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Bonding structure and optical properties of a-CN_x:H films deposited in CH_4–NH_3 system

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ABSTRACT

Hydrogenated amorphous carbon nitride (a-CN_x:H) films were deposited by plasma enhanced chemical vapor deposition (PECVD) in CH_4–NH_3 system. The chemical composition and bonding configuration were investigated by XPS and FTIR. The results indicated that both sp^2CN and sp^3CN bonds generally increased with the increase of the nitrogen concentration, and the N atoms bonded to C atoms through C–N, C=N and C≡N bonds. Remarkably, for FTIR spectra, two peaks (2125 and 2200 cm^{-1}) were obviously observed, corresponding to C≡N bond which was found to predominantly exist in the isonitrile structure. As more nitrogen atoms were incorporated, the optical band gap was found to vary from 1.8 to 2.5 eV. Finally, the conduction mechanisms were discussed at low and high temperature, respectively.

1. Introduction

Numerous attempts to synthesize carbon nitride films have been stimulated by the prediction proposed by Liu and Cohen that a new superhard phase β-C_3N_4 would have bulk modulus and hardness higher than those of diamond [1,2]. Since 1989, various synthesis methods have been adopted to grow CN_x films, including magnetron sputtering [3,4], ion implantation [5], plasma enhanced chemical vapor deposition (PECVD) [6,7], laser ablation [8,9] and ion beam deposition [10]. On the other hand, amorphous carbon nitride (a-CN_x) films are also interesting materials in themselves, since they have properties such as high hardness and antiwear, chemical inertness to both acid and alkaline environments, lack of magnetic response, and an optical gap ranging from 0 to a few eV depending upon the nitrogen concentration and deposition conditions [11].

In these previous reports of carbon nitride films, a broad absorption band having a single absorption peak around 2200 cm^{-1} has been observed by most authors [12,13]. As far as the optical band gap was concerned, Corkill and Cohen [14] found the lowest indirect band gap to be 6.4 eV and the direct band gap to be 6.75 eV by the quasiparticle electronic band calculation. However, the relationship between optical band gap, electrical conductivity and the nitrogen concentration are still not very clear.

In this paper, hydrogenated amorphous carbon nitride (a-CN_x:H) films were prepared by plasma enhanced chemical vapor deposition (PECVD) in CH_4–NH_3 system. The bonding structure, the optical band gap and the electrical conductivity of the films were investigated by XPS, FTIR, UV–vis and electrical conductivity measurements.

2. Experimental details

Fig. 1 shows the schematic diagram of the deposition system. As shown in Fig. 1, the reactive gases were regulated downstream in vacuum chamber, using mass flow controllers, 50 sccm full scale for the mixture of ammonia and hydrogen (99.999% purity each and the volume ratio of NH_3 to H_2 was 1:9) and 5 sccm full scale for methane (99.999% purity), respectively. During the deposition, the gas flow rate of CH_4 kept constant at 1 sccm, while the mixture of NH_3 and H_2 varied from 5 to 10 sccm. The other parameters were kept the same for all the films: the cathode-substrate distance was 2 cm, the starting pressure before deposition was about 7 Pa, the deposition pressure was controlled at 1.0×10^2 Pa by a leaf valve, and a −350 V voltage was continuously applied.

The samples used for XPS and FTIR measurements were deposited on silicon substrates, while samples deposited onto quartz substrates were used for UV–vis and electrical conductivity measurements. Prior to film deposition, the silicon substrates were

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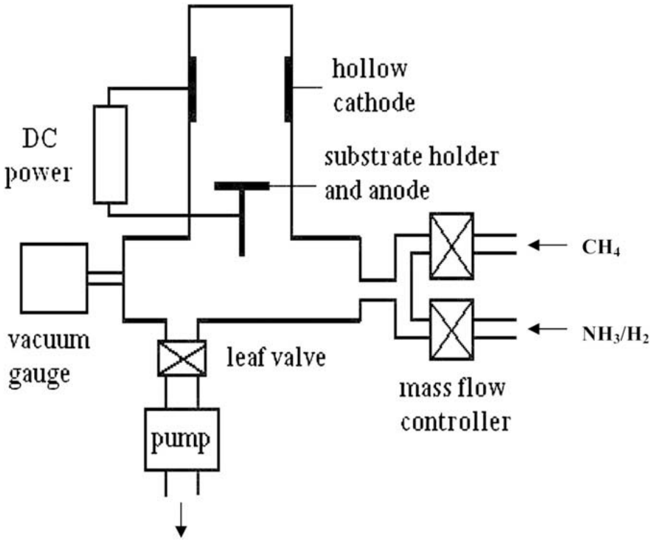

Fig. 1. The schematic diagram of the deposition apparatus.

