Article

Effects of Surface Engineering of Copper Catalyst on the CVD Growth of Boron-Doped Graphene with a Solid Carbon and Boron Source

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Abstract: Chemical doping of boron atoms is essential to modify the electrical properties of graphene films. The synthesis of large-scale boron-doped graphene with high uniformity and good electrical properties is still a great challenge. To improve the quality and uniformity of boron-doped graphene, we introduced several methods to engineer the surface of the copper catalyst for chemical vapor deposition. The ethylic acid treatment proved to be more effective to remove surface impurities than the hydrochloric acid treatment. Moreover, electrochemical polishing showed the best performance in reducing the impurities and surface roughness in all the methods. The sheet resistance and carrier mobility of the boron-doped graphene film grown on the electropolished copper foil were $2.35 \text{ k}\Omega/\square$ and $1.15 \times 10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature, respectively. Our results suggest that the boron-doped graphene grown on the electropolished copper catalyst possesses a high carrier mobility and less structural defects, which makes it suitable for application in optoelectronics.

Keywords: boron-doped graphene; surface engineering; electrochemical polishing

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1. Introduction

The outstanding optical [1,2] and electrical [3,4] properties of graphene have triggered numerous interests in its application as transparent electrodes [5–7] in photoelectric devices. Still, chemical doping of boron and nitrogen in graphene is necessary to create a band gap, tune the work function, and modify the carrier concentration and other useful properties [8–10]. For graphene, boron is a proper candidate that could be used to substitute carbon atoms, since it is carbon's neighbor in the periodic table and expected to induce p-type doping. Boron-doped graphene film was reported to be a potential candidate as the electrode in display screen, solar cells, and other electronic devices [11]. Thus, the synthesis of large-scale boron-doped graphene with high uniformity and good electrical properties is of great importance [12,13]. Compared to mechanical cleavage and chemical exfoliation [14], chemical vapor deposition (CVD) [15–17] is the more promising and scalable approach to produce high-quality graphene at a relatively low cost. At present, copper foil, among all the transition metals, is commonly used as the catalyst and substrate for the growth of single-layer graphene, due to its low cost and low carbon solubility [18–20]. Recent studies have demonstrated that the grain size and defects density of polycrystalline graphene could present a strong correlation with copper surface morphology, such as atomic steps and copper grain boundaries [21–23]. The surface state of the copper foil is of great importance to the growth of graphene and its physical properties [24]. Pretreatment of the copper surface can significantly reduce contamination and surface roughness, and promote the growth of high-quality graphene [25]. The removal of carbon contamination on surface and in bulk by oxygen passivation and electropolishing was reported to greatly reduce the graphene nucleation density and promote the growth of large-scale

single-crystal graphene [26–28]. However, it is still a challenge to prepare large-scale boron-doped graphene with high quality and uniformity. The aim of this study was to produce boron-doped graphene films with high-quality and tunable electrical properties for optoelectrical application. Herein, we focused on the surface engineering of the copper catalyst to modify the electrical properties of the boron-doped graphene. Three surface treatments of chemical etching and electrochemical polishing were applied to remove the impurities and smooth the copper surface before graphene growth. Among these methods, electrochemical polishing of copper catalyst proved to effectively reduce the structure defects in the boron-doped graphene with high carrier mobility.

2. Materials and Methods

Here, 25- μm -thick copper foil (Alfa Aesar, 99.8%) was used as the catalyst for the growth of the boron-doped graphene. Before deposition, the copper foil was cleaned with acetone and ethanol. Then, the copper foil was treated by being immersed in 2% hydrochloric acid (HCl) for 2 min or in 20% ethylic acid (CH_3COOH) for 10 min, or electrochemically polished in 85% phosphoric acid (H_3PO_4) aqueous solution for 2 min. After being processed by these different methods, the copper foil was loaded into a double-temperature-zone tube furnace (KJMT, 1200X-S, Hefei, China) with a quartz tube. Ethylboronic acid ($\text{C}_6\text{H}_7\text{BO}_2$, Aladdin, 98%) was used as the only solid-state carbon and boron source, and placed at the center of the low-temperature zone, while the copper foil was loaded at the center of the high-temperature zone. Then, the tube was pumped down to 2 Pa and cleansed three times with hydrogen (H_2). The high-temperature zone was heated to 980 $^\circ\text{C}$ with a heating rate of 15 $^\circ\text{C}/\text{min}$, and the low-temperature zone was heated to 220 $^\circ\text{C}$. H_2 was used as the carrier gas with a flow of 50 sccm during the 15-min growth. The system was naturally cooled down to room temperature under the same H_2 flow with an average cooling rate of 8 $^\circ\text{C}/\text{min}$. For graphene transfer, polymethyl methacrylate (PMMA, Alfa Aesar, molecular weight of 450 K, 30 mg/mL dissolved in anisole) was spin coated on the surface of the boron-doped graphene on the copper foil. After being cured at 120 $^\circ\text{C}$ for 10 min, the samples were floated on ferric chloride (FeCl_3) aqueous solution (0.5 mol/L) to remove the copper foil. The floating PMMA/graphene films were rinsed in deionized water for several times before transferred onto quartz glass or Si substrates with a 300-nm silicon dioxide (SiO_2) cap layer. Finally, acetone was used to remove PMMA.

