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Short communication

Comparative analysis of graphene grown on copper and nickel sheet by microwave plasma chemical vapor deposition

Xiao Zhao, Li Gou*

College of Materials Science and Engineering, Sichuan University, Chengdu, China

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ABSTRACT

Microwave plasma chemical vapor deposition (MPCVD) is expected to prepare graphene film at a low temperature and a short growth time. So the same and different process conditions were designed to deposit graphene on Cu and Ni sheets. Despite the atom arrangement of Cu (111) and Ni (111) corresponding to graphene, the different films were obtained at the same process due to the difference in electron configuration of 3d shell of two elements. Carbon atoms penetrated into Ni sheet and segregated to form graphene while graphene film was grown on Cu surface directly. The different growth mechanism resulted in different preparation conditions on substrates where graphene grown on copper sheet preferred mild conditions. It is high energy and large density of microwave plasma that leads to dense surface of substrate and strong etching on graphene film, which is different from chemical vapor deposition (CVD) process.

Graphene with different outstanding properties and well-prospective applications has attracted researchers' attention [1–3], which is synthesized by mechanical exfoliation [4], oxidation-reduction, epitaxial growth over SiC [5,6], and chemical vapor deposition (CVD) [7]. Among these methods, the CVD technique gives promise for large-area graphene growth and large-scale production [8–10]. In the process of preparing graphene, copper and nickel metal are commonly used as substrates where the growth mechanism of graphene is different owing to lower carbon solubility in copper and higher carbon solubility in nickel [11,12]. Xuesong Li [13] reported that carbon diffused into the Ni first and then segregated and precipitated at the surface of Ni, while graphene was grown on Cu foil by surface adsorption using ^{12}C and ^{13}C isotope labeling. Compared to CVD, microwave plasma chemical vapor deposition (MPCVD) is considered as a highly efficient and stable method for the deposition of graphene at a low temperature, short growth time and continuous production [14–18]. However, the growth mechanism of graphene was usually discussed in the CVD method, for example, the effect of the crystal structure of copper. As reported that the Cu (111) facet was proposed to be the ideal surface to produce uniform monolayer graphene with high-quality [19,20]. Copper and nickel were used as substrates in both MPCVD and CVD, but the related mechanisms were studied more in CVD and less in MPCVD. MPCVD with the features such as large density of plasma and high energy might lead to different effect on the graphene growth from CVD process.

In the present paper, graphene is to be grown on Cu and Ni sheet by MPCVD under same process conditions and different conditions. It is noticed that copper and nickel has same crystal structure and different 3d shell of the electron configuration. In addition, MPCVD has much impact on Cu and Ni substrate compared with CVD process. So it is important to study what's the difference and why is different for the graphene growth using MPCVD method in order to grow graphene with high quality.

Graphene film synthesis was performed in a self-made bell jar type MPCVD system [21] with H_2 and CH_4 as feed gases. Copper or nickel sheet (0.4 mm thick, 99.99% purity) as the substrate was polished to the mirror by abrasive paper with different specifications, then ultrasonically washed in acetone for 5 min and ethanol for 10 min, respectively, and dried. The whole deposition generally involved three phases. First, the substrate was pretreated in H_2 (200sccm) plasma for 30 min to clean the substrate and remove the surface oxide. Second, CH_4 was introduced to deposit film in short time about 5–10 min. The surface morphology of substrate varied with the pretreatment and duration. After that, in order to etch graphite, microwave plasma post-treatment was directly performed for 5 min in the hydrogen at a lower microwave power.

The composition of graphene films was obtained by Raman

* Corresponding author.
E-mail address: gouli@scu.edu.cn (L. Gou).

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spectroscopy (LabRAM HR, France) with 532 nm excitation wavelength. X-ray diffraction (XRD, X'Pert Pro MPD, Netherlands) was used to characterize crystal orientation of the substrate at grazing incidence angle of 2°. Additional surface morphology and uniformity of graphene films were observed by scanning electron microscope (SEM, JSM-7500 F, Japan).

Fig. 1 shows the SEM micrographs of graphene grown on nickel substrate without pretreatment and pretreatment of 30 min. The graphene film was prepared at a gas pressure of 2.7 KPa, a microwave power of 1300 W, 1.67% of methane diluted in hydrogen for 5 min. It can be seen that loose surface without pretreatment is gone instead of dense surface due to re-crystallization and grain growth after hydrogen plasma treatment. In the MPCVD process, it is the pretreatment that acted as a significant factor in graphene synthesis. Initial preheating and annealing of substrate led to re-crystallization at the nickel surface where graphene film was grown continuously. Fig. 1d also exhibits multilayered graphene film on nickel with pretreatment for 30 min at a high magnification. Fig. 2a compares the Raman spectra of graphene shown in Fig. 1. There are three obvious resonant peaks, a D-band near 1350 cm^{-1}, a G-band near 1580 cm^{-1} and a 2D-band at 2700 cm^{-1}, among which G and 2D band are intrinsic resonant modes of graphene and can be designated as in-plan doubly degenerate phonon mode with E_{2g} symmetry and inter-valley process [22–24]. The defects resulted in the appearance of D-band. As reported that the peak intensity ratio (both I_G/I_D and I_{2D}/I_G), the shape and full width at half maximum (FWHM) of the 2D peak have been used to characterize single- and few-layer graphene [25]. Raman spectra of obtained film are the indicatives of multilayer graphene, such as a 2D-band to G-band intensity ratio (I_{2D}/I_G) less than 1, and a symmetric 2D-band with FWHM value of 71–83 cm^{-1}. According to Fig. 2a, the I_{2D}/I_G of graphene with treatment for 30 min and without pretreatment are 0.54 and 0.52, respectively, indicating the number of graphene layers is more than 4. Fig. 2b shows the XRD of two nickel sheets after graphene deposition. There is no difference in crystal structure between pretreatment and without pretreatment. The crystallographic plane orientation of substrate is still dominated by (111) plane after treatment. However, the grains on nickel substrate grew and surface became denser, which promoted the growth of graphene with the higher ratio of I_{2D}/I_G shown in Fig. 2a.

