

Effect of reaction temperature on carbon films prepared by a hydrothermal electrochemical method

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Carbon films were synthesized under hydrothermal electrochemical conditions using sugar as the carbon source at temperature ranging from 170 °C to 180 °C. The reaction temperature affects the degree of sugar decomposition, the concentration of carbon ions, supersaturation and overpotential of the solution, thereby affecting the morphology, orientation, and crystallinity of the films. The graphitic content (sp^2) increases with increasing the processing temperature and vice versa. The higher the synthesizing temperature the less the amount of amorphous carbon (sp^3). The graphite in thin films prepared at 170 °C and 175 °C shows a (101) preferred orientation, whereas those prepared at 180 °C show a fairly random orientation. The mechanism of this synthesizing process seems to consist of three stages.

Keywords: carbon, thin film, supersaturation, overpotential, hydrothermal electrochemical method

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1. Introduction

Carbon has many allotropic forms such as amorphous carbon [1, 2], graphite [3, 4], diamond [5], chaoite [6], fullerenes and carbon nanotubes [7]. Recently, amorphous carbon films and graphite films have attracted much attention not only due to their unique electronic properties but also due to their potential application to nanoelectronic devices [1–4].

Usually, carbon thin films are prepared by chemical vapor deposition (CVD) [8], pulsed laser deposition [9], filtered cathodic vacuum arc [10], ion beam deposition [11], sputtering [12, 13] and electrolysis [14, 15].

In this study, a hydrothermal electrochemical process was developed for preparing carbon thin films. During the hydrothermal electrochemical process, the temperature and the resulting vapor pressure are key factors affecting the degree of sugar decomposition, supersaturation and overpotential of the solution, which affects

the initial nucleation on the substrate and the subsequent growth of the grains. The nucleation and growth of crystal significantly influence the morphology, orientation, and crystallinity of the grains in the as-deposited carbon films.

2. Experiment

Pt substrates of 99.9% purity with $10 \times 10 \times 0.1$ mm³ dimensions were mechanically polished and degreased with acetone using an ultrasonic cleaner. Guaranteed reagents of absolute ethyl alcohol solution containing sugar were used to prepare synthetic solutions. The solutions were prepared by dissolving/suspending 1.0 g (0.005 mol) of sugar into 100 ml of the absolute ethyl alcohol solution.

The detailed description of the deposition facility and the growth method has been given elsewhere [16]. A typical preparation process was carried out for 20 h in galvanostatic conditions, at the current density of 0–5 mA/cm² and the processing temperature of 170~180 °C. After each experiment, the Pt substrate was covered with a tawny film. The film was washed with water,

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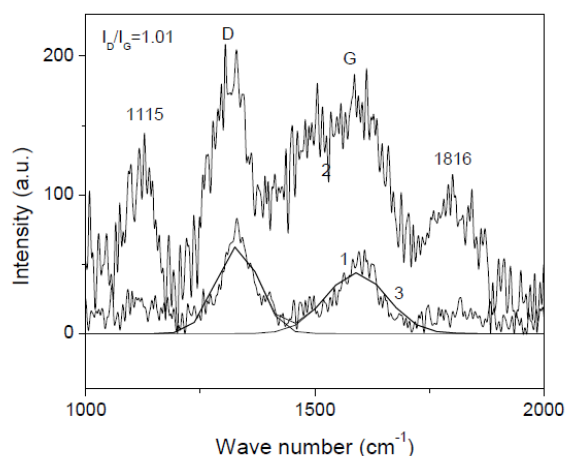


Fig. 1. Raman spectra of carbon film prepared at 170 °C (sample A).

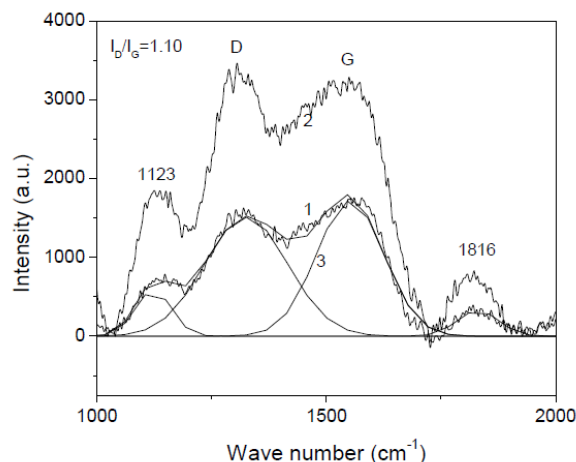


Fig. 2. Raman spectra of carbon film prepared at 175 °C (sample B).

ultrasonically in ethanol, and air-dried prior to characterization.

