The effect of copper pretreatment on graphene synthesis by ion implantation into Ni/Cu substrate

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Received 28 February 2018, revised 25 April 2018
Accepted for publication 14 May 2018
Published 4 June 2018

Abstract

Synthesis of graphene on Ni/Cu bilayer substrate by ion implantation is sensitive to the quality of the Ni/Cu substrate. In this work, different pretreatments of Cu foils were implemented to elucidate the role of Cu pretreatment on graphene synthesis. Four types of pretreatments including polishing, annealing at 950 °C, annealing at 1000 °C, and annealing at 1050 °C were conducted prior to the growth of the Ni coating layer. Four different Ni/Cu substrates were implanted by carbon ions and annealed to obtain monolayer graphene. It shows that the impurity particles emerging on the Cu foils annealed at 1000 °C and 1050 °C affect the crystalline quality of the synthesized graphene. In addition, the increase in roughness due to the polishing process induces non-uniformity of the obtained graphene. Overall, annealing at 950 °C is proven to be the proper pretreatment for Cu foil, and the corresponding graphene film has excellent crystalline quality and uniformity compared to those obtained on the substrates with other pretreatments.

Supplementary material for this article is available online

Keywords: graphene, ion implantation, impurity precipitation

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene has attracted intense research interest in nanoelectronics and optoelectronics due to its extraordinary physical properties [1–3]. As a building block for the graphene-based device, the synthesis of graphene with good uniformity and controllable layer numbers is an essential prerequisite [4–6]. However, it is still challenging to precisely control the layer numbers of graphene using the traditional chemical vapor deposition (CVD) method. It is reported [7], that by conducting carbon ion implantation with a specific dose into the Ni layer of Ni/Cu bilayer substrate, graphene with good uniformity and tunable layer numbers can be synthesized by the subsequent annealing. In this Ni/Cu bilayer substrate, Ni has a high carbon solubility of 1.3 at% at 1000 °C, while the solubility of carbon in Cu is extremely low (<0.001 at%) at 1000 °C [8]. The inter-diffusion of Ni and Cu at high temperature formed Cu-Ni alloy with reduced carbon solubility, making the implanted carbon ions in Ni layer expelled to the surface and transformed to graphene [7]. As the carbon...
content is solely determined by the implantation dose, the ion implantation approach is less sensitive to thermal processing conditions compared to CVD method. It is known that the industrial Cu foils have high surface roughness and many impurities [9]. The pretreatment of Cu foil is found to influence the uniformity and quality of graphene obtained by ion implantation into Ni/Cu bilayer substrate, but scarcely studied.

In this work, the influence of Cu pretreatments, including polishing and annealing, on the graphene synthesis by ion implantation into Ni/Cu bilayer substrate is intensively studied. It is found that the crystalline quality of graphene is degraded due to the precipitates of impurities on the Cu foils after annealing at 1000 °C and 1050 °C. Furthermore, the polishing-induced roughness increment results in the non-uniformity of graphene. In comparison, Cu foil annealed at 950 °C possesses good roughness and less impurity precipitate, therefore the graphene film with excellent crystalline quality and uniformity is obtained on Ni/Cu bilayer substrate by ion implantation.

2. Experimental methods

The Cu foils (25 μm, Alfa Aesar, Item No.046365) were firstly washed in dilute acetic acid, acetone, and isopropyl alcohol for 10 min. Then, four types of Cu pretreatments were implemented. The first Cu sample was pretreated by mechanical polishing and then electrochemical polishing. The Cu sample was firstly mechanical polished to reduce its roughness and then loaded into home-made electrochemical polishing equipment for 15 min to further reduce the roughness and contaminations. The electrochemical polishing solution was phosphoric acid and the electrode was a clean copper plate. To improve the surface flatness and grain size, three Cu foils were loaded into a furnace tube and annealed in a mixture of Ar/H₂ (200/50 sccm) flow at 950, 1000 and 1050 °C for 1 h. After different pretreatments, a 300 nm thick Ni layer was deposited on Cu foils using an electron beam evaporator to form Ni/Cu bilayer substrates. Carbon ions were implanted into the Ni/Cu bilayer substrate with an energy of 60 keV and a dose of \(4 \times 10^{15}\) atoms/cm². According to the SRIM Monte Carlo Code [10], the projected range of the implanted carbon ions with 60 keV energy in Ni is about 73 nm with a spread of 31 nm, which is within the thickness of evaporated Ni film. The implantation dose was designed to obtain a monolayer graphene film. The implanted samples were then annealed at different temperatures for 30 min in a horizontal quartz tube (50 mm inner diameter) with a mixture of Ar/H₂ (200/5 sccm) flow. After annealing, the furnace was cooled down to room temperature under the same gas flow rate, as schematically shown in figure 1.

