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Effects of acetylene/ammonia mixtures on the properties of carbon films prepared by thermal chemical vapor deposition

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ABSTRACT

Effects of the $C_2H_2/(C_2H_2+NH_3)$ ratio on the properties of thermal chemical vapor deposition (CVD) carbon films are investigated. Experimental results indicate that the deposition rate of carbon films increases with increase of the $C_2H_2/(C_2H_2+NH_3)$ ratio. Ten NH_3 molecules will suppress about one C_2H_2 molecule to form carbon films, and the deposition rate of carbon films is proportional to the partial pressure of acetylene with a power of fourth order. A model description of the kinetics of this thermal CVD process is proposed. Moreover, the ordering degree, nano-crystallite size, and the number of sp^2 carbon sites decrease with increase of the $C_2H_2/(C_2H_2+NH_3)$ ratio, while the electrical resistivity increases. Few nitrogen atoms and no hydrogen are incorporated in the carbon films. When the carbon films are very thin, the carbon atoms would be uniformly deposited on a silica glass plate which results in surface smoothening. Nevertheless, when the carbon films are getting thicker, the surface roughness increases. As the $C_2H_2/(C_2H_2+NH_3)$ ratio increases, the decrease of the water contact angle on a carbon film surface is mainly resulting from the decrease of the number of sp^2 carbon sites in the carbon films. The deposition temperature and working pressure of thermal CVD carbon films using the C_2H_2/N_2 or C_2H_2/NH_3 mixtures are smaller in comparison to those using a CH_4/NH_3 mixture. Usually, when the deposition temperature is above 1073 K, NH_3 is decomposed into NH_2, which would suppress the growth of carbon films. However, as the deposition temperature is below 1073 K, NH_3 serves as the dilute gas in the described processes.

1. Introduction

Carbon films have many excellent properties including wide band gap, infrared transparency, high hardness, inertness to chemical attack, and high water-repellency [1,2], and have been intensively studied. One kind of carbon films called pyrolytic carbon films can be formed by decomposing hydrocarbons in a heating reactor and depositing them on optical fibers [3–6] or graphite particles [7,8] using thermal chemical vapor deposition (CVD); such materials were employed as hermetic optical fiber coatings [3–6] and for graphite anodes in lithium ion secondary batteries [7,8]. Among the precursor gases, methane (CH_4) remains a popular choice because it is available in high purity [1]. Therefore, adopting CH_4 as the precursor gas, the effect of deposition temperature [6], substrate size [9], nitrogen (N_2) addition [10], and ammonia (NH_3) addition [11] on the properties of thermal CVD carbon films had been studied previously by our group. Alternatively, acetylene (C_2H_2) is a very useful source gas for low pressure deposition, because its strong C≡C bond means it has a simple dissociation pattern, giving mainly $C_2H_n^+$ ions [2]. Hence, we had also investigated the effects of different C_2H_2/N_2 ratios on characteristics of thermal CVD carbon films [12].

The dissociation of NH_3 in CVD process is easier than that of N_2 [13,14], so NH_3 was often added in the precursor gas to form various kinds of nitrides [15–19]. Alternatively, NH_3 was also used as an etchant in hydrocarbon gases to etch away graphitic carbon films that continuously form during the CVD growth process; this is helpful for the alignment of carbon nanofibers [20] or in shaping a carbon nanostructure that consists of a nanocylinder grown directly on a nanocone [21]. In the literature, N_2 admixtures were often used as the precursor gases to prepare carbon films using different methods including thermal CVD [11], hot-filament assisted CVD [22,23], plasma enhanced CVD [24], and so on. Nevertheless, we found no evidence of previous works to study the influences of NH_3 addition with C_2H_2 on the properties of thermal CVD carbon films. Hence, this study investigated the effect of the $C_2H_2/(C_2H_2+NH_3)$ ratio on the properties of thermal CVD carbon films deposited on silica glass plates. Additionally, the thermal CVD carbon deposition using a C_2H_2/NH_3 mixture is compared with those using CH_4/NH_3 [11] and C_2H_2/N_2 mixtures [12].