X-ray diffraction (XRD, D/max 2400 with $\text{CuK}\alpha$ radiation) and Raman spectroscopy (Labram HR 800, Jobin-Yvon) were employed to characterize the structure and bond parameters. The observation of the morphology of the films was conducted using scanning electron microscopy (SEM, JSM-6301F) and atomic force microscopy (AFM).

3. Results and Discussion

3.1. Raman spectroscopy

Figs. 1, 2, 3 show the Raman spectra of carbon films prepared by the hydrothermal electrochemical method at different temperatures. Curve 1 is the result of the first Raman scan, curve 2 is the result of the second scan, and curve 3 is the fitting Gaussian of the first scan. Four broad bands, named D peak, G peak, 1100 cm^{-1} peak and 1820 cm^{-1} peak can be observed in curve 1. Both D and G peaks are related to sp^2 C (graphite) [17], the peaks around 1100 cm^{-1} are attributed to disordered sp^3 C (amorphous carbon or nanodiamond) [18], and the peaks around 1820 cm^{-1} are attributed to sp^1 C (carbon chains or allenes) [19, 20].

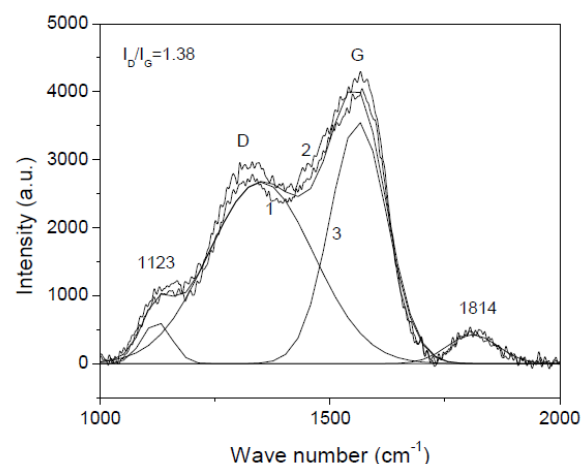


Fig. 3. Raman spectra of carbon film prepared at 180 °C (sample C).

By calculating the relative intensities of the four peaks (1100 cm^{-1} , D, G, and 1820 cm^{-1}), the information on the three kinds of carbon fractions i.e. sp^1 , sp^2 and sp^3 was obtained. The I_D/I_G ratios of the films grown at 170 °C (sample A), 175 °C (sample B) and 180 °C (sample C) were about 1.01, 1.10 and 1.38, respectively. The G peak from sample A was located at 1550 cm^{-1} with a full-width half-maximum (FWHM) value of 130 cm^{-1} whereas the G peaks from sample B and sample C were located at 1552 cm^{-1} (FWHM = 129 cm^{-1}) and 1562 cm^{-1} (FWHM

$= 124 \text{ cm}^{-1}$). The increasing in the ratio of I_D/I_G , along with G peak shifting to higher wave numbers and the narrowing of G peak indicate an increase of graphite-like sp^2 bonding in the sample [21]. So it could be deduced that graphite phase increased with the increase in the processing temperature. The I_{1100}/I_G ratios of the films grown at 175°C and 180°C were about 0.18 and 0.09, respectively. It could be deduced that there was more sp^3 C in the films grown at 175°C than in the films grown at 180°C . The I_{1820}/I_G ratios of the films grown at 175°C and 180°C were about 0.12 and 0.11, respectively. It could be deduced from the approximately equal values that the two films have the same fraction of sp^1 C.

