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COMMUNICATION

Precise control of chemical vapor deposition graphene layer thickness using $\text{Ni}_x\text{Cu}_{1-x}$ alloys

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We investigated a simple but effective method to precisely control the desired number of graphene layers on the $\text{Ni}_x\text{Cu}_{1-x}$ alloy substrates by thermal chemical vapor deposition. Our method could be utilized to precisely control the number of graphene layers without altering growth conditions such as growth temperature, and the cooling rate.

Graphene, a two-dimensional nanostructure of sp^2 -bonded carbon atoms, has attracted worldwide interest owing to its novel and unique properties such as its high charge mobility, quantum Hall effect, and high optical transparency, flexibility, and electrical and thermal conductivities.¹⁻⁵ However, the realization of graphene-based optoelectronic, electronic, and chemical devices requires the development of a reproducible, large-scale method to produce single- or few-layer graphene films with high crystalline quality. In particular, it is well recognized that one of the most promising application areas of graphene is in transparent electrodes for solar cells or touchscreen displays. For these applications, the precise control of graphene layer growth is essential to achieve uniform electrical and optical properties. Accordingly, intensive efforts have been devoted to develop an economic and reproducible method allowing the synthesis of graphene with the appropriate quality. Since graphene mechanically exfoliated from graphite flakes was introduced by Geim et al. in 2004, many graphene synthesis methods have been demonstrated such as chemical exfoliation from bulk graphite powders, chemical reduction from graphene oxides, and chemical vapor deposition.^{3, 6-11} Among these, chemical vapor deposition (CVD) of hydrocarbons on transition metal substrates is believed to be the most promising because of its simplicity, scalability, and its ability to produce large graphene sheets at a relatively low cost, and with reasonable crystalline quality.¹²⁻¹⁴ The CVD of graphene on various transition metals such as Pt, Co, Ru, Cu, and Ni has been explored extensively and great progress has been achieved.^{15,16} In recent work, primarily Cu and Ni have been used as catalysts and the growth mechanism of graphene on Cu and Ni substrates has been investigated^{13, 17-21} With a Cu catalyst, since the solubility of carbon in Cu is very low or negligible even at a high growth temperature of 1000 °C, it is utilized mainly to form a graphene monolayer through carbon adsorption on the Cu surface from the decomposition of hydrocarbon gas.^{13,21} However, the

formation of small regions of double- or multilayers on Cu substrates has also been reported.^{22, 23} The reasons why multilayer regions are formed on Cu substrates are not yet clear. On the other hand, with a Ni catalyst having a high carbon solubility of about 1.3 at.% at 1000 °C, carbon is dissolved in the metal at this growth temperature. As the substrate is cooled, the solubility of carbon in Ni decreases such that graphene segregates and then grows on the surface.²¹ Hence, in order to obtain the desired number of graphene layers, both the substrate temperature and cooling rate must be adjusted precisely.

Accurately controlling the thickness (that is, the number of layers) and the uniformity of graphene is important if it is to be used as a substitute for transparent conducting oxides such as indium tin oxide (ITO). Recently, Reina et al. reported the possibility of growing one or two graphene layers by controlling both the carbon concentration and the substrate cooling rate during the CVD process.²⁴ On the other hand, Chen et al. reported the synthesis of graphene films on commercial Cu-Ni alloy foils by CVD with methane and hydrogen gas as precursors.²⁵ They tried to control the thickness and quality of the graphene and graphite films by varying both the deposition temperature and the cooling rate. However, in the cases mentioned above, the simultaneous control of two different growth parameters suggests a great deal of work is required to obtain the desired thickness of graphene. Moreover, the growth parameters need to be adjusted and optimized for each CVD growth system, which requires tedious and laborious efforts. In this study, we present a new growth method to precisely control the number of graphene layers without altering any growth parameters other than the catalytic metal substrate. $\text{Ni}_x\text{Cu}_{1-x}$ alloys are used as substrates whose composition is varied systematically to obtain the desired number of graphene layers.