In order to evaluate the quality of synthesized graphene, the graphene films were transferred by a conventional PMMA-assisted wet-transfer method. A PMMA solution was spin coated onto the top side of the sample at 2500 rpm. Then the PMMA film was baked at 120 °C for 3 min. The PMMA/graphene/Cu-Ni alloy sample was then placed onto the surface of a 0.1 M ammonium persulfate aqueous solution for 1 h to etch away the Cu-Ni alloy substrate. After the Cu-Ni substrate was completely etched away, the PMMA/graphene was scooped out with SiO₂ substrate and then the PMMA film was removed by acetone.

Raman scattering (HORIBA Jobin Yvon HR800) using an Ar⁺ laser with a wavelength of 514 nm and a spot size of 1 μm was carried out to characterize the thickness, quality, and uniformity of the graphene films. FE-SEM (Field-Emission Scanning Electron Microscope) was used to characterize the surface morphology of pretreated Cu foils. EDS (Energy Dispersive Spectrometer) was used to analyze the impurity precipitate on the pretreated Cu foils. AFM (Atomic Force Microscope) was utilized to characterize the roughness of polished Cu foils and annealed Cu foils.

3. Results and discussions

3.1. Raman characterization of the as-synthesized graphene films

Figure 2 shows the Raman spectra of the graphene films obtained on differently pretreated Ni/Cu bilayer substrates, which are implanted with C ions after the subsequent growth annealing at 900 °C, 920 °C and 940 °C. The Raman spectra exhibit the D, G and 2D peaks at \(~1350, \sim1580\) and \(~2700\) cm⁻¹, respectively, which are the main characteristics of graphene [11, 12]. The intensities and shapes of the Raman peaks strongly depend on the growth annealing temperature. In general, the graphene with adequate crystalline quality is obtained at the growth annealing temperature of 940 °C. For Cu foil pre-annealed at 1050 °C, the main characteristics of the graphene film obtained are barely observed, indicating the corresponding crystalline quality is considerably poor. As the pre-annealing temperature decreases to 1000 °C, the D, G and 2D peaks emerge, but the intensity of the D peak is enhanced, suggesting the crystalline quality is improved, but still degraded. Figure S1, available online at stacks.iop.org/SST/33/074001/mmedia, shows the \(I_{2D}/I_G\) and \(I_D/I_G\) Raman mappings of the graphene obtained by ion implantation into Ni/Cu bilayer substrates with Cu pretreatment at 1000 °C, which further confirms the low quality of the synthesized graphene. When Cu foil pretreatment temperature further decreases to 950 °C, the obvious G and 2D peaks appear, and the D peak is barely observed, suggesting the crystalline quality is significantly improved. In addition, for Cu foil pretreated by the polishing process, the obtained graphene possesses considerably high crystalline quality as well.

3.2. FE-SEM and EDS characterizations of pretreated Cu foils

To investigate the effect of Cu pretreatment on the synthesis of graphene by ion implantation into Ni/Cu bilayer substrate, FE-SEM was utilized to characterize the surface morphology of differently pretreated Cu foils. As shown in figure 3(a), the polished Cu foil has some recessed areas due to the polishing process. While Cu foils pre-annealed at high temperatures...
show a rather smooth surface without recessed areas, there are some impurity particles emerging on the Cu foils annealed at temperatures above 1000 °C which may affect the synthesis of graphene, as shown in figures 3(b)–(d). For polished Cu and Cu pre-annealed at 950 °C, EDS line scans show that, in addition to Cu element, only trace amounts of Si, Ca and O elements are distributed on the surface, as shown in figures 3(e) and (f). As the pre-annealing temperature increases to 1000 °C and 1050 °C, a considerable amount of impurity elements including Si, Ca and O are detected on the surfaces other than the Cu element, and the intensities of Si, Ca and O elements reach the maximum on impurity particles.
as displayed in figures 3(g) and (h). It is well known that the industrial Cu foils inevitably contain impurities such as Si and Ca [13], therefore, it is hypothesized that the impurity particles mainly originate from the precipitation of impurities that are already present inside the industrial Cu foils. During the annealing process, the impurities in the Cu foils may precipitate at the Cu surface and be oxidized by the residual O2 during the growth annealing process [13]. According to the Ellingham diagram, Si oxidized at any oxygen partial pressure higher than $\sim 10^{-26}$ atm at 1000 °C and Ca oxidized at any oxygen partial pressure higher than $\sim 10^{-40}$ atm at 1000 °C [13, 14]. However, even 99.999% pure Ar gas still contains 1–2 ppm of oxygen, which is high enough to oxidize Si and Ca [13]. As shown in figure S2, the number and size of impurities on the Cu surface becomes higher with the increase of annealing temperature. When the annealing temperature is 950 °C, almost no impurity particle precipitates to the Cu surface. When the annealing temperature rises to 1000 °C and 1050 °C, large impurity particles with a diameter ranging from 200 nm to 400 nm emerge and higher annealing temperatures yield more large particles. Due to the fact that the thickness of deposited Ni layer is only 300 nm, the impurity particles with large diameter have disastrous effects on the synthesis of graphene on the Ni/Cu bilayer substrate by ion implantation and severely disturb the uniform inter-diffuse of the Ni and Cu layer. In the subsequent growth annealing process after carbon ion implantation, small holes are observed on the Ni/ Cu pre-annealed at 1000 °C and Ni/ Cu pre-annealed at 1050 °C, which is the consequence of inhomogeneous inter-diffuse of Ni and Cu (as shown in figure S3). The formation of small holes on the Ni-Cu alloy surface promotes the accumulation of carbon atoms and then leads to the formation of few-layer graphene or amorphous carbon.