The changes in the spectra for various scan times are also shown in Figs. 1, 2, 3. It was found that the maxima of relative intensities of the first scan were about 100, 1900 and 4000 for sample A, sample B and sample C, respectively. The maximum values of relative intensity increased sequentially with the increase in temperature. The relative intensity of the second scan revealed a similar tendency. More amorphous carbon could absorb more incident laser energy and Raman scattered energy and consequently, the incident laser energy could lead to burning or transformation of the amorphous carbon (sp^3 C). The absorption, taking place in sample A, reduced the Raman intensity greatly and produced a “noisy” spectrum (Fig. 1) because of a big fraction of amorphous carbon (sp^3 C). The spectra indicate that the higher the processing temperature, the less amorphous carbon in the films.

3.2. XRD analysis

Fig. 4 shows the XRD patterns of the experimental films obtained at different temperatures. The samples have the characteristics of XRD spectrum of graphite phase (sp^2 C). As shown in Fig. 4(c), the peaks at ca. 26.5° , 44.6° and 77.5° are related to the graphite phase (JCPDS number: 23-0064) for (002), (101) and (110) diffraction peaks, respectively. The relative intensity of the three XRD peaks is found to agree with the standard XRD data (JCPDS 23-0064). It

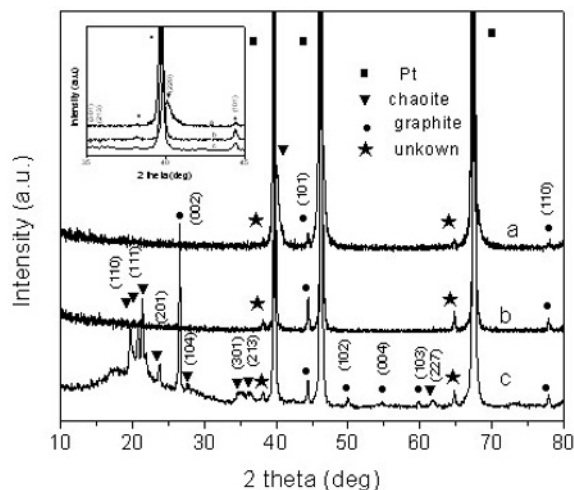


Fig. 4. XRD analysis of carbon films obtained at (a) 170°C , (b) 175°C and (c) 180°C .

indicates that the graphite grains with the random orientation have been crystallized at 180°C . There are only 44.6° and 77.5° peaks and no apparent (002) graphite peak is observed in Fig. 4(a) and Fig. 4(b). The relative intensity of the peak at 44.6° is higher than that of peak at 77.5° . So, the (101) preferential orientation of graphite could be obtained at 170°C and 175°C .

As shown in Fig. 4(c), the peaks at $2\theta \approx 19.7^\circ$, 20.7° and 23.6° are related to the chaoite phase (JCPDS number: 22-1069) for (110), (111) and (201) diffraction peaks, respectively. It is found that the relative intensity of the peaks is in agreement with that of standard chaoite powder. It means that the chaoite grains obtained at 180°C are randomly oriented. The peak at 40.2° in Fig. 4(a) is related to (220) chaoite peak. There is no other chaoite peak in Fig. 4(a), so the chaoite obtained at 170°C is (220) preferentially oriented.

In Fig. 4(c), the intensity of the peak observed at $2\theta \approx 20^\circ$ is characteristic of the presence of amorphous phases in the carbon film.

It is obvious that the carbon films containing (101) preferentially oriented graphite grains and (220) preferentially oriented chaoite grains were obtained at 170°C . The films obtained at 175°C showed the (101) preferential orientation of graphite, parallel to the substrate surface. The

randomly oriented chaoite and graphite grains were obtained at 180 °C.

3.3. SEM and AFM characterization

Fig. 5 shows the SEM micrographs of carbon films prepared at different temperatures. It can be seen that the surfaces of the films obtained at 170 °C and 175 °C are smooth. No ripples, swelling, corrugation or coating delamination can be found on the surface shown in Fig. 5(a) and Fig. 5(b). However, the films prepared at 180 °C exhibit the spherical particles distributed on the smooth surface (Fig. 5(c)).

Fig. 6 shows the surface roughness of the films obtained at various temperatures. Except some abnormal coarse grains in Fig. 6(c), the grains in the films are uniform. The abnormally coarse grain in Fig. 6(c) can form the spherical particles shown in Fig. 5(c). Not considering the abnormal grains, the grain size and surface roughness decrease with the increase in the processing temperature.