2. Experimental details

2.1. Preparation of carbon films

The preparation of carbon films proceeded as follows. The silica glass plates (length = 12 mm, width = 12 mm, height = 1 mm) were cleaned

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in ultrasonic baths of acetone and de-ionized water, in that order, to improve the adhesion of carbon films onto these substrates. Then, the silica glass plates were coated with carbon films by thermal CVD. The thermal CVD system adopted a quartz tube as the reaction chamber, which has a length of 900 mm, an internal diameter of 25 mm, and a wall thickness of 1.5 mm. The deposition zone length of the reaction chamber was 60 mm, and the substrate was placed in the reaction chamber so that the middle portion of the substrate's length coincides with that of the deposition zone. 99.90% C_2H_2 and 99.99% NH_3 were used as the precursor gases. The mass flow rates of $(C_2H_2+NH_3)$ were kept at 40 sccm (standard cubic centimeter per minute, cm^3/min), and five carbon films were prepared with the $C_2H_2/(C_2H_2+NH_3)$ ratios at 60, 70, 80, 90, and 100%. The working pressure was maintained at 8 kPa by a mechanical pump. The temperature rose from room temperature to deposition temperature at a rate of 15 K/min. The deposition temperature and deposition time were set to 1113 ± 1 K and 8 min, respectively. In a previous work, deposition temperature of the thermal CVD process using C_2H_2/N_2 mixtures was set at 1003 K [12]. However, Matsumoto et al. [25] reported that large amounts of ammonia were decomposed as the temperature was above 1073 K, so the deposition temperature of this work was set at 1113 K. To verify the decomposition temperature of NH_3, an extra experiment was executed as follows. As both $C_2H_2/(C_2H_2+N_2)$ and $C_2H_2/(C_2H_2+NH_3)$ ratios were fixed at 80%, the total mass flow rate of precursor gases, working pressure, and deposition time were set as 40 sccm, 8 kPa, and 8 min, respectively. Alternatively, the deposition temperature was varying from 1073 to 1153 K. During the deposition process, a residual gas analyzer (Extorr-XT200M) was used to measure the partial pressures of the residual gases. After the deposition process was finished, the temperature was quickly reduced to room temperature at a rate of 250 K/min by cooling in air with a fan.

2.2. Characterization of carbon films

The thicknesses and morphologies of the carbon films were obtained by measuring the cross sections of the glass plate located at the middle position of the reactor using a field emission scanning electron microscope (FESEM, JEOL JSM-6700F). The operating voltage of the FESEM was 3 kV. The structural and chemical characterizations of the carbon films were investigated by X-ray diffractometer (XRD, Bruker MXP-III), Raman spectroscopy (Jobin Yvon Triax 550), and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI 5000 VersaProbe). All these experiments were done on carbon films located at the middle position of the reactor of the substrate. XRD was performed using $Cu\ K_\alpha$ radiation ($\lambda=0.154$ nm) in grazing incident diffraction mode, and the incident angle is 0.5°. Diffraction peaks from the carbon films were discerned by 2θ angles ranging between 10 and 50°. Data from the Joint Committee on Powder Diffraction File (JCPDF) database (numbers: 75–1621) were used to identify the microstructure of the carbon films from the diffraction peaks. XRD patterns were decomposed by Gaussian functions, and a linear background has been considered. The peak of the silica glass substrate (amorphous SiO_2) was extracted from the XRD patterns to obtain the (002) peak of graphite. The Raman spectra (RS) were measured in back-scattering geometry with the 633 nm line of a He–Ne laser at room temperature in the spectral range of 800–2000 cm^{-1}. The laser power of the Raman spectrometer was 25 mW, and a damper was adopted to weaken the laser power. When the irradiation time of the laser on the carbon films was set to 10 s/point, the surface morphologies of carbon films examined by optical microscope showed no significant damage. The RS were decomposed by Lorentzian and Gaussian functions, and a linear background has been considered. The photoelectron spectra of carbon films were acquired with $Mg\ K_\alpha$ radiation (photon energy = 1253.6 eV). All carbon core line ($C\ 1s$) spectra were acquired at the X-ray incident angle of 54°. Before collecting XPS data, all carbon films were sputtered by Ar^+ ions for surface cleaning. The sputtering time, energy, and pressure were 2 min, 3 kV, and 1.5×10^{-8} Pa, respectively. XPS spectra were decomposed by Gaussian functions, and a linear background has been considered. The electrical properties of the carbon films were measured using the four point probe (FPP) method at room temperature. Four probes were arranged with intervals of 1 mm along a straight line and these probes were connected to a source meter (Keithley 2400). A direct current of 1 mA was applied to the carbon film, and the output voltage was then measured. The sheet resistance was obtained from the relationship between output voltage and input current. With the application of the correction factors, sheet resistance, and film thickness, the electrical resistivity can be calculated. The surface roughness of carbon films was examined by the atomic force microscopy (AFM, Veeco D5000). The value of surface roughness, R_{rms}, was evaluated in tapping mode over an area of 5×5 μm. Each data point was obtained from the average value of three different positions on the same specimen surface. Meanwhile, the wetting behavior of carbon films was characterized by contact angle measurements with the sessile drop technique. A DI water droplet with a volume of 2 μl was released onto the surface of the sample from a syringe needle. Each measurement was repeated 10 times and the reproducibility was never worse than ±1°.