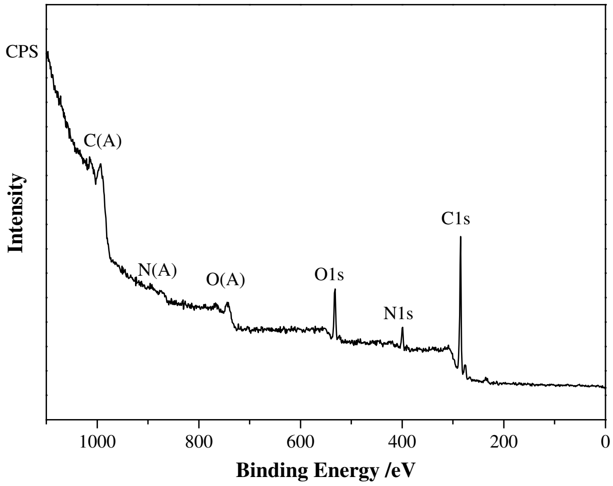

Fig. 3. XPS survey scan of the entire binding energy.

cleaned consecutively using ultrasonic in the acetone, absolute alcohol bath, then etched by HF acid for 1 min to stripe of the oxide and finally rinsed with distilled water.

The XPS data were obtained using an ESCALAB-250 spectrometer with a monochromatic Al K_α ($h\nu = 1486.6$ eV, energy resolution of 0.6 eV) X-ray source. No sputtering etching was performed before the measurement. The FTIR absorption was completed with MAGNA750 from 400 to 4000 cm^{-1}. The transmittance spectra were measured using a UV–vis spectrophotometer in the range of 190–1100 nm. Films deposited onto quartz substrates were used for the electrical conductivity measurements. Aluminium electrodes were evaporated onto the specimen surface in a co-planar manner, with a separation of 2 mm.

3. Results and discussion

3.1. XPS analysis

Based on the XPS measurement, samples with N content of 3.5–8.6 at.% were obtained. The variation of N content in the films with NH_3 (H_2)/CH_4 flow rate is shown in Fig. 2. Generally, the N content decreases with the increasing of the $NH_3(H_2)$ flow. This phenomenon can be easily explained because the standing time of ion species in the plasma reduced largely when the NH_3 (H_2) flow increased, due to the volume ratio of 1:9 in the mixture. Accordingly, the concentration of chemically active nitrogen atoms in the plasma dropped remarkably.

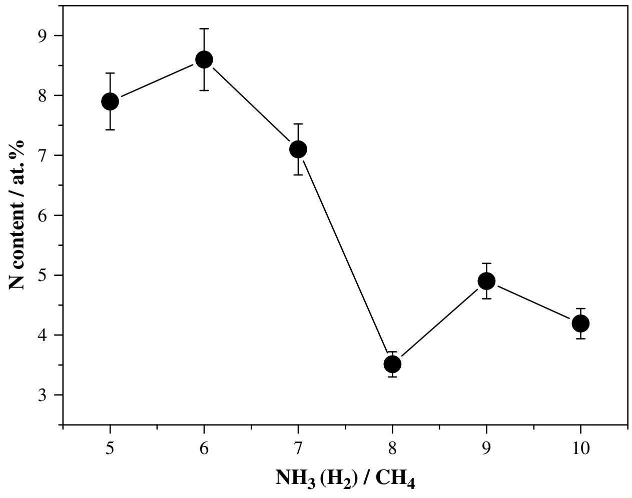

Fig. 2. The relationship between N content and $NH_3(H_2)/CH_4$ gas flow ratio.

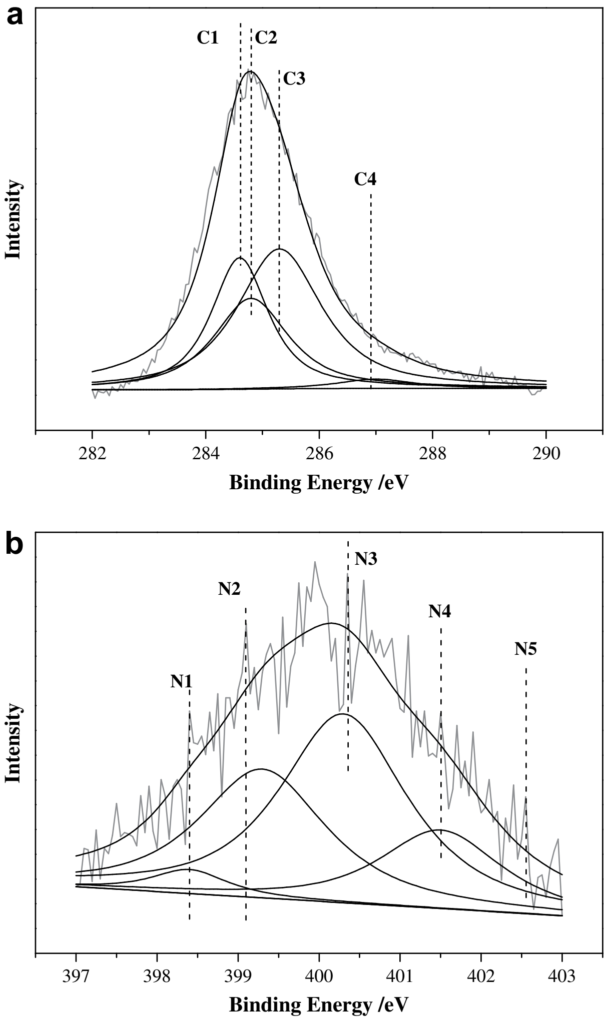

Fig. 4. The deconvoluted XPS spectra: (a) C1s (b) N1s.