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Effect of C_2H_2 flow rates and microwave powers on the synthesis of sp^3 carbon on glass substrates

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In this research, sp^3 and sp^2 carbon was deposited on glass substrates in 10-100 ml/min flow rates of C_2H_2 at 650, 750 and 900 W microwave for 5 sec each. Raman analysis revealed the presence of sp^3 and sp^2 carbon at 1534-1599 and 1325-1377 cm^{-1}, corresponding to the G and D bands, respectively. Both sp^3 and sp^2 contents were controlled by the C_2H_2 flow rates and microwave powers. By using X-ray diffraction (XRD), selected area electron diffraction (SAED), atomic force microscopy (AFM) and scanning electron microscopy (SEM), the carbon films of nanoparticle colonies were detected.

Key words: sp^3 carbon, Microwave-assisted synthesis, Raman analysis, Nanoparticles.

Introduction

Diamond-like carbon (DLC) is a material that has very attractive properties, such as high hardness, good resistance to wear, low friction coefficient, chemical inertness, electrical insulator and optical transparency [1, 2]. It has attracted a lot of interest for application in microelectromechanical (MEM) devices, magnetic storage disks and optical parts [2]. There are different methods used to produce DLC: magnetron sputter-type negative ion source [1], radio frequency-plasma enhanced chemical vapor deposition [3], low energy dense plasma focus [4] and microwave ECR plasma CVD [5].

Microwave-assisted synthesis is very attractive process used for producing materials. It is able to reduce reaction times which lead to very high temperatures and have the influence to accelerate reaction rate. When microwave radiation was supplied to chemicals, their components were capable of coupling with a vibrating electric field of the radiation. Vibrations of the reactants play the role in the reaction to proceed with efficiency. Finally, pure products were produced [6]. The purpose of the present research was to produce sp^3 carbon thin films on glass substrates using a microwave radiation, which is simple, rapid, environmentally benign and effective.

Experiment

Each of 1 cm × 1 cm glass substrates was put in a quartz chamber which was tightly closed. The air was evacuated to 1.425 kPa pressure, and 20 ml/min Ar was fed into the chamber until at 101 kPa (1 atm) pressure and kept on flowing through this chamber for 20 min. Then different C_2H_2 flow rates (10-100 ml/min) were added, and the pressure was also regulated to be at 2.125 kPa by evacuation. The deposition was done using 650, 750 and 900 W microwave for 5 sec each. In the end, the samples were left cool down to room temperature in 20 ml/min Ar and brought for further analysis.

The products were characterized by X-ray diffractometer (XRD, SIEMENS D500) operating at 20 kV, 15 mA, and using Cu-K_α line, in combination with the database of the Joint Committee on Powder Diffraction Standards (JCPDS) [7]; scanning electron microscope (SEM, JEOL JSM-6335F) operating at 15 kV; transmission electron microscope (TEM, JEOL JEM-2010) and selected area electron diffractometer (SAED) operating at 200 kV; atomic force microscope (AFM, NanoScope IIIa, MMAFML N, Veeco) with silicon tip driven at a frequency of 200-300 kHz tapping mode; and Raman spectrometer (T64000 HORIBA Jobin Yvon) using a 50 mW and 514.5 nm wavelength Ar green laser.

Results and Discussion

Raman spectroscopy is a common technique used to characterize DLC films [3, 4, 8], produced using 650, 750 and 900 W microwave and 10-100 ml/min flow rates of C_2H_2 for 5 sec. The spectra (Fig. 1) were composed of two prominent G and D peaks [4] at 1534-1599 and 1325-1377 cm^{-1}, respectively. They were specified that the deposited films were composed of a mixture of sp^3 or C-C (diamond) and sp^2 or C = C (graphite) bonded carbon [1, 8-11]. The G peaks [8, 12] correspond to the symmetric E_{2g} C-C stretching mode of sp^3 carbon [1, 12].