The compositions of the $\text{Ni}_x\text{Cu}_{1-x}$ alloys were regulated by varying the thickness ratio of Cu and Ni layers. In order to obtain specific $\text{Ni}_x\text{Cu}_{1-x}$ alloy compositions, Ni (purity 99.995%, Alfa Aesar) films with different thicknesses were deposited on SiO_2/Si substrates prior to the deposition of the Cu (purity 99.999%, Alfa Aesar) film using a thermal evaporator. Table 1 shows the FE-SEM results of Cu and Ni thicknesses and its thickness ratio. Low pressure CVD was employed to anneal the metal substrate and

synthesize the graphene layer. After loading a 2×2 cm² single (Cu or Ni) or Cu/Ni double-layer substrate, the reactor was evacuated to approximately 50 mTorr and then filled with 1600 sccm Argon (Ar, 99.999% purity) and 200 sccm Hydrogen (H₂, 99.999% purity). Then, the reactor was heated to the growth temperature of 900 °C at a rate of 30 °C/min for 30 min then maintained for 20 min of annealing to form Ni_xCu_{1-x} alloys. For the synthesis of graphene, 20 sccm of C₂H₂ gas was injected for 20s into the reactor at 900°C. However, for the analysis of the Ni_xCu_{1-x} alloys, the reactor was air-cooled down to room temperature on completion of the annealing process. X-ray diffraction (XRD, X'Pert PRO MPD, PANalytical) analysis was performed to measure the crystalline structure, lattice parameter, and composition of the Ni_xCu_{1-x} alloys. The graphene samples were coated with polymethyl methacrylate (PMMA, Sigma Aldrich) diluted in chlorobenzene (Sigma Aldrich) at 4.31 wt.% to protect the graphene films. The PMMA was spin coated for 30s at 4000 rpm. The metal films were detached from the SiO₂/Si substrate using a buffer oxide etchant (BOE) solution to remove the silicon oxide, and then floated in diluted ammonium persulfate ((NH₄)₂S₂O₈) solution (1 M) to remove the metal alloys. After the metal film was etched, the PMMA/graphene film was rinsed 5 times using deionized water (DIW). The floating PMMA/graphene films were transferred onto glass slides and placed over blowing N₂ gas to eliminate the DIW. The film was then soaked in acetone for 30 min to remove the PMMA. The synthesized graphene was analysed a lab-made laser confocal Raman spectroscopy with spectrometer, and its optical transmittance and sheet resistance were also measured by UV/Vis spectrometer (S-3100, Scinco) and 4-point probe system (1 mm-spacing, 40-70 gms- spring force, 250 μm- radii osmium probe head, C4S 54/1S).

Figure 1 shows cross-sectional and plane view field-emission scanning electron microscopy (FE-SEM, Hitachi S-4300SE) images of Cu (sample S1), Cu/Ni bilayer (samples S2–S6), and Ni (sample S7) thin films deposited on SiO₂/Si substrates, whose compositions are given in Table 1.

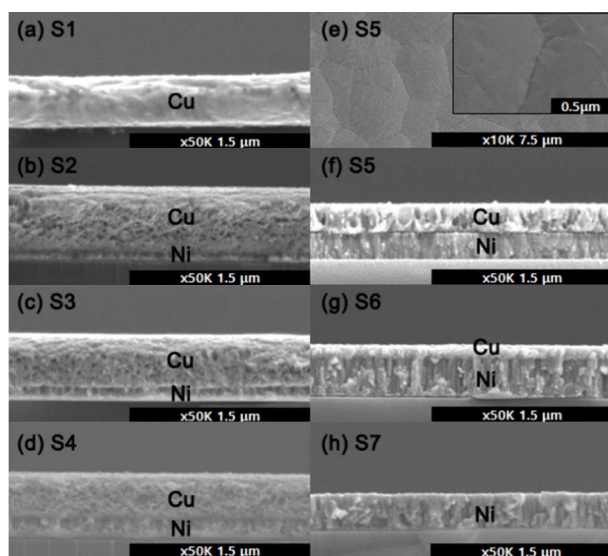


Figure 1. Cross-section SEM images at 50k magnification of Ni-Cu layers with Ni accounting for (a) S1: 0%, (b) S2: 10%, (c) S3: 18%, (d) S4: 33% (f) S5: 46%, (g) S6: 75%, and (h) S7: 100% of the total thickness. (e) S5 is plain view image of the after graphene growth with clear wrinkles and grain boundary. Inset shows high magnification (50k) image of grain boundary of Ni-Cu alloy and covered with uniform graphene surface and wrinkles on the surface.

Table 1. The FE-SEM results of Cu and Ni thicknesses and its thickness ratio.

