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Attempt to deposit carbon nitride films by electrodeposition from an organic liquid

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Carbon nitride films were synthesized by electrodeposition from an organic liquid on silicon substrates at temperatures lower than 80 °C. The N/C ratio in the films is about 0.25. The x-ray diffraction measurement indicates that the film contains some C_3N_4 polycrystalline phases. The Fourier-transform infrared spectroscopy, x-ray photoelectron spectroscopy, and Raman spectroscopy analyses suggest the presence of both single and double carbon-nitrogen bonds. The deposition mechanisms are also discussed. Our paper shows that the electrodeposition technique may hold some promise for synthesizing the metastable compound C_3N_4 in the liquid phase. [S0163-1829(99)05403-X]

I. INTRODUCTION

Recently there has been considerable interest in the synthesis of carbon nitride materials. This upsurge of research activities was stimulated by the theoretical prediction of the existence of a covalent-bond carbon nitride solid β-C_3N_4, with characteristics comparable to or better than those of the diamond.[1,2] Many attempts have been made to synthesize this superhard carbon nitride compound, such as shielded arc-ion plating,[3] laser ablation,[4] shock-wave compression,[5] plasma chemical-vapor deposition[6] and filtered-arc deposition.[7] The above-mentioned methods all involved vapor deposition techniques, and by these techniques, various carbon nitride materials were obtained. These methods generally require complex equipment, strict experimental conditions, and high temperatures, which is unfavorable to the synthesis of the metastable compounds, such as C_3N_4, because they need to be ''quenched'' to avoid undesirable atomic rearrangements.[8] In our paper we attempt to use a simple electrochemical-deposition method to synthesize the carbon nitride films from an organic liquid on Si(100) substrates. We have successfully deposited diamondlike carbon films from the liquid phase.[9,10] Electrodeposition from the liquid phase has a number of advantages over other methods, such as the simplicity of apparatus and low-depositing temperature, avoiding difficulties the conventional methods generally confront.[9–12] Thus, to synthesize carbon nitride (CN_x) materials from the liquid phase not only can broaden their applications but also has scientific significance.

II. EXPERIMENTAL DETAILS

The apparatus used in our experiment is an electrolytic cell system. The schematic diagram of the system is shown in Fig. 1. The Si substrate is mounted on the positive electrode. The counter electrode is a graphite plate. The distance between the two electrodes is 7 mm. In our experiments, the silicon (100) wafer we use as substrates has a size of $10 \times 20 \times 0.3\ \mathrm{mm}^3$. The substrates were treated with dilute HF solution before deposition. A dc power supply, which can be changed from 0 to 3000 V was used to apply high voltages to the substrate. The current density was in the range of 0–50 $\mathrm{mA/cm}^2$. During deposition we kept the voltage constant. The current density may change on itself during the process. The range of the substrate temperature was from 20 to 80 °C. Analytically pure acetonitrile (CH_3CN) was used as the source material because it contains both carbon and nitrogen elements. Besides, acetonitrile has a large dielectric constant (37.5) and dipole moment (3.92). The films were all deposited under an applied potential 1500 V and temperature 50 °C.

The films were characterized by Fourier transform infrared (FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and x-ray diffraction (XRD).

III. RESULTS AND DISCUSSION

In the range of 0–2000 V the current density increases linearly with the applied potential below the boiling point of acetonitrile (81.6 °C). During the deposition process the substrate current density changes obviously. Figure 2 shows the typical time-dependence curve of the current density under an applied potential of 1500 V and at the temperature of 50 °C. It can be seen that the current density decreases remarkably at the initial stage of the deposition. It takes only about 10 min for the electric-current density to decrease from 23 to 5 $\mathrm{mA/cm}^2$, and then it undergoes nearly no changes. This phenomenon may be ascribed to the increasing resis-