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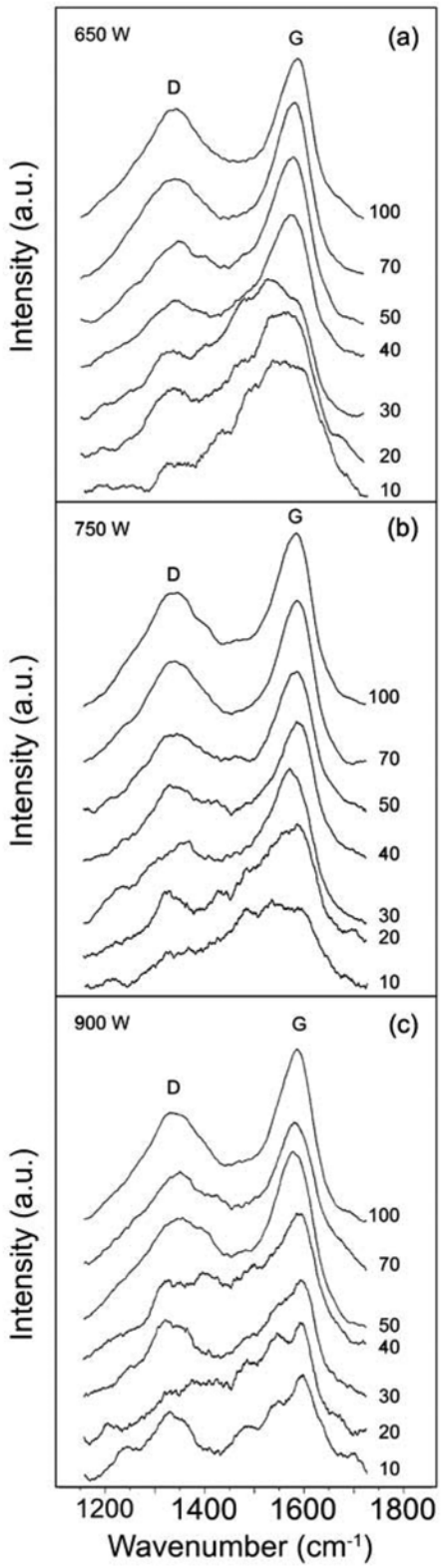

Fig. 1. Raman spectra of thin films produced in 10-100 ml/min flow rates of C_2H_2 at (a-c) 650, 750 and 900 W microwave for 5 sec, respectively.

The D peaks [8] were caused by the breathing mode of six-fold rings [13]. They are the zone edge A_{1g} modes which become active only in the distorted system [14]. Intensity ratios of the G to D peaks (I_G/I_D) were used to specify the sp^3 (C-C) content [4, 8]. A larger I_G/I_D ratio corresponds to the higher sp^3 content. The ratios reflected the concentration of the graphite crystals in the films as well [15]. At a constant microwave power of 650, 750 and 900 W each and 10 ml/min flow rate of C_2H_2, I_G/I_D ratio was the highest. The films were mainly composed of sp^3 carbon. The sp^2 (C = C bonding) [1] was very low. When the C_2H_2 flow rates were increased from 10 ml/min to 100 ml/min, both sp^3 and sp^2 contents became higher. The ratios were decreased with the increase in the C_2H_2 flow rates. Decreasing of the ratios was caused by the increasing rate of sp^2 content that was higher than that of the sp^3. The I_G/I_D ratio was the lowest at 100 ml/min. The films were thickened and more internal stress developed. The stress may also develop by a mismatch between carbon film and the substrate [16]. The analysis indicated that sp^3 carbon firstly originated as thin films. At higher C_2H_2 flow rates and microwave powers, some of sp^3 transformed into sp^2. The increasing rates and contents of sp^3 and sp^2 carbon have the influences on the I_G/I_D ratios. Thus, the change in microwave powers and C_2H_2 flow rates can lead to the variation of the film structures and sp^3/sp^2 bonding (σ bonding : π bonding) ratios. Considering the DLC films deposited on 2024 aluminum alloy by increasing in the electrical powers at pulsed negative substrate bias voltages over the range of 0 V and −200 V, the Raman spectra exhibited the typical peaks of DLC with some difference. The shoulders at about 1360 cm^{-1} was weakened with the increasing in the bias voltage until they were no longer detected at −100 V. The bias voltage was further increased and the shoulder was detected once again at -200 V [17]. The results were in good accordance with the C1s XPS core level spectra of the films deposited by different bias voltages. The C1s XPS core level spectra were composed of three main components at 284.5, 285.3 and 287.7 eV, specified as the sp^3 carbon, sp^2 carbon and C-O or C = O of adsorbed gas on top, respectively [17]. The DLC film is enable to exist in a variety of different forms, of which the hardest one is tetrahedral amorphous carbon (t-C) -ideally consisting of purely sp^3 bonded carbon. For the present configuration, each carbon is connected by four strong covalent bonds with its neighboring carbon atoms. These bonds are symmetrically arranged in three dimensions to produce tetrahedral configurations, forming structured units similar to diamond structure. Comparing to the sp^2 carbon, the bonds are covalent arranged in the same plane with 120 deg apart by forming a two dimensional configuration. Each plane is held together by a weak van der Waals force to form graphitic lattice [18]. Another interesting allotrope of carbon is graphene which is a one-atom thick layer of carbon atoms stacked together as a two-dimensional honeycomb lattice. The main features in the Raman spectra of graphene are