Fig. 3 shows the Raman spectra of films on copper and nickel substrate pretreated for 30 min in hydrogen plasma and deposited 5 min in the mixture of methane and hydrogen simultaneously. It can be seen that a 2D-band at 2714 cm^{-1} and G-band at 1583 cm^{-1} appears in the Raman spectrum of graphene film on Ni sheet. The I_{2D}/I_G ratio (0.54) and FWHM (83 cm^{-1}) of 2D peak indicate a multilayered graphene film on Ni (111). For the film grown on Cu (111) with same process, the intensity of 2D peak is extremely low and the G to D peak intensity ratio (I_G/I_D) is around 1.34. It seems that few graphene films are grown on Cu (111) at the condition suitable for Ni. The broaden D-band and G-band proved the formation of amorphous carbon on the copper substrate. As shown in the inset in Fig. 3a, the Raman spectra of free-standing graphene film free Ni and Cu displayed D band, G band and obvious 2D band, which indicated there is no significant difference between the Raman spectra of the graphene on substrates and free substrates. Fig. 3b shows the XRD pattern of copper sheet with a (111) orientated plane after graphene growth. The structure match was presented to explain the growth of graphene. Fig. 4a shows the graphene grown on copper or nickel substrate in terms of structure correspondence. The atoms arrangement on the Cu or Ni (111) plane is corresponding to carbon atoms of graphene. The location of the three carbon atoms was determined by the location of metal atoms, and then these three carbon atoms were bonded to other carbon atoms to form graphene by sp^2 hybridization. The Cu (111) and Ni (111) substrates are suitable for the graphene deposition in structure. However, the different films were obtained under the same conditions. There must be other factors affecting graphene growth. We proposed to explain this phenomenon from the electron configuration of the atom.

As shown in Fig. 4b, the electron configurations for Cu and Ni are [*Ar*] $3d^{10}4s^1$, and [*Ar*] $3d^84s^2$, respectively. The 4s electrons of Cu

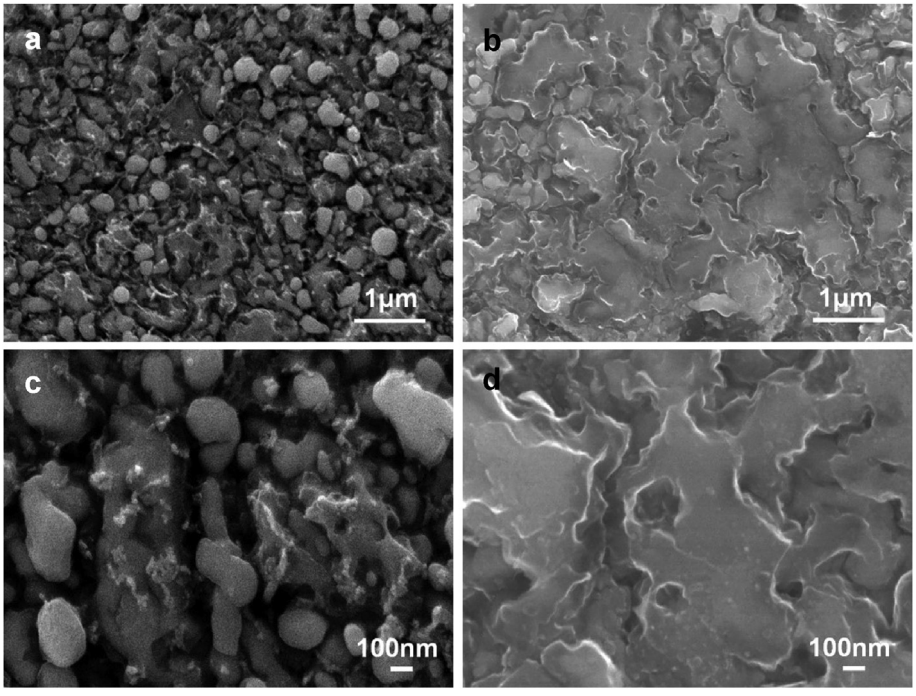

Fig. 1. SEM images of graphene films on Ni, (a, c) without pretreatment, (b, d) pretreated for 30 min.