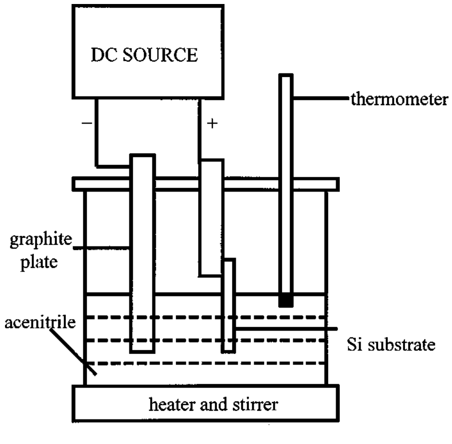

FIG. 1. The schematic diagram of the apparatus for the deposition of CN_x films used in our experiment.

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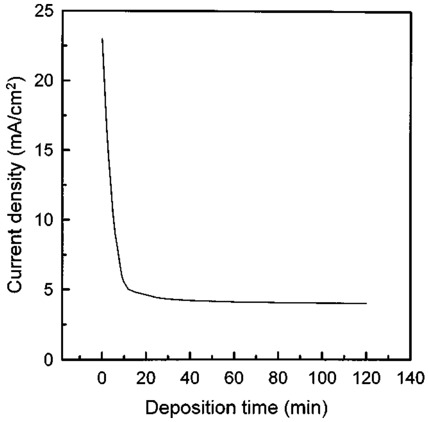

FIG. 2. Dependence of the current density with deposition time.

tance of the deposited film on the substrate. The resistance of the film was measured by the standard four-point probe method. The results show that the body resistivity of the film is higher than 10^6 Ω cm.

The XPS measurements indicates that the films (film A) contain mainly C, N, and a small amount of O and Si elements. Apparently, the O element is from the surface absorption of the films. The ratio of N/C is about 0.25, which is much lower than the stoichiometry of the theoretical material C_3N_4 (1.33). But this experiment verifies the practicability of depositing CN_x films from the liquid phase at low temperatures. For comparison, we mounted the Si substrate on the negative electrode and the deposition took place under the same conditions. The XPS spectrum of the deposited film shows that its main composition is C and the ratio of N/C is much lower than 0.04. This experimental result rules out the possibility that the N composition in the CN_x film is from the absorption, thus, we can conclude that the N element in the anodic deposits is mainly from the bonded N in the film instead of from the contamination from an organic liquid. At the same time, it is interesting to notice that the carbon and CN_x films can be prepared by cathodic and anodic deposition from the acetonitrile liquid, respectively. This paper is still under research and will be described later.

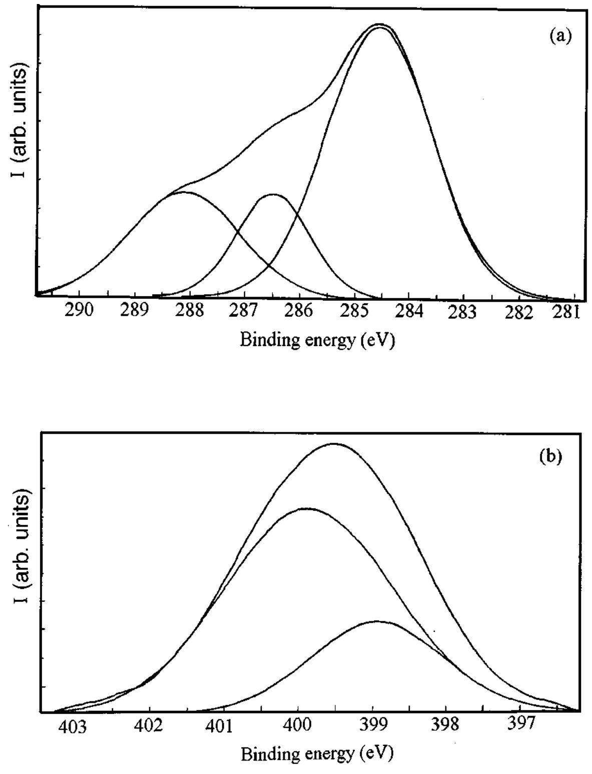

FIG. 3. The binding energy and the deconvoluted spectra of (a) C 1s and (b) N 1*s* of the CN_x films.