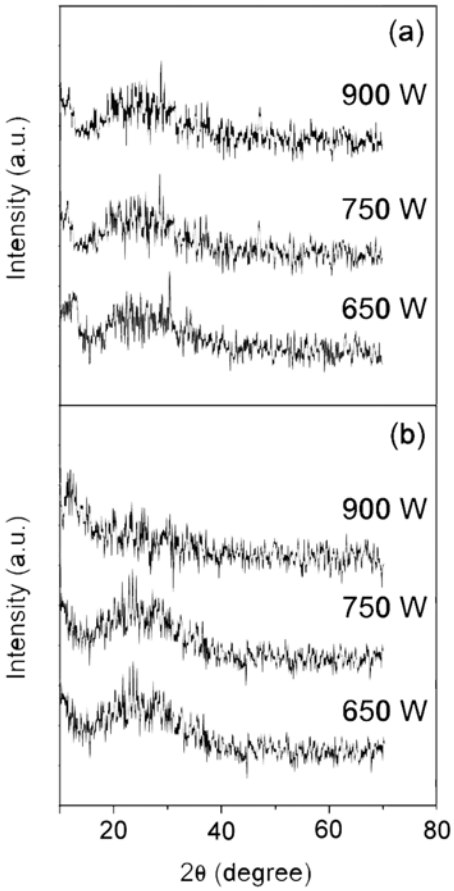

Fig. 2. XRD spectra of thin films produced in (a) 10 ml/min C2H2 and (b) 100 ml/min C_2H_2 at 650, 750 and 900 W microwave powers for 5 sec.

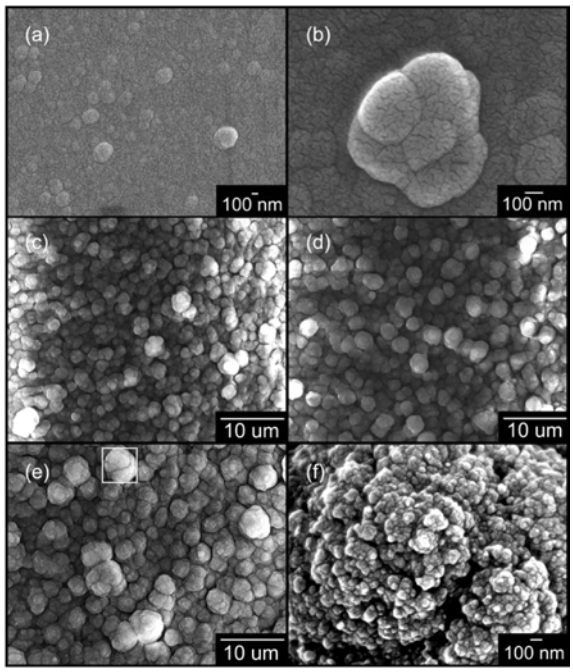

Fig. 3. SEM images of thin films produced using (a, b) 10 ml/min C2H2 at 650 W, and (c-e) 100 ml/min C_2H_2 at 650, 750 and 900 W for 5 sec, respectively. (f) the enlarge image at the square in (e).

from the phonon branch related to the zone-center Raman-active mode, i.e. to the optical phonon branch related to in-plane stretching of the C-C bonds. The strong Raman peaks of graphene are at 1583 cm^{-1} and 2700 cm^{-1}, corresponding to the G and G' peaks, respectively. The most prominent peak of graphene is detected by Raman spectroscopy at 2700 cm^{-1}, at about 2D peak [19-22].

Thin films deposited on glass substrates and the as-received glass substrates were characterized by XRD. By subtracting these spectra, the spectra of only thin films produced in 10 ml/min C_2H_2 and 100 ml/min C_2H_2 at 650, 750 and 900 W microwave for 5 sec are shown in Fig. 2. The spectra are rather broad with a wide package over the diffraction angles of 2θ ranging from 17 to 34 deg. No diffraction peaks were clearly detected. These spectra were specified that the films were amorphous [9, 23], although they were produced in 10 and 100 ml/min C_2H_2 at a power as high as 900 W. The detections of carbon using Raman and XRD analyses are in good accordance. XRD analysis did not differentiate between sp^3 and sp^2 carbon containing in these thin films, but Raman analysis did.

SEM images (Fig. 3) show surface morphologies of thin films deposited on glass substrates, produced using 650, 750 and 900 W microwave and 10 and 100 ml/min flow rates of C_2H_2 for 5 sec. They have the characteristics of deposited films containing a number of particles that protruded from their surfaces. At 10 ml/min C_2H_2 and 650 W microwave (Fig. 3(a) and 3(b)), a number of particles with different sizes were detected. Sometimes the particles were produced so close that they clustered themselves into colonies (Fig. 3(b)). These showed that the colonies grew in a random manner. When 100 ml/min C_2H_2 was used in the process, the particles (Fig. 3(c)) became larger. Their sizes (Figs. 3(c-e)) were also increased by the increasing of the microwave powers from 650 W to 900 W, which led the particles (Fig. 3(f)) to condense together.

