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Evolution of morphology and defects of graphene with growth parameters by PECVD

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Abstract

The morphology of graphene has an important impact on its applications such as sensing and energy storage. In this study, the evolution of the surface morphology and defect types of graphene that was directly grown on Al₂O₃ by plasma enhanced chemical vapor deposition (PECVD) was investigated by controlled growth conditions. It was found that the defect type of graphene was determined by the ion source power while the surface morphology of graphene was determined by the combination of growth temperature and ion source power. The type of defects of graphene changed from vacancy-like to boundary-like as the ion source power increased, and the morphology of graphene changed from two-dimensional (2D) to three-dimensional (3D) as the temperature rose or the power of the ion source increased. The hydrophobicity of graphene was well correlated with surface morphology, in which the contact angle of graphene changes from 78° to 132° with the change of graphene from 2D to 3D.

1. Introduction

Graphene, due to its high carrier mobility, superior thermal conductivity, and the richness of optical properties [1–3], has the potential to be used in important areas such as sensors [4, 5], solar cells [6, 7], energy storage [8], and electronic devices [9]. Due to the excellent properties and extensive applications of graphene, many methods have been developed for synthesizing graphene, which include mechanical peeling [10], SiC sublimation [11], graphene oxide reduction [12], chemical vapor deposition (CVD) [13] and PECVD [14]. PECVD is a catalyst-free direct growth method, which avoids complex and fuzzy transfer process for applications. Currently, PECVD has become a widely used method for the synthesis of graphene. Due to its low synthesis temperatures, direct growth of graphene has been demonstrated on different substrates, such as metallic substrates of Cu and Ni [15, 16], semiconducting substrates of Ge, Si, and GaN [17–19], and dielectric substrates of SiO₂ [20]. The synthesis of graphene with 2D and 3D structures has been reported by PECVD. In 2011, without using any catalyst, 2D-graphene with a size about tens of nanometers was directly grown on different substrates (such as insulators, semiconductors, and even metals) by PECVD at a relatively low temperature of 550 °C. The resistance and optical properties of graphene was characterized, in which a transmittance of higher than 92% and 85%, and a relatively low resistance of 40 and 7 kΩ/square was obtained at a wavelength around 550 nm, on quartz and glass, respectively [21]. 3D-graphene which was vertically erected graphene walls was also grown by direct PECVD at 900 °C on SiO₂ substrates without using any catalyst [20]. It was found that the qualities and properties of 3D-graphene are strongly dependent on the plasma power and growth time. The morphology and microstructure of 3D-graphene evolved with different growth times revealed a two-level growth process which is composed of continuous vertically erected graphene sheets (the second level) on a nanocrystalline graphene film.
(the first level) in PECVD. With the decrease of plasma power, the 3D-graphene structure became sparser. Song et al. [22] further investigated the effect of the 3D-graphene morphology on different substrates by PECVD at 750 °C, in which Si, SiO2, GaAs, Ge, and carbon fiber substrates were employed. It was found that the morphology of 3D-graphene was not sensitive to substrates, in which similar morphologies and structures can be obtained on different substrates with the same preparation process. The evolution of 3D-graphene was also studied at different growth stages [23], from which the relationship between morphology and growth time was revealed. It was found that as the growth time increased, the height of 3D-graphene increased while the number density and the defect density decreased. Recently, Ghosh et al. [24] reported on the effect of the key process parameters such as deposition temperature, discharge power and distance from plasma source to substrate on the catalyst-free growth of 3D-graphene and found that the increased growth temperature was conducive to the formation of stable nanostructures in the interconnected vertical network normal to the substrate, and the number density of vertical sheets decreased while the dimensions of the sheets and inter-sheet spacing of 3D-graphene increased with the increased distance. The growth rates and areal density can be controlled by changing the ion source power. Physically, the growth mechanism of graphene with 2D or 3D structure in PECVD as reported in recent years involves multiple factors and the complicated coupling effect of these factors [24–27], such as stress relaxation and defects accumulated through multilayer graphene films or nanographitic islands [25, 26], inherent electric field [26, 27] and thermophoretic force along with supersaturation of the carbon source [24] and a simultaneous etching process by nascent hydrogen [27]. Due to the complexity of the growing mechanism and its related growing conditions, precise preparation of 2D and 3D structures of graphene, which are required for different applications, is difficult. So far, there are many investigations on the morphology of graphene, further effort is required to understand on the evolution of surface morphology and defect types of graphene from 2D to 3D with growth parameters. In this paper, the evolution of the surface morphology and defect types of graphene is investigated, in which the graphene structure was directly grown on Al2O3 by PECVD. The defect type and surface morphology of graphene were studied by controlling growth conditions. It was found that the defect types of graphene were only related to the power of the ion source rather than the growth temperature and gas flow rate. The morphologies of graphene from 2D to 3D were strongly dependent on growth temperature and ion source power. To visually verify the fabricated 2D or 3D structures of graphene, experimental hydrophobicity of the graphenes is conducted, in which the contact angle of graphene changes from 78° to 132° with the change of graphene from 2D to 3D structure. This work provides the variational trend of surface morphology and defect types of graphene with the changing of growth conditions which is useful for guiding the fabrication of different type of graphene.