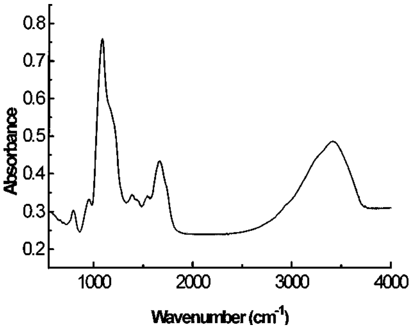

FIG. 4. The FTIR spectrum of the typical as-deposited CN_x film.

To determine the type of the chemical bonds in our CN_x films, the binding energy of the C 1*s* and N 1*s* in the XPS spectra were recorded and deconvoluted. Figures 3(a) and 3(b) show the C 1*s* spectrum, which was deconvoluted into three lines peaked at 284.57, 286.50, and 288.11 eV, and the N 1*s* spectrum, which was deconvoluted into two lines peaked at 398.93 and 399.85 eV, respectively. We assign the C 1*s* peak at 284.57 eV to the adventitious carbon and surface carbon, the peak at 286.5 eV to the sp^2 trigonal CN bonding, and the peak at 288.11 eV to the sp^3 tetrahedral CN bonding.[13] The N 1*s* peak located at 399.85 eV corresponds to the N bonded to sp^2 C. However, for N 1*s* peaked at 398.6 eV, there is some controversy in the assignment. Kobayashi *et al.*[14] and Rossi *et al.*[15] assigned this peak to N≡C (nitrile), while Caricato *et al.*[4] and Li *et al.*[16] attributed this peak to the N surrounded by the sp^3-coordinated C atoms. We prefer the later opinion, i.e., the peak is due to the N bonded to the sp^3 C, which is supported by our IR and Raman results.

The FTIR spectrum of the CN_x film is shown in Fig. 4, where absorption peaks at 3400, 1669, 1540–1560, 1380, and 1100 cm^{-1} can be seen. The broad band at 3400 cm^{-1} is due to the NH_x ($x=1,2$) stretching. The absorption at 1669 cm^{-1} suggests the existence of C═N bonds. The two bands

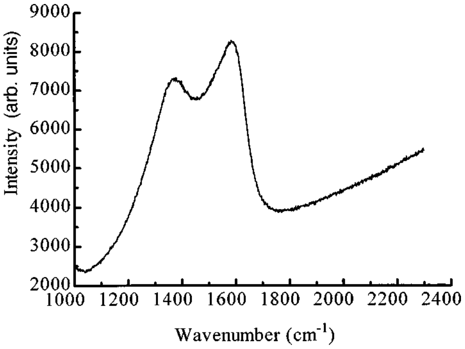

FIG. 5. The Raman spectrum of the as-deposited CN_x film.

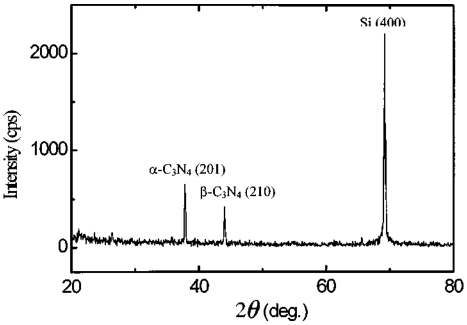

FIG. 6. The XRD pattern of the CN_x film deposited on the Si substrate.