AFM images (Fig. 4) of thin films, produced using 650, 750 and 900 W microwave and 10 and 100 ml/min flow rates of C_2H_2 for 5 sec, show traces of the thin films composing of a number of colonies of particles produced at random, which reflected their surface properties. The analyses using AFM and SEM are in good accordance. Root mean square (RMS) value, mean roughness and maximum height of thin films were increased with an increase in the microwave powers and C_2H_2 flow rates, caused by carbon deposition on the substrates. These values are the highest at 900 W microwave: RMS values = 9.4 nm and 463.4 nm, mean roughness = 7.1 nm and 363.8 nm, and maximum heights = 55.7 nm and 3,760 nm, for the 10 ml/min and 100 ml/min flow rates of C_2H_2, respectively.

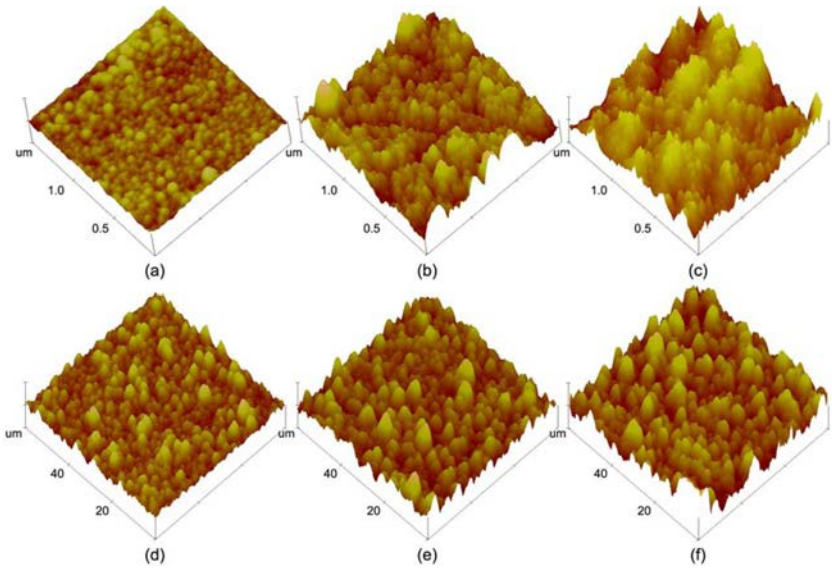

Fig. 4. AFM images of thin films produced in (a-c) 10 ml/min C_2H_2, and (d-f) 100 ml/min C_2H_2 at 650, 750 and 900 W microwave for 5 sec, respectively.

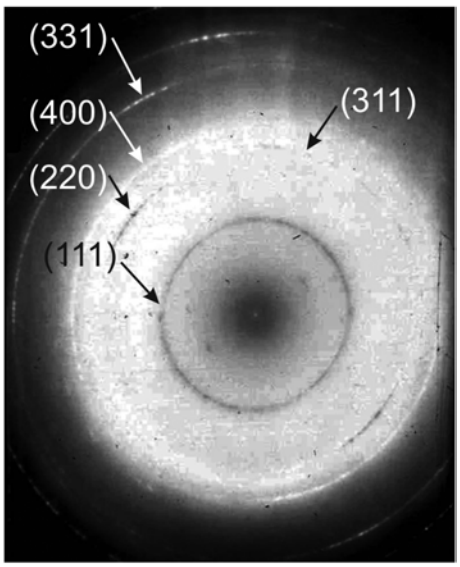

Fig. 5. SAED pattern of thin film produced in 100 ml/min C_2H_2 at 900 W microwave for 5 sec.

SAED pattern (Fig. (5)) of thin film, produced in 100 ml/min flow rate of C_2H_2 at 900 W microwave for 5 sec, is diffuse and hollow although the deposition was done at a power as high as 900 W. The analysis showed that the film was mainly amorphous. Diameters of the traces of diffraction rings were interpreted [24, 25]. Their d spaces were compared with those of the JCPDS database (reference code no. 01-1249) [7]. The traces were specified as the (111), (220), (311), (400) and (331) planes, corresponding to cubic diamond C [7].

Conclusions

The sp^3 and sp^2 carbon thin films were produced on glass substrates using 650, 750 and 900 W microwave and 10-100 ml/min flow rates of C_2H_2. The process was very successful although the microwave power was as low as 650 W. It was the rapid process, which was done within 5 sec. The films were respectively composed of two prominent G and D peaks at 1534-1599 and 1325-1377 cm^{-1}, corresponding to the sp^3 and sp^2 carbon. They were amorphous in nature, which reflected their surface properties. They were composed of cubic diamond C, when they were produced using 900 W microwave and 100 ml/min C_2H_2.

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