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Simultaneous formation of diamond-like carbon and carbon nitride films in the electrodeposition of an organic liquid

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Abstract

Diamond-like carbon (DLC) and carbon nitride (CN_x) films have been simultaneously prepared on the cathode and the anode in the electrodeposition of an acetonitrile liquid at atmospheric pressure and temperatures below 80°C. The deposits were analyzed by X-ray photoelectron spectroscopy, Raman spectroscopy and X-ray diffraction. The deposits on the cathode were amorphous DLC films consisting of sp^2 and sp^3 carbon, while the deposits on the anode were CN_x films in which the N/C ratio was about 0.25. The mixed phases of α-C_3N_4 and β-C_3N_4 may exist in the CN_x films. The related reaction mechanism is also discussed in this Letter.

1. Introduction

Because of the extraordinary physical and chemical properties of diamond and the realization of depositing the material at low pressures, research into diamond and diamond-like films has become an area of intense interest in the field of condensed matter physics since the 1980s. Recently, the first-principle pseudopotential approach was used by Liu and Cohen [1,2] to predict a hypothetical covalent sp^3 bonded compound β-C_3N_4, with characteristics comparable to or better than those of diamond. Hereafter, an intense new interest in the synthesis of β-C_3N_4 has been stimulated. Many research groups have tried to synthesize these materials using various techniques and great progress has been made [3–6]. However, these methods are all vapor deposition techniques. The high vacuum required in the vapor deposition makes the equipment rather complicated and the control of the experiments difficult. At the same time, the comparatively high substrate temperature also limits the application of these materials. Compared to the vapor deposition techniques, the electrodeposition in the liquid phase can be performed in an atmospheric environment and at room temperature, bringing many advantages. Increasing attention has been attracted to by liquid phase electrodeposition research.

In recent years following the pioneering work of Namba [7], several attempts have been made in the field of electrodepositing diamond and the related materials in the liquid phase [8–10]. However, the depositing liquid was mainly limited to alcohol or alcohol–water systems, and carbon materials were the only deposits. Therefore, the synthesis of diamond and the related materials besides carbon materials from a new liquid system may have great scientific and technological significance.

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In our present work acetonitrile was chosen as the depositing liquid and DLC and CN_x films were prepared simultaneously on the cathode and the anode using electrodeposition. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman spectroscopy were applied to study the deposited films. The reaction mechanism is discussed in detail.

2. Experimental

The experimental setup comprised an electrolytic cell system, which is similar to that reported in Ref. [8]. The difference is that in this research the cathode and anode are both used as substrates. Silicon (100) wafers with a resistivity of 20 Ω cm and a size of $10 \times 20 \times 0.3$ mm^3 were selected as substrates, as well as the both electrodes. They were both mounted on graphite plates and the distance between the two electrodes was 7 mm. Before deposition, the substrates were cleaned by ultrasonic treatment and were then treated by a dilute HF solution. After several random trials with acetonitrile, propionitrile and acrylonitrile, analytically pure acetonitrile was used as the depositing liquid.

A DC power source was used to supply the high voltage applied to the substrates, which can be regulated from 0 to 4000 V. The reaction current recorded was in the range of 0–50 mA cm^{-2} and the reacting temperature was between 20°C and 80°C. In this work, the samples were deposited at 50°C and 1500 V.

3. Results and discussion

After deposition for a certain length of time pale gray films (deposits A) and pale yellow or deep gray films (deposits B) were obtained on the cathode and anode, respectively. The resistance of the films was measured by the standard four-point probe method. We found that the body resistivities of the films were all above 10^6 Ω cm. The scratch tests suggested that the both deposits on the Si substrates were qualitatively hard [4].

The composition of the deposits was investigated by XPS analysis. The results revealed that the cathodic deposits A consisted mainly of carbon with the N content being less than 3%, and N may come from the adsorption of acetonitrile; in contrast, the anodic deposits B consisted of both C and N and the N/C ratio was about 0.25. This indicates that the carbon film was deposited on the cathode, while the CN_x film was deposited on the anode.