Sample I.D.	S1	S2	S3	S4	S5	S6	S7
Cu thickness (nm)	428	534	491	400	246	119	0
Ni thickness (nm)	0	60	106	200	213	351	301
<u>Ni thickness</u> total thickness	0.0	0.10	0.18	0.33	0.46	0.75	1.0

Both 20 min annealing of alloying for the Cu/Ni bilayer and 20 s graphene growth process on Ni_xCu_{1-x} alloys were performed in a CVD reactor at 10^{-3} Torr and 900 °C as described above. For annealing for alloying, the diffusion lengths of Cu in Ni and Ni in Cu were found to be 668.7 nm and 1106 nm, respectively, demonstrating that 20 min of annealing leads to well alloyed samples (see the electronic supplementary information 2, EIS 2). In this experiment, our concern is not so much for the total thickness of the metal but for the thickness ratio of Ni and Cu. Because the mole fraction of the Ni_xCu_{1-x} alloy is determined by the thickness ratio of the metal as far as the total thickness of the metal is within the diffusion length of carbon atom in it under our growth conditions. The diffusion lengths of carbon species in Ni_xCu_{1-x} alloys at 900 °C were calculated to find out whether 20 min annealing for alloying were sufficient for the formation of Ni_xCu_{1-x} alloys (S2–S6)²⁶. Based on our calculation, see the EIS 2, the total thicknesses of metals (S2 to S6) used in this experiment are found to be within the diffusion length of carbon species in the metal under our growth conditions.

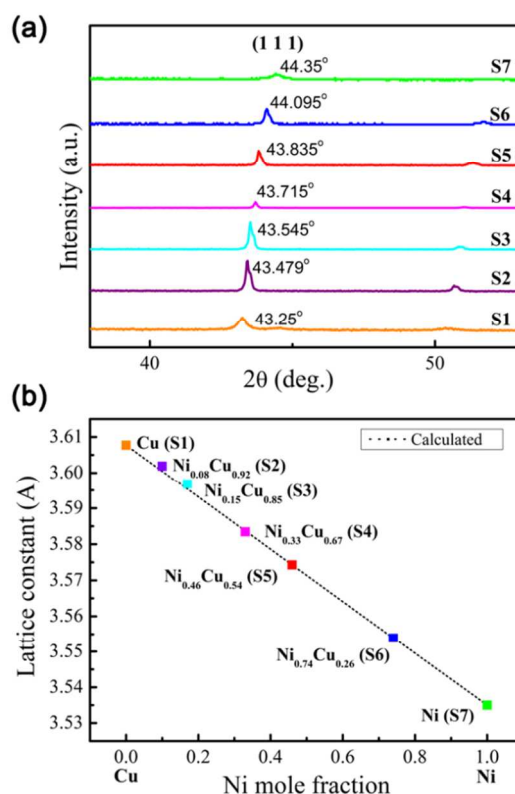


Figure 2. After annealing, (a) XRD spectra of Ni-Cu films with different thickness ratios, and (b) graph of the Ni mole fraction calculated from Vegard's law for Ni_xCu_{1-x} alloys.

X-ray diffraction analysis was carried out to confirm the Ni_xCu_{1-x} compositions after alloying. Figure 2 (a) shows the 111 reflection peak positions obtained for the Cu (S1), Ni_xCu_{1-x} alloys (S2–S6),

and Ni (S7) samples. The peaks at 2θ of 43.25° for sample S1 and 44.35° for sample S6 correspond to the 111 reflections of Cu and Ni, respectively, whereas peaks are observed at 43.479° , 43.545° , 43.715° , 43.835° , and 44.095° for the $\text{Ni}_x\text{Cu}_{1-x}$ alloy samples S2, S3, S4, S5 and S6. The lattice parameters and alloy compositions for samples S2, S3, S4, S5 and S6 were calculated using the XRD data and plotted in Figure 2 (b). In Figure 2 (b), the black dotted line and the squares respectively represent the theoretical values calculated from the Cu and Ni lattice parameters using Vegard's law, and the experimental results from the XRD peaks. The Ni mole fractions in samples S1 through S7 are found to be 0.0, 0.08, 0.15, 0.33, 0.46, 0.74, and 1.0, respectively. Thereby, the Ni mole fractions obtained by XRD are almost coincident with the Ni thickness ratios measured by SEM, indicating that the mole fractions of the $\text{Ni}_x\text{Cu}_{1-x}$ alloys can be controlled effectively by varying the Ni/Cu thickness ratios.