between 1350 and 1600 cm^{-1} correspond to the *D* and *G* bands of pure amorphous carbon, which become infrared active due to the incorporation of nitrogen atoms into the carbon network.[17] The band at 1000–1200 cm^{-1} can be attributed to the C—N single bond.[18] There are no evidences of the existence of the C—H and C≡N groups in the spectrum. The absence of stretching mode at 2200 cm^{-1} indicates that the concentration of the *sp* C must be very low.[4] The Raman spectrum of the CN_x film is shown in Fig. 5. There are two peaks located at 1365 cm^{-1} (*D* band) and 1580 cm^{-1} (*G* band), respectively. They are almost identical with those of the graphitelike microcrystalline carbon. But due to the bonds with nitrogen atoms, the carbon atoms sp^2 bond angles become more disorderly, thus they have a stronger *D* peak than that of the diamondlike carbon film.[3] The absence of peaks at 2200 cm^{-1} indicates the absence of the C≡N bond. From XPS, IR, and Raman spectra, we conclude that the CN_x film mainly contains C═N, C—N, C═C bonds, but no C≡N bonds.

The XRD pattern of the film is shown in Fig. 6. In order to confirm that the diffraction peaks are from the synthesized film, we also measured the used Si substrate. Except for the substrate-diffraction peaks, there are two diffraction peaks that come from the film. They can be attributed to α-C_3N_4 ($d_{\mathrm{exp}}=0.2377$ nm, $d_{\mathrm{cal}}=0.2375$ nm, $hkl=201$) and β-C_3N_4 ($d_{\mathrm{exp}}=0.2054$ nm, $d_{\mathrm{cal}}=0.2043$ nm, $hkl=210$), respectively.[19] The N/C ratio of the CN_x films is only 0.25, much lower than that of the theoretical stoichiometry of C_3N_4 (1.33), and the Raman result confirms the existence of the amorphous carbon. From these results, we speculate that some mixed polycrystalline phases of α-C_3N_4 and β-C_3N_4 are contained in the amorphous carbon matrix. Since the XRD is sensitive to crystalline phases, a small amount of polycrystalline C_3N_4 has been detected.

The above results indicate that the CN_x films are synthesized by anodic electrodeposition from the acetonitrile liquid. The deposition mechanism may be inferred as follows: the acetonitrile molecules are absorbed on the surface of the substrates randomly, regardless of which electrode the substrate was mounted on. When the electric potential is applied to the substrate, the absorbed molecules become polarized, i.e., CH_3CN becomes polarized $CH_3^{\delta+}\cdots CN^{\delta-}$. Because the dipole moment *D* (3.92) of acetonitrile is rather large, the polarization takes place rather easily. The potential direction determines the polarization direction of the molecules. When the Si substrates are used as the anode, the potential applied to the substrates is positive and the negative end of the $CH_3^{\delta+}\cdots CN^{\delta-}$ turns towards the surface of the substrate. If the energy becomes high enough, the C-C bonds would be broken and the cyano groups (−CN) react to form carbon-nitride films on the substrate surface. On the contrary, when the potential applied to the substrates is negative, the direction of the absorbed molecules would be reversed. The groups reacted on the substrate should be the CH_3, and finally carbon films form on the negative electrode.

Although our paper is still very preliminary and the N/C ratio is relatively low, because of the very low temperatures and the simplicity of equipment, this experiment is believed to be very promising in the synthesis of the metastable materials, such as C_3N_4, etc.

IV. CONCLUSIONS

We first verified that CN_x film can be synthesized from an organic liquid at atmospheric pressure and temperatures lower than 80 °C. The ratio of N/C in the deposited CN_x films is about 0.25. The XPS and IR analyses indicate that the nitrogen and carbon atoms are mainly bonded together in single- and double-bonding states. The XRD result indicates that the film contains some mixed polycrystalline phases of C_3N_4. Our paper shows that electrodeposition technique may hold some promise for synthesizing the metastable compound C_3N_4. Further research will be focused on the increase of the N content in the CN_x film and further identification of the deposition mechanism.

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