3. Results

3.1. Deposition rate

Fig. 1 shows FESEM images of cross sections of the carbon films that are deposited on silica glass plates with different $C_2H_2/(C_2H_2+NH_3)$ ratios. The thicknesses t_p of the carbon films are obtained by measuring cross sections of the silica glass plate located at the middle position of the reactor. The results show that the carbon films are uniformly deposited on silica glass plates, and the standard deviation of the measured values of the film thickness was within 5%. The thickness of the carbon films was determined by using FESEM, and then, the deposition rate r_p of the carbon films can be calculated from the film thickness and deposition time. Table 1 shows the thickness t_p and deposition rate r_p of carbon films on silica glass plates that are prepared with different $C_2H_2/(C_2H_2+NH_3)$ ratios, and reveals that the deposition rate r_p of carbon films on the silica glass plate increases from 14.4 to 125 nm/min as the $C_2H_2/(C_2H_2+NH_3)$ ratio increases from 60 to 100%. Thus the deposition rate of carbon films increases with increase of the $C_2H_2/(C_2H_2+NH_3)$ ratio. In order to find the threshold ratio of C_2H_2/NH_3 for carbon film formation, an additional experiment with the $C_2H_2/(C_2H_2+NH_3)$ ratio below 60% was executed. We found that if the C_2H_2/NH_3 ratio is less than 0.1, no carbon film is formed. This implies that ten NH_3 molecules will suppress about one C_2H_2 molecule to form the carbon film. Hence, the relation between the deposition rate of carbon films and mass flow rates of C_2H_2 and NH_3 can be expressed by a power function as

$$r_f=k_1[(C_2H_2-0.1NH_3)/(C_2H_2+NH_3)]^n, \tag{1}$$

where k_1 and n are constants to be determined. After curve fitting using the data shown in Table 1, k_1 and n are obtained as 126.4 nm/min and 3.72, respectively. This indicates that this CVD reaction is controlled by a process of about fourth order. The details of residual gases analysis (RGA) results and kinetics of this thermal CVD process are described in Appendix A. RGA results show that the main residual gas in the gas phase is C_2H_2, so it is also the main species to deposit carbon atoms on the substrate.

Fig. 1 also illustrates that the carbon films exhibit a laminar structure. Pyrolytic carbon films prepared by thermal CVD usually exhibit a laminar structure [26]. Notably, when the $C_2H_2/(C_2H_2+NH_3)$ ratio is above 90%, there appear many particles on the carbon-coated surface.

The growth of these particles should proceed as follows [9,27]. Initially, a small (nanoscale) particle is nucleated on the carbon film. The laminar carbon film is then deposited around the small particle, extending the shape of the particle to that of a headstand cone with a spherical base. The spherical base of the cone can be evident from