2. Experimental

The PECVD apparatus consists of vacuum CVD chambers, a plasma generator and a high temperature furnace. Al2O3 was washed in acetone for 5 min, then rinsed with deionized water and dried for use. The graphene layers were directly grown on an Al2O3 substrate in a PECVD reactor. Different parameters included growth temperature, ion source power, and flow rate of CH4/H2/Ar were changed to see the effect of Graphene synthesis. Firstly, to investigate the effect of growth temperature, samples were grown by changing growth temperature from 650 °C to 800 °C with ion source power of 100 W, growth time of 90 min and CH4 flow rate of 10 sccm. Secondly, to investigate the effect of ion source power, samples were grown by changing ion source power from 20 to 200 W with growth temperature of 700 °C, growth time of 90 min and CH4 flow rate of 10 sccm. Finally, to investigate the effect of gas flow rate, samples were grown on different CH4/H2/Ar flow rate of 10/0, 10/2, 10/4/4, 10/8/8, 10/16/16 and 10/4/64 sccm, with growth temperature of 700 °C, ion source power of 60 W and growth time of 90 min and CH4 flow rate of 10 sccm. The surface morphology of graphene was characterized by SEM (FEI Quanta 400 FEG, 20 KV, and S-4800, 3 KV) and AFM (Veeco; Dimension 3100). Raman spectroscopy (JY; LabRam HR 800) was carried out as a convenient tool at room temperature, in which a 532 nm diode-pumped solid-state green laser was focused on the surface of the sample through a 100x objective. Hydrophobicity of samples was measured by a contact angle measurement instrument (JCY-4).

3. Result and discussion

Raman patterns in figure 1 showed the bulk structural information of samples grown on Al2O3 substrates for growth temperature of 650 °C, 675 °C, 700 °C, 725 °C, 750 °C, and 800 °C, respectively, with ion source power of 100 W and growth time of 90 min As shown in figure 1(a), Raman spectrum with a growth temperature of 650 °C did not have any peaks. Raman spectra with growth temperatures of 675 °C–800 °C showed three obvious peaks, which were indexed at ~1352 cm−1, ~1592 cm−1 and ~2700 cm−1, corresponding to the D band, G band, and 2D band [28]. The D band represents the degree of defects in the crystal structure. The G band
is attributed to in-plane sp² phonon vibration, indicating the formation of graphitized structure. The 2D band is a second-order Raman spectrum. It should be noted that D' band that locates at about 1620 cm⁻¹ is associated with finite-size graphite crystals and graphite edges [28]. It shows that graphene can be obtained under different temperature from 675 °C to 800 °C. For defect types, the value of ID'/IG was reported to be related to the defects of graphene, in which a maximum (≈13) of ID'/ID for defects is related to sp³ hybridization, a decreased value (≈7) of ID'/ID is related to vacancy-like defect and a minimum value (≈3.5) is related to boundary-like defects in graphite [29]. As shown in figure 1(b), it was found that the value of ID'/IG stayed within 3.5 to 5 in the growth temperature range of 675 °C–800 °C, which indicated that these were boundary-like defects and defect types were not sensitive to growth temperatures. The Raman ID'/IG ratio was extensively used to estimate the quality of graphene and the degree of disorder, because of inversely proportional to crystallite or grain size [30, 31]. From figure 1(b), the grain size of graphene can be estimated to be ∼12.8 nm, according to the formula [30]

$$\text{La(nm)} = 2.4 \times 10^{-10} \times \lambda^4 \times (\text{ID'/IG})^{-1},$$

when the wavelength of the excitation laser, $\lambda$, is 532 nm and the ID'/IG ratio is around 1.5 shown in figure 1(b). At the same time, it indicated that the defect density hardly changed with the rising of growth temperature.