3.3. Raman characterization of the transferred graphene films

To better visualize the crystalline quality and uniformity of graphene, all graphene films were transferred onto oxidized silicon substrates for further Raman characterization. Raman spectra of graphene transferred from Ni/polished Cu show poor uniformity (shown in figure 4(a)). Raman spectra of graphene transferred from Ni/ Cu pre-annealed at 950 °C shows better uniformity with weak D peaks and intensity of $I_{2D}/I_G$ over 1.2, as shown in figure 4(b). A representative Raman spectrum of the monolayer graphene film transferred from Ni/ Cu pre-annealed at 950 °C is also provided in figure S4. The Raman intensity ratios of the 2D/G peak and the D/G peak are 1.94 and 0.11, respectively. In addition, the Raman spectrum of monolayer graphene also has a symmetric 2D band with a full width at half maximum (FWHM) of $\sim 31.7$ cm$^{-1}$, which can be well fitted by a single Lorentzian curve [11], which proves the synthesized graphene is monolayered with few defects.

Raman mapping measurements at a 12 μm $\times$ 12 μm scale were also detected to further confirm the uniformity of graphene films. Figure 5 depicts the Raman mappings of $I_{2D}/I_G$ and $I_D/I_G$ for the graphene films transferred from Ni/ polished Cu and Ni/950 °C annealed Cu. For the graphene film transferred from Ni/polished Cu (as shown in figures 5(a) and (b)), more than 52.9% of the graphene area has an $I_{2D}/I_G$ ratio $> 1.2$, and more than 85.1% of the graphene area has an $I_D/I_G$ ratio $< 0.1$. For the graphene film transferred from Ni/ Cu pre-annealed at 950 °C (as shown in figures 5(c) and (d)), more than 95.4% of the graphene area has an $I_{2D}/I_G$ ratio $> 1.2$, and more than 80.8% of the graphene area has an $I_D/I_G$ ratio $< 0.1$. These two kinds of graphene films show low defect density, but the uniformity of graphene film transferred from Ni/ Cu pre-annealed at 950 °C is much better than that transferred from Ni/polished Cu.
3.4. AFM characterizations of polished Cu and Cu pre-annealed at 950 °C

To study the effect of Cu pretreatment on the uniformity of graphene, AFM characterizations were conducted on polished Cu and Cu pre-annealed at 950 °C. The arithmetic mean deviation (Ra) at a scale of 5 μm × 5 μm is used to compare the roughness of different Cu samples. The Ra of polished Cu and Cu pre-annealed at 950 °C are 2.53 nm and 0.83 nm, respectively, as depicted in figure 6. For Cu pre-annealed at 950 °C.
450 °C, the surface has very low roughness without recessed areas compared to the polished Cu foil, thus leading to the synthesis of graphene with better uniformity.

4. Conclusion

In summary, we studied the effects of Cu pretreatments on graphene synthesis by ion implantation into Ni/Cu bilayer substrates. It was found that the impurity precipitation on Cu foils pre-annealed at 1000 °C and 1050 °C significantly affect the crystalline quality of the obtained graphene films. In addition, the roughness increase induced by the polishing pre-treatment resulted in non-uniformity of the graphene. However, Cu foil pre-annealed at 950 °C has rather low roughness and no impurity precipitation, thus yielding graphene film with excellent crystalline quality and uniformity.

Acknowledgments

The authors thank the Program of Shanghai Academic/Technology Research Leader (16XD1404200), Key Research Project of Frontier Science, Chinese Academy of Sciences (QYZDB-SSW-JSC021), National Science and Technology Major Project (2016ZX02301003), National Natural Science Foundation of China (11574338 and U1530402) and the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (Grant No. XDB04040300), City University of Hong Kong Strategic Research Grant (SRG No. 7004644) and City University of Hong Kong Applied Research Grant (ARG No. 9667122) for financial support. Partial support was also provided by the Center for Integrated Nanotechnologies (CINT), a US DOE nanoscience user facility jointly operated by Los Alamos and Sandia National Laboratories.

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