3.4. The formation mechanism

The mechanism of this synthesizing process seems to consist of three stages. In the first step, sugar chains decompose; furfural and hydroxymethylfurfural (HMF) form as the first and the main decomposition intermediates under the hydrothermal treatment [22]. Subsequently, the first intermediates electrolytically decompose to form carbon ions [23]. At the third stage, the carbon ions move from the solution to the electrode and nucleate on the electrode surface. The concentration of carbon ions depends on the intermediates. The growth rate of the intermediates strongly depends on the melting point of the sugar.

The sugar used in this study contains about 98% sucrose and its melting point is about 180 °C. Below 180 °C, the decomposition speed of sugar chains is slow [24], so that at 170 °C and 175 °C, the concentration of ions in the solution is below saturation. In these conditions, a homogeneous nucleation of carbon in the solution is hardly possible. When the carbon ions move to the electrode surface and cause supersaturation near the electrode, the heterogeneous nucleation and

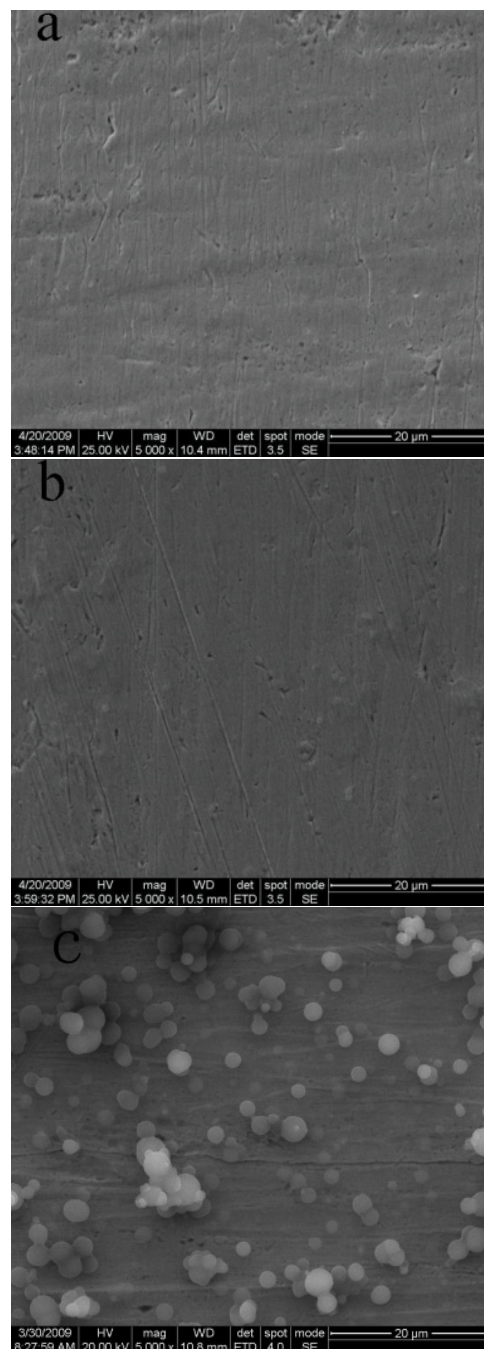


Fig. 5. SEM micrographs of carbon films prepared at (a) 170 °C, (b) 175 °C and (c) 180 °C.

growth of carbon take place on the electrode (substrate). As sugar decomposes violently at 180 °C, the concentration of carbon ions is above its saturation. In these conditions, some of carbon ions contact each other and the homogeneous