The effect of ion source power on epitaxial graphene and defect types was also investigated and shown in figure 2. Raman spectra of graphene samples on Al₂O₃ substrates with ion source powers ranging from 20 to 200 W at 700 °C in 90 min were shown in figure 2(a). It is seen that when the ion source power is 20 W, the D and G peaks can be seen without 2D peak in figure 2(a), indicating that only carbon is deposited on the Al₂O₃ substrate. When the ion source power was increased between 40 W and 200 W, significant 2D peaks showed up, which meant that graphene could be formed under these power conditions. As shown in figure 2(b), it was found that the ratio of ID'/IG was around 7 when the ion source power was between 40 W and 60 W, which suggests a vacancy-like defect as mentioned above. When the ion source power was increased to between 80 W and 200 W,
the defect types of graphene had transformed to boundary-like defects from vacancy-like defects. In other words, the defect types could be effectively controlled by changing the ion source power. The Raman ID/IG ratio indicated that the defect density for graphene is relatively high when compared with that of 0.05 of low defect density by CVD \[32\]. The ratio of I_{2D}/IG was between 0.55 and 0.90, which represented that the thickness of graphene was between 3 and 10 layers \[33\].

Then, we investigated the effect of the flow rate of CH\(_4\)/H\(_2\)/Ar on the graphene quality. Figure 3(a) shows the Raman spectra of the grown graphene with different flow rate of CH\(_4\)/H\(_2\)/Ar at 10/0/0, 10/2/2, 10/4/4, 10/8/8, 10/16/16 and 10/4/64 sccm, respectively, with a plasma power of 60 W and growth time of 90 min at 700 °C. The peaks of D, G and G’ band could be seen clearly in these six spectra. It suggested that the flow rate of CH\(_4\)/H\(_2\)/Ar hardly affect the synthesis of graphene within this gas flow rate range. As shown in figure 3(b), in which samples were labeled as S1, S2, S3, S4, S5 and S6 for different gas flow rate of 10/0/0, 10/2/2, 10/4/4, 10/8/8, 10/16/16 and 10/4/64 sccm respectively, I_{2D}/I_G was always about 7 when the ratio of CH\(_4\)/H\(_2\)/Ar varied, which suggests a vacancy-like defect as mentioned above, indicating that the type of defect is independent of the gas flow rate of CH\(_4\)/H\(_2\)/Ar. The ratio of I_{2D}/IG was significantly increased from S1 (i.e., no H\(_2\) flow introduced) to S2, and then remained basically unchanged with the increasing of H\(_2\) flow rate from S2 to S6, indicating that the defect density of graphene was increased in the H\(_2\) atmosphere, regardless of the H\(_2\) flow rate.

The uniformity analysis was also performed for a typical grown graphene sample using Raman mapping. Figure 4 shows the Raman mapping of a one-step growth sample over 10 μm × 10 μm area with growth temperature of 700 °C, ion source power of 40 W, growth time of 90 min and CH\(_4\)/H\(_2\)/Ar flow rate of 10/0/0 sccm. In Raman analysis, the excitation laser spot was about 1 μm, and the Raman data were obtained at every 0.5 μm over the 10 μm × 10 μm area. The graphene Raman mapping data was obtained by Gaussian fitting.
The maps of $I_D/I_G$ and $I_{2D}/I_G$ were shown in figures 4(a) and (b), respectively. As can be seen from figures 4(a) and (b), good uniformity of the grown graphene can be obtained with the average values of $I_D/I_G$ and $I_{2D}/I_G$ being about 2.712 and 1.072, respectively, which suggests that the average grain size was $\sim 7.1$ nm and the thickness of graphene was about 3 layers according to Raman data reported in the literature as mentioned before.