The deconvoluted C_{1s} and N_{1s} XPS spectra of deposits A and deposits B are given in Fig. 1. The C_{1s} spectrum has a main peak at 284.5 eV, which corresponds to the C–C bond [10]. Three additional smaller peaks are also observed in this spectrum, which are due to the C bonded to the oxygen and to Si in the substrate (Fig. 1A). The N_{1s} spectrum consists of only one peak at 399.6 eV (Fig. 1B). This value is identical to that of nitrile [11], which suggests that the N element in the film A come from the absorbed acetonitrile. Due to the incorporation of nitrogen, the C_{1s} spectrum (Fig. 1C) shows an increase in intensity of the high binding energy components. The spectrum can be deconvoluted into three lines peaked at 284.57, 286.50 and 288.11 eV. We have assigned the peak at 284.57 eV to C–C bonds, the peak at 286.50 eV to sp^2 trigonal CN bonding and the peak at 288.11 eV to sp^3 tetrahedral CN bonding [12]. The N_{1s} spectrum (Fig. 1D) has two peaks located at 398.6 and 399.85 eV, which correspond to the N surrounded by sp^3-coordinated C atoms and sp^2-coordinated C, respectively [12,13].

Fig. 2A,B shows the Raman spectra for the carbon film and the CN_x film. Spectrum A is composed of an asymmetric broad band at 1575 cm^{-1} (G band) with a shoulder peak at 1350 cm^{-1} (D band), which is a typical DLC characteristic spectrum and indicates the existence of the sp^2 C as well as the sp^3 C in the film [14,15]. Spectrum B also consists of two similar bands at 1595 and 1355 cm^{-1}. The presence of nitrogen makes the bond angles of the sp^2 carbon atoms in the CN_x films more disordered, and consequently the CN_x films have an more intense D peak than that of the DLC film [16]. In all the Raman spectra of the CN_x films the peaks at about 2200 cm^{-1}, corresponding to the characteristic peak of the $C \equiv N$ bonds [15], have not been detected, which is similar to the IR results. The IR spectra also show no characteristic peaks of the C–H groups in the carbon and CN_x films.

The two films were studied by XRD (Fig. 3). The pattern of the carbon film (Fig. 3A) indicates that the

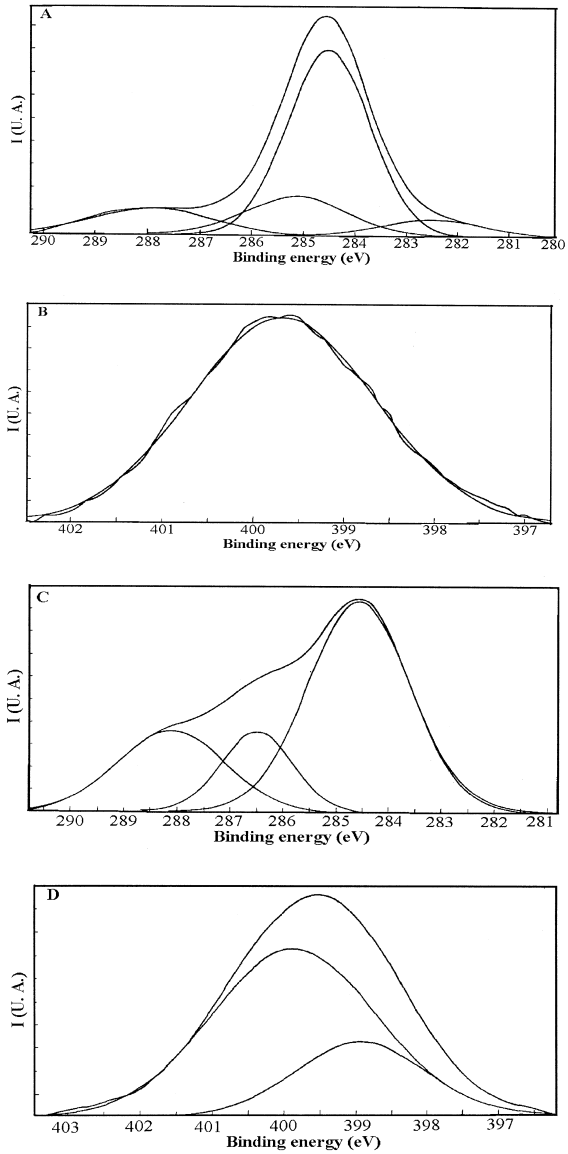

Fig. 1. The deconvoluted binding energy spectra of the deposits: (A) C_{1s} spectrum of the carbon film; (B) N_{1s} spectrum of the carbon film; (C) C_{1s} spectrum of the CN_x film; (D) N_{1s} spectrum of the CN_x film. The spectra were recorded using MgK_α with a Perkin–Elmer PHI 5300 ESCA.