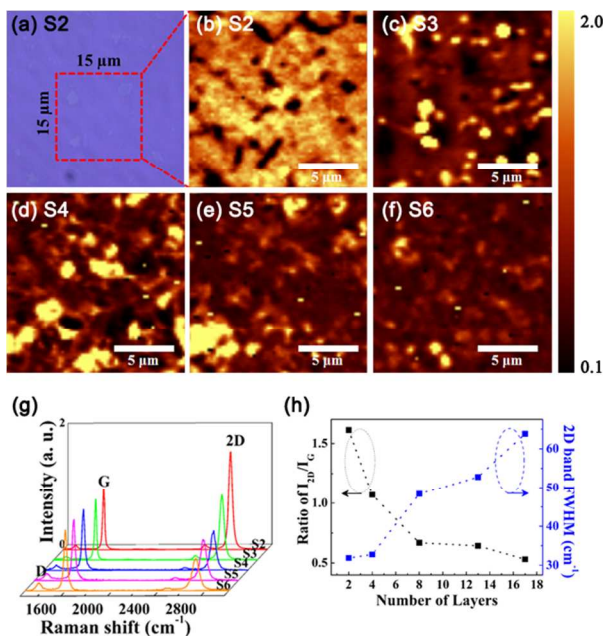


Figure 3. The optical image (a), the I_{2D}/I_G Raman mapping of the S2, S3, S4, S5 and S6 (b) ~ (f). The Normalized average Raman spectrum of the S2, S3, S4, S5 and S6 (g), the intensity ratio of 2D/G band and the FWHM of 2D band corresponding to the number of graphene layers on $\text{Ni}_x\text{Cu}_{1-x}$ substrates (h). The Raman maps have the same scale ($15\ \mu\text{m} \times 15\ \mu\text{m}$) and scale bar (0.1~2.0) for I_{2D}/I_G ratio.

The results of the confocal Raman spectroscopy are shown in Fig. 3. The confocal Raman spectroscopy was used to determine the relationship between the Ni mole fractions of the $\text{Ni}_x\text{Cu}_{1-x}$ alloys (samples S2–S6) and the uniformity and thickness of the synthesized graphene films. Figure 3 (a) shows optical image of S2, Fig. 3 (b) ~ 3 (f) represent the variations in the I_{2D}/I_G peak ratios for samples S2, S3, S4, S5 and S6, respectively. The mapping results were obtained over a relatively large central area of $15\ \mu\text{m} \times 15\ \mu\text{m}$, where darker areas represent increased number of graphene layers. As can be seen in the figure, the distributions of graphene layers with defects such as darker or lighter pixels were confirmed through all samples. In case of samples S4, S5 and S6, relatively large number of graphene layers compared to samples S2 and S3 were distributed across the surface, varying thickness as indicated by the contrast observed. Fig. 3 (g) shows the normalized average Raman spectra of mapping each area for samples S2, S3, S4, S5 and S6, with a D band at $\sim 1342\ \text{cm}^{-1}$, a G band at $\sim 1581\ \text{cm}^{-1}$, and a 2D band at $\sim 2680\ \text{cm}^{-1}$. From S2 to

S6, the average 2D/G intensity ratio over the areas analysed is reduced from 1.61 to 0.53 and the full width at half maximum (FWHM) of the 2D peak is increased from 31.86 to $63.82\ \text{cm}^{-1}$. The average intensity ratio of 2D/G band and the variations in FWHM of 2D band corresponding to the number of graphene layers was shown in detail in Fig. 3 (h). Thereby, as the Ni mole fraction increases from 0.08 to 0.74, the average I_{2D}/I_G ratio is reduced from 1.61 to 0.53, which means that the number of synthesized graphene layers increases with the Ni content. As the number of graphene layers increases, the crystalline quality is found to improve, as indicated by the decreased D band intensity.

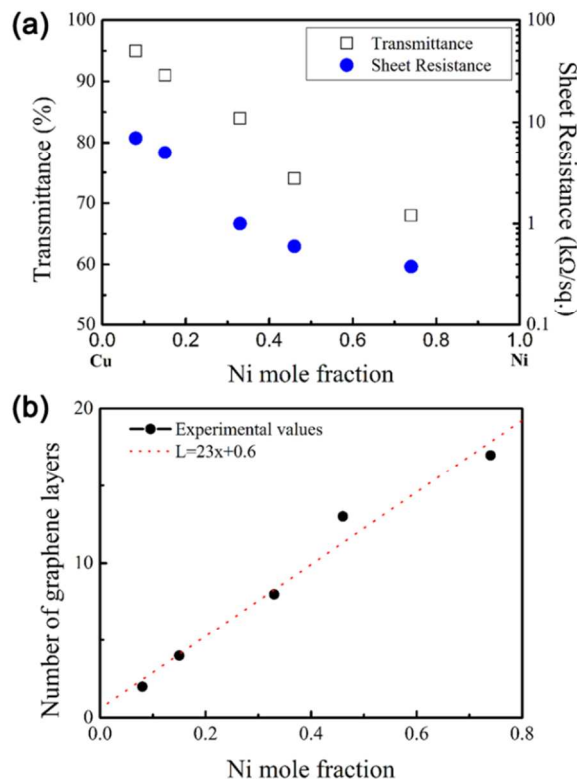


Figure 3. (a) Transmittance at 546 nm and sheet resistance of graphene, and (b) the number of graphene layers as a function of the Ni mole fraction.

