITO conductive glasses are 10^{12}–10^{16} $\Omega \cdot cm$. The electrical resistivity of hydrogenated DLC film on ITO glass was in the 10^{10} $\Omega \cdot cm$ range, three orders higher than that of the films deposited on the Si substrate [17, 18]. The resistivity of CN_x film is much higher than that of DLC film, perhaps due to the incorporation of nitrogen atoms into the carbon network. The resistivities of CN_x films on ITO glasses are much higher than those of films on Si substrates, perhaps because there is more CN structure and less amorphous carbon structure in the films on ITO glasses than those on Si substrates. Of course the film microstructure formed during the growing process is also an important factor in electric properties.

4. Conclusion

From the analysis of the experimental results, the CN_x films were deposited by electrodeposition on silicon and glass substrates and the N/C ratios were approximated to or larger than 1 from XPS. The FT-IR spectra of them indicated that there are N─H, C≡N, C═H, C═C, C═N, C─N bonds. The obvious difference is that there is nearly no C≡N absorption band in the film on glass compared to that on Si substrate. The PL analysis shows broad bands during 2.5–3.5 eV are observed on the CN_x films, and the band at 3.35 eV became stronger and stronger with the increase of N/C ratio. From absorbance spectra, the optical band gaps of deposited films are between 1.1–1.6 eV which are affected by nitrogen content. The electrical resistivities of the films on Si wafers are in the 10^9–10^{10} $\Omega \cdot cm$ range, and those on ITO glasses are in the range of 10^{12}–10^{16} $\Omega \cdot cm$.

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