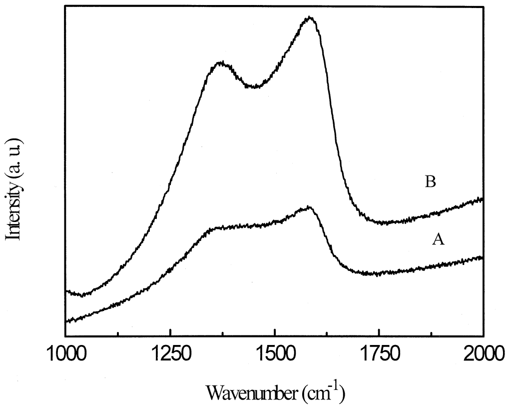

Fig. 2. Raman spectra of carbon film (A) and CN_x film (B). Raman measurements were carried out by using a Renishaw-1000 type confocal Raman spectrometer. The 514.5 nm radiation of an argon ion laser was focused to spots of about 1–2 μm in diameter.

film was amorphous. The CN_x film has a polycrystalline structure (Fig. 3B). In the pattern of the CN_x film there are two new peaks besides the Si substrate peak. The *d* values of the two peaks are identical to the calculated data [17], which are attributed to α-C_3N_4 (201) ($d_{exp} = 0.2377$ nm, $d_{cal} = 0.2375$ nm) and β-C_3N_4 (210) ($d_{exp} = 0.2054$ nm, $d_{cal} = 0.2043$ nm), respectively. The results indicate that the deposited CN_x films may contain mixed phases of α-C_3N_4 and β-C_3N_4 in the amorphous carbon matrix.

According to the above results, DLC and CN_x films have formed on the cathode and the anode simultaneously in the electrodeposition of liquid acetonitrile. The deposit on the cathode was amorphous DLC films consisting of sp^2 and sp^3 carbon. The deposit on the anode was CN_x film, in which the N/C ratio was about 0.25; mixed phases of

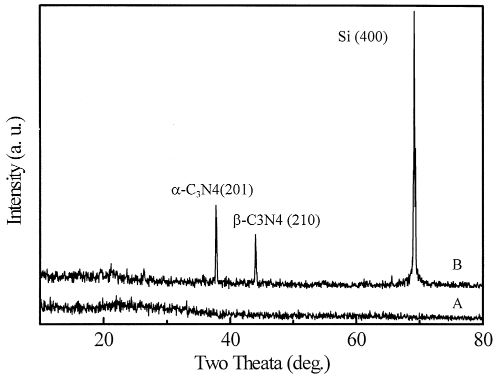

Fig. 3. The XRD patterns of the carbon film (A) and CN_x film (B) (using X'Pert MRD, Philips).

α-C_3N_4 and β-C_3N_4 may exist in the CN_x films. Accordingly, the deposition mechanism may be inferred as follows: in the beginning, the acetonitrile molecules are absorbed on the substrates randomly. When high voltages are applied to the substrates the absorbed molecules become polarized because of the large dielectric constant ε (37.5) and dipole moment D (3.92) of acetonitrile, i.e. CH_3CN becomes polarized $CH_3^{\delta+} \cdots CN^{\delta-}$. The potential direction determines the polarization direction of molecules. When the substrate is selected as the anode, the potential applied to the substrates is positive and then the negative end of the polarized molecule ($CH_3^{\delta+} \cdots CN^{\delta-}$) turns towards the surface of the substrates. If the energy reaches a certain value the C–C bonds in the polarized acetonitrile molecules will break first, under the high electric field, as the bond energy of the C–C (347 kJ/mol) is much lower than that of the C≡N (879 kJ/mol). Thus certain amounts of CN species are produced near the surface of the anode, which react on the substrate to form carbon nitride films. On the contrary, when the substrate is selected as the cathode, the potential applied to the substrate is negative. The CH_3 species would react on the electrode and thus carbon films form on the cathode.

In the vapor deposition process the formation and excitation of the CN species play a critical role for the N incorporation in the CN_x films [18,19]. Similarly, as the specific additive species for the growth of carbon films in the vapor phase, the formation of CH_3 species is also very important [3]. In our electrodeposition process the high voltage is applied to the two electrodes, and then the CN and CH_3 species can be easily formed by breaking the covalent bonds of the organic precursors at the electrode surface under the high electric field. For the electrochemical reaction, the high fields at the electrode surface are critical for many reactions which are impossible to take place using the conventional methods at the same temperatures [20–22]. We speculate that the high electric field in our procedure may contribute to fabrication of the carbon and carbon nitride networks on the electrodes at low temperatures.

To our knowledge carbon nitride and carbon materials can only be prepared separately at higher temperatures in different reaction systems. In this experiment we have obtained the both materials simultaneously using a high voltage electrodeposition technique in a suitable liquid phase system. Our present results demonstrate exciting prospects for this further research into simple but effective technique.

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