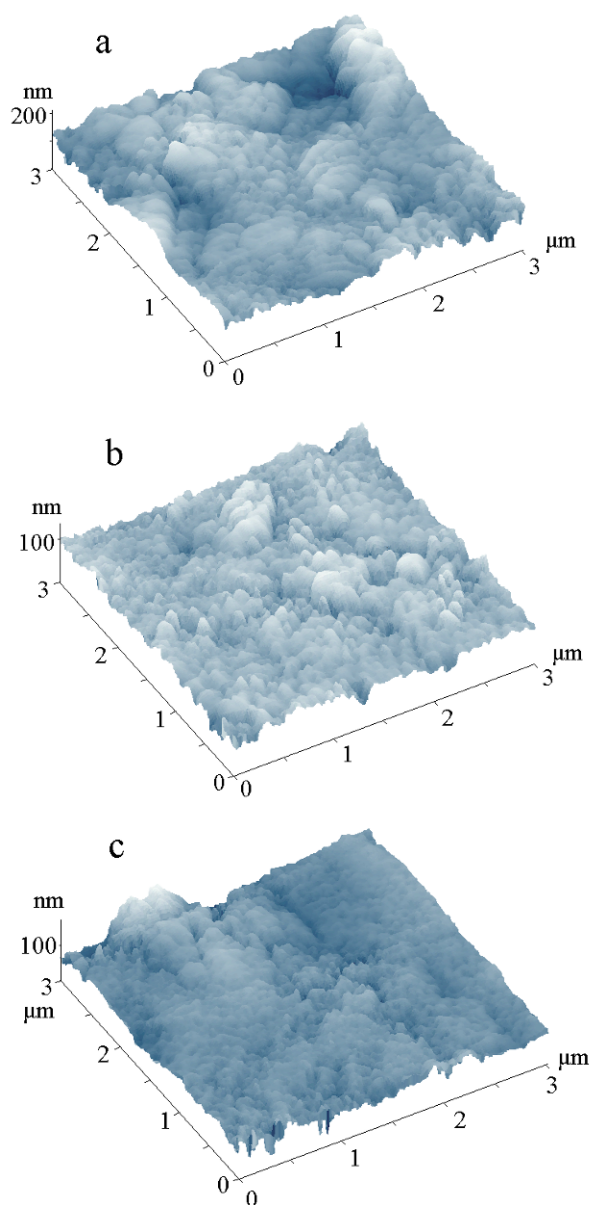


Fig. 6. AFM topography images of the films deposited at (a) 170 °C, (b) 175 °C and (c) 180 °C.

nucleation takes place in the solution, while some of the ions move to the electrode to form the carbon films. Some homogenous crystal nuclei formed in the solution move to the electrode in the electric field and grow to spherical particles on the surface of the carbon film as shown in Fig. 5(c).

As the processing temperature increases, high concentration and high supersaturation are

obtained. The high supersaturation results in a high nucleation density. The high density of nuclei restricts the further growth of grain sizes. A smooth continuous film with small grains is formed on the substrate, as shown in Fig. 6.

The volume fraction of graphite (sp^2) phase increases with the increasing of the processing temperature. It is because the amorphous carbon and metastable phase could be transformed into a stable crystal phase as the temperature and pressure increase, according the carbon P-T diagram. Generally, there are two kinds of crystalline carbon phases: graphite and diamond. The growth rate of graphite is faster than that of diamond under ethanol saturation pressure at temperatures ranging from 170 to 180 °C [25]. So, the graphite crystal is easy to nucleate and grow at 180 °C.

According to the mechanism proposed by Pangarov, the plane with the preferred orientation in hexagonal phase is (001) at low overpotential and it is then shifted to (101) and (110) as the overpotential for hexagonal phase deposition increases [26, 27]. The graphite structure is hexagonal. For graphite with random orientation, the intensity of (002) peak approaches its maximum value, as shown in Fig. 4c. The overpotential determined in this manner includes the overpotential for carbon deposition and the resistance overpotential, derived from the ohmic resistance of the electrolyte. At the same current density, the overpotential for carbon deposition decreases with the increase in the concentration of carbon ions. The concentration of carbon ions increases with the increase of temperature. As the temperature increases, the overpotential decreases and the preferred orientation of the as-deposited carbon film changes from the (101) and (110) to the (002) plane.

4. Conclusions

Carbon thin films consisting of graphite, chaoite and amorphous carbon were prepared by the hydrothermal electrochemical technique using sugar as the carbon source in this study. Graphite phase (sp^2 C) increases with increasing the process

temperature, while the amorphous carbon (sp^3 C) is formed during the low temperature process. The preferential orientation of the films disappears for in the films prepared at 180 °C. The grain sizes and roughness decrease with increasing the process temperature.

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