The morphology of the grown graphene at different temperatures and ion source powers was further investigated. Figure 5 shows the SEM images (figures 5(a)–(c)), AFM images (figures 5(d)–(f)) and height profiles (figures 5(g)–(i)) of graphene on Al$_2$O$_3$ at 700 $^\circ$C/100 W, 700 $^\circ$C/200 W, and 800 $^\circ$C/100 W, respectively. The growth time and the gas flow rate are the same for all the samples, which are fixed at 90 min and CH$_4$/H$_2$/Ar flow rate of 10/0/0 sccm. In figures 5(a) and (d) (i.e., sample at 700 $^\circ$C/100 W), there was no fold and the depth of graphene was about 1.5 nm as shown in profile AA’ in figure 5(g). The root-mean-square (RMS) roughness of the graphene was 0.53 nm over the selected 10 $\mu$m $\times$ 10 $\mu$m area, which meant that the graphene had a 2D morphology. In figures 5(b) and (e) (i.e., sample at 700 $^\circ$C/200 W), a 3D morphology was observed, in which the surface structure was similar to vertical graphene nanosheets with the sizes of vertical graphene nanosheets ranging from 50 to 350 nm and the height of vertical graphene nanosheets ranging from 15 to 50 nm, as clearly shown in profile BB’ in figure 5(h). The RMS roughness of the graphene in figure 5(e) was 5.91 nm over the 10 $\mu$m $\times$ 10 $\mu$m area, which indicated that graphene was transformed from 2D to 3D structure with the increased ion source power. At higher growth temperatures or ion source powers, it is favorable for the migration and chemisorption of carbon atoms, a nanocrystalline graphene film is quickly obtained as a buffer layer, the further nucleation occurs at the mismatch of a nanocrystalline graphene film (a buffer layer) and the active sites for growth can be the surface steps as well as the edges at the top. graphene is grown in normal to the substrate, which eventually forms a stable nanostructure in interconnected vertical networks normal to the substrate [24]. In figures 5(c) and (f) (i.e., sample at 800 $^\circ$C/100 W), the nanosheets of the 3D-graphene were further connected with each other and then formed a wall-like network. The height of graphene was about...
120 nm as shown in profile CC’ in figure 5(i). The RMS roughness of the 3D-graphene was 24.8 nm over the measured 10 μm × 10 μm area. Compared figure 5(a) with figure 5(c), it is also seen that the graphene could be transformed from 2D to 3D structure with increasing growth temperature. As a result, it can be concluded that the different morphologies of graphene from 2D to 3D structure can be controlled by changing the growth temperature or ion source power.

To visually verify the fabricated 2D or 3D structures of graphene, experimental hydrophobicity of the graphene was conducted, in which a water contact angle test was performed. As shown in figure 6(a), the surface of a naked Al₂O₃ was completely wet, the water droplet brought into contact with the solid spontaneously formed a film with a water contact angle of ∼27°. When graphene was grown on Al₂O₃ at 700 °C with ion source power of 100 W, the surface contact angle was increased to 78°, as shown in figure 6(b), which is a typical contact angle of a 2D graphene [34]. The contact angle of the fabricated graphene with ion source power of 200 W at 700 °C reached 99° (figure 6(c)), which suggests a 3D morphology was formed, consistent with that seen in figure 5(b). When the growth temperature was increased to 800 °C with an ion source power of 100 W, the contact angle of the graphene further reached 132° as seen in figure 6(d). This means the 3D morphology of the fabricated graphene was further enhanced with the increased growth temperature, which is also consistent with that observed in figure 5(c). The results of the hydrophobicity of the graphene fabricated at different conditions give us a correlation between the morphology and hydrophobicity, which permits estimation of the surface morphology and defect types of the graphene from 2D to 3D by ion source power and growth temperature, which has practical significance in future applications.

4. Conclusions

In summary, we revealed the evolution of the surface morphology and defect types of graphene by controlling growth temperature, ion source power, and gas flow rate. It was found that defect types can be adjusted by changing the ion source power, which changes from vacancy-like to boundary-like when the ion source power is increased from 40 W to 200 W. The defect density of graphene is increased in the H₂ atmosphere, regardless of the H₂ flow rate. 2D-graphene can be obtained at the growth temperature of around 700 °C and the ion source power of around 60 W. As the temperature increases or the power of the ion source increases, the morphology of graphene transforms from 2D to 3D. The surface morphology of the fabricated graphene was further correlated with the hydrophobicity, in which the contact angle of graphene is well consistent with the surface morphology from 78° to 132° with the structure change of graphene from 2D to 3D. This provides an effective way to regulate the surface morphology and defect types of graphene from 2D to 3D by ion source power and growth temperature, which has practical significance in future applications.

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