CVD Growth of Mono- and Bi-Layer Graphene from Ethanol

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1. Introduction

Graphene, a monolayer of sp^2-bonded carbon atoms with a honeycomb structure, has triggered numerous fundamental studies due to its unique properties such as superb mechanical strength and quantum transport. Due to the fact that mechanically-exfoliated graphene [1] cannot fulfill the requirement of electronic applications, the development of large-scale, high-quality graphene production methods have been motivated.[2-5] Among these methods, chemical vapor deposition (CVD) on polycrystalline metal substrates has attracted most attention recently, because of its low cost and operation simplicity.

Many kinds of carbon precursors have been employed to synthesize graphene, such as methane [6], ethane [7] and ethanol [8]. Here we report a systematic study on CVD growth of graphene on Cu and Ni substrates from ethanol. Ethanol has proven effective in the synthesis of high-purity single-walled carbon nanotubes, and it is expected that these advantages would also apply in the synthesis of graphene. Results show that compared with widely-used methane, ethanol is also capable of synthesizing high-quality, large-scale graphene. We track the carbon atoms during the CVD process using $^{12}C_2H_5OH$, $^{13}C_2H_5OH$, and $^{13}CH_3{}^{12}CH_2OH$ precursors, and investigate the growth mechanism on Cu and Ni substrates using Raman spectroscopy.

2. Experiments

We adopt commercially available Cu foils and thermally evaporated/deposited Ni films as substrates. A 10-μm-thick Cu foil is first cleaned using HCl solution, acetone and 2-proponal before it is placed in hot-wall CVD chamber, and then heated to the reaction temperature of 900-1050°C. The foil is then annealed for another 1 hour to increase the grain sizes and obtain a smooth surface. 3% H_2 in Ar is used throughout the heating and annealing processes. After flowing ethanol vapor with different flow rate and pressure, the CVD chamber is cooled to room temperature (~25°C).

As to Ni film substrate, after it is heated to 900°C, ethanol vapor flow is immediately introduced into the CVD chamber without any further annealing process. After a short CVD period, the ethanol flow is stopped and the system is rapidly cooled (~10-20°C/s) to room temperature.

Various ethanol flow rates, pressures, and cooling rates have been investigated for both types of substrates. As-grown graphene film is then transferred by spin-coating a thin protection layer of poly(methyl methacrylate) (PMMA) and then etching the metal layer. We characterize the transferred graphene samples by scanning electron microscope (SEM), micro-Raman spectroscopy, and atomic force microscopy (AFM).

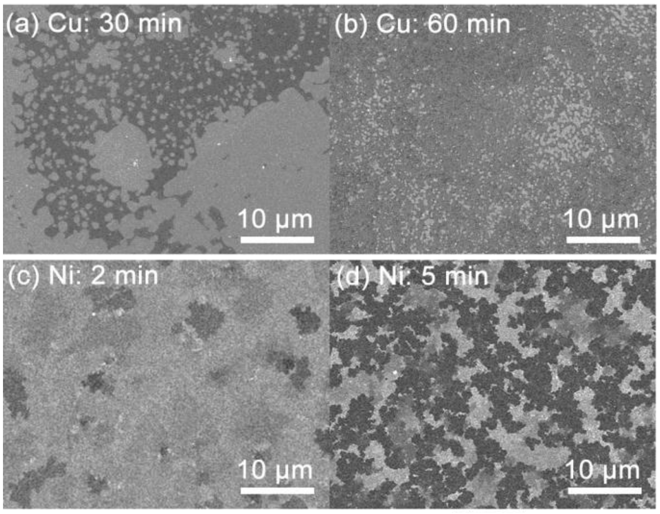

Fig. 1: SEM images of graphene with different morphologies grown on (a, b) Cu and (c, d) Ni substrates.

3. Results and discussion

SEM images of as-grown graphene films on metal substrates are shown in Fig. 1. For graphene growth on Cu relatively long CVD reaction time is required. When 30 minutes ethanol flow is introduced, graphene flakes are formed on Cu surface with a low coverage [Fig. 1(a)], whereas 60 minutes ethanol flow increases this coverage to more than 90% [Fig. 1(b)]. Fig.1(c) and (d) show the graphene morphology on Ni substrates, in which a CVD reaction time of 2 minutes has already achieved a full coverage of graphene films, whereas extended growth time only increases the number of graphene layers.