In order to further evaluate the graphene layers, the optical transmittance and sheet resistance were measured for graphene films transferred onto glass slides. As shown in Figure 4 (a), the transmittance at 546 nm is approximately 95% for sample S2, which corresponds to approximately two layers of graphene considering an absorbance of $\sim 2.3\%$ for an individual graphene layer.²⁷ As the mole fraction of Ni increases, the transmittance decreases indicating increasing numbers of graphene layers, as expected. The transmittance at 546 nm is found to be about 68% for sample S6. The sheet resistance decreases logarithmically as the Ni mole fraction increases. The lowest sheet resistance of $\sim 355\ \Omega/\text{sq}$ was measured for sample S6, which has a Ni mole fraction of 0.75. The thickness of graphene was calculated using the Beer-Lambert law, $T = \exp(-4\pi kd/\lambda)$, where T is the transmittance, k is the extinction coefficient (1.3), d is the graphene thickness, and λ is the wavelength (546 nm). Figure 4 (b) shows the number of graphene layers as a function of the Ni mole fraction. The number of graphene layers was obtained by dividing the calculated thickness by the thickness of a graphene monolayer. The number of graphene layers is thereby found to be 2, 4, 8, 13, and 17 for samples S2, S3, S4, S5 and S6,

respectively (see the ESI 5), such that the number of graphene layers increases linearly with the Ni mole fraction. In Figure 4 (b), the linear dotted line represents the function $L = Ax + B$, where L is the number of graphene layers, A represents the slope, B the intercept, and x is the Ni mole fraction. Using the fitting program (Microcal Origin 6.0), $L = 23x + 0.67$ was obtained. When $x = 0.0$ (Cu substrate) $L = 0.67$, meaning that a single layer of graphene is grown on the Cu substrate. On the other hand, when $x = 1.0$ (Ni substrate), the resulting number of graphene layers is 23. This demonstrates that the Ni mole fraction can be adjusted to obtain the desired number of graphene layers by using this linear equation. Then, the thickness ratio of Cu and Ni required to grow the desired number of graphene layers can be derived from the Ni mole fraction. Thereby, the number of graphene layers can be controlled precisely by modulating the Cu/Ni thickness ratio -which is almost coincident with the Ni mole fraction in the $\text{Ni}_x\text{Cu}_{1-x}$ alloys- without changing any other growth parameters such as the temperature or the cooling and gas flow rates. Furthermore, once the number of graphene layers grown on the Ni substrate is confirmed by experiment for all growth conditions, the Ni mole fraction, x , can be calculated using the above equation and the desired number of graphene layers obtained using the appropriate $\text{Ni}_x\text{Cu}_{1-x}$ alloy substrate.

Conclusions

In summary, we introduce a simple but effective method to precisely control the number of graphene layers by using $\text{Ni}_x\text{Cu}_{1-x}$ alloy substrates in which the mole fraction, x , is determined by the thickness ratio of Cu and Ni layers. Cu (sample S1) and Ni (sample S7) substrates, as well as four different thickness ratios of Cu and Ni (samples S2 through S6) were deposited on SiO_2/Si substrates using a thermal evaporator. The as-deposited Cu/Ni bilayer films were alloyed in a CVD growth chamber. We found that the Ni mole fraction in the $\text{Ni}_x\text{Cu}_{1-x}$ alloys coincided well with the Cu/Ni thickness ratio. It is therefore possible to control the mole fraction, x , of $\text{Ni}_x\text{Cu}_{1-x}$ alloys by modulating the thickness ratio of Cu/Ni bilayer substrates. We also found that the number of graphene layers was linearly proportional to the Ni mole fraction in the $\text{Ni}_x\text{Cu}_{1-x}$ alloys, growing as $L = 23x + 0.67$. We believe that the desired number of graphene layers can be obtained by modulating the Cu/Ni thickness ratio without changing any other growth parameters such as the temperature or the cooling and gas flow rates.

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Notes and references

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