The Raman spectra of graphene films grown on Cu and Ni also confirm that graphene films have been successfully synthesized from ethanol (Fig. 2). The Raman spectrum feature measured from a graphene sample provides direct information about its number of layers, e.g., a monolayer graphene (MLG) usually displays a very high intensity ratio between the 2D and G peaks (I_{2D}/I_G), as well as a very narrow symmetric 2D peak [9]. Recently, it was revealed that Raman features of twisted bi-layer graphene (BLG) are similar to those of MLG [10]. Here we temporarily discuss MLG and BLG from classical Raman assignment. To investigate the graphene quality grown from ethanol, we plot the contour maps of I_{2D}/I_G and 2D full-width at half-maximum (FWHM) for both Cu- [Fig. 2(a, b)] and Ni-

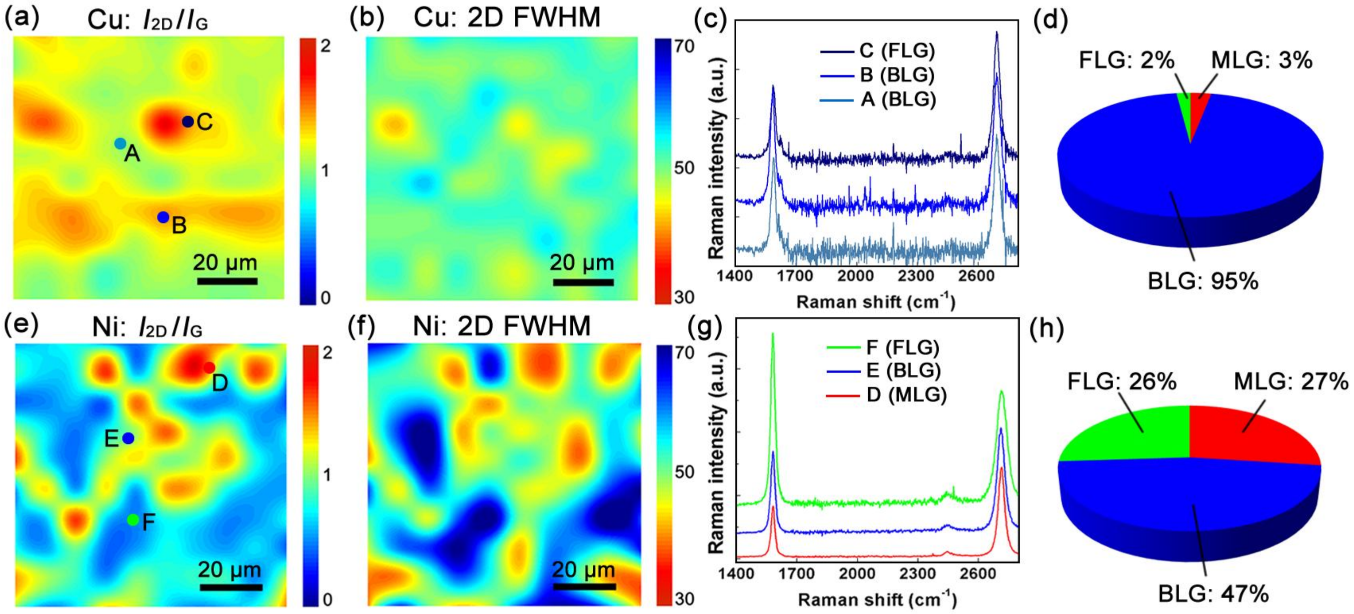

Fig. 2: Raman spectroscopic analyses of as grown graphene after transferred on Si/SiO$_2$ substrates. Raman maps of I_{2D}/I_G and 2D FWHM of graphene grown on (a, b) Cu and (e, f) Ni. (c, g) Raman spectra of three corresponding points in (a, e). The percentages of MLG, BLG and FLG graphene grown on (d) Cu and (h) Ni.

derived [Fig. 2(e, f)] graphene transferred on Si/SiO$_2$ substrates. Typical Raman spectra of the graphene films with different numbers of layers are shown in Fig. 2(c) and (g) for Cu and Ni, respectively. Graphene films grown on copper are predominantly composed of BLG, with a small portion of mono- and few-layer graphene (FLG, layer number >2) [Fig. 2(d)]. On the other hand, for graphene films grown from Ni, their numbers differ significantly from MLG to FLG [Fig. 2(h)]. The CVD conditions of the samples we show here are 80 Pa, 100 sccm ethanol flow and 1000°C for Cu, and 300 Pa, 50 sccm ethanol flow and 900°C for Ni.

More parametric studies show that the growth mechanisms of graphene for both Cu and Ni using ethanol as precursor are different from those using methane. These differences are probably due to the low bond-dissociation energies and various decomposition products of ethanol, which complicate the solid-gas interface reaction for the graphene formation. Additional experiments using isotope labeling of ^{12}C and ^{13}C ethanol also show that at least for Ni-derived graphene from ethanol, surface adsorption growth process plays a dominant role rather than a segregation/precipitation process that occurs for graphene from methane. [11]

5. Conclusion

We have synthesized graphene films on both Cu and Ni substrates using ethanol as the CVD precursor. SEM images and Raman spectroscopy confirm the quality of the grown graphene, which is at least comparable with those derived from methane. Systematic studies help understand the effect of CVD parameters on the quality and number of layers of graphene, and possible growth mechanisms are investigated.

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