To characterize the boron-doped graphene, an optical microscope (OM, KEYENCE, VK-9710, Shanghai, China), field-emission scanning electron microscope (SEM, FEI Quanta 600, Hillsboro, OR, USA), and transmission electron microscope (TEM, Hillsboro, OR, USA) were used to examine the surface morphology and uniformity. Raman measurements were performed using a Thermo Scientific DXR Raman microscope spectrometer (Shanghai, China) with a laser wavelength of 532 nm at room temperature. For square resistance measurements, we used a semiconductor analyzer (Agilent, B1500A, Beijing, China) combined with a four-probe station (CASCADE, alessi REL-4800, Livermore, CA, USA). Hall measurement was carried out in a physical properties measurement system (PPMS, Quantum Design, Beijing, China). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Shanghai, China) was also conducted. Before the XPS measurements, the samples were annealed in a tube furnace at 250 $^\circ\text{C}$ for 30 min with H_2 as the protective gas to remove PMMA and other possible carbon residues.

3. Results

Figure 1a,c,e exhibit the optical images of the original and acid-treated copper foil surfaces. The original surface of the copper foil is not suited for graphene growth due to its bad surface state. The copper surface without any treatment was covered with impurities and stripes with a surface arithmetic mean roughness (R_a) of 0.36 μm . The surface roughness, impurities, and defects of copper foil were reported to be of vital importance to the grain size and defects density of graphene [21,22]. Acid treatments were introduced to improve the surface of copper foil. Figure 1c,e display the optical images

of the HCl-etched copper surface and the CH₃COOH-etched copper surface, respectively. Since HCl can easily react with copper, we chose 2% HCl aqueous solution to treat the copper foil for 2 min. A higher concentration or longer time of the HCl treatment resulted in the surface residue of copper chloride and increased the surface roughness. On the other hand, the weak acidity of CH₃COOH allowed us to use the CH₃COOH aqueous solution with a high concentration of 20% and a 10-min treatment. After the treatments of the acids, the copper foil was ultrasonic cleaned in deionized water for 10 min. The HCl treatment did not form a cleaner or smoother surface, compared to the original surface, since the R_a value of the HCl-etched copper surface is 0.35 μm . On the other hand, CH₃COOH treatment evidently removed most of the impurities on the copper surface and formed a smoother surface, with an R_a value of 0.27 μm , compared to the original and HCl-etched copper surfaces. The Raman spectrum of the boron-doped graphene films synthesized on these three types of copper surfaces are displayed in Figure 1b,d,f. The intensity ratios of the D and G bands (I_D/I_G) of the boron-doped graphene grown on the original (BGO), HCl-treated (BGH), and CH₃COOH-treated (BGC) copper foil is 0.39, 0.16, and 0.27, respectively. The relatively high D band can be attributed to the combination of boron doping and structure defects [29,30]. The intensity ratios of the 2D and G bands (I_{2D}/I_G) of the graphene grown on the original, HCl-treated, and CH₃COOH-treated copper foil are 2.17, 1.52, and 2.28, respectively. These results suggest that the BGO film possesses the highest defect density in all these samples. The low I_{2D}/I_G suggests the existence of a large portion of multilayer boron-doped graphene in the BGH films, which means the HCl treatment introduced many active sites on the surface of the copper foil for the nucleation of multilayer graphene. On the other hand, the CH₃COOH treatment seems to result in more defects than the HCl treatment due to the higher I_D/I_G of the BGC film than that of the BGH film. From the comparison of the Raman spectrum, although the CH₃COOH and HCl treatments reduced the defect density, they did not produce boron-doped graphene with high quality and uniformity.

For further improvement, electrochemical polishing of the surface of the copper foil after organic solvent cleaning was introduced. The 85% H₃PO₄ aqueous solution was used as the electrolyte. The copper foil for growth was used as the anode, while another copper foil was used as the cathode. A voltage of 5 V was applied between the anode and the cathode with a distance of 4 cm during the electrochemical polishing for 2 min. For comparison with the original and acid-treated copper surfaces, the optical image of the surface of the electropolished copper foil is shown in Figure 2a. The color difference of Figure 2a with the optical images in Figure 1 is a result of the replacement of the halogen bulb for optical observation in the optical microscope. The electropolished surface is much smoother without any visible impurities, compared to the original surface as well as the acid-treated surfaces. The R_a value of the electropolished surface is 0.18 μm . Further extension of the polishing time did not lead to a reduction of the surface roughness of the copper foil. After CVD growth, the boron-doped graphene was transferred onto a copper grid for TEM analysis. For electrical application, it is necessary to transfer graphene films onto dielectric substrates. In Figure 2c, the SEM image of the boron-doped graphene transferred onto the silicon substrate with a 300-nm oxide layer is displayed. Both the TEM (Figure 2b) and SEM (Figure 2c) images show high uniformity in the boron-doped graphene grown on the electropolished copper foil (BGE). In Figure 2c, the wrinkles of boron-doped graphene are shown, which is caused by the mismatch of the coefficients of thermal expansion between the copper foil and the boron-doped graphene.

Figure 1. The optical images of the original (a), hydrochloric acid- (c), and ethylic acid-treated (e) copper foil. The Raman spectrum of the boron-doped graphene films synthesized on the original (b), hydrochloric acid- (d), and ethylic acid-treated (f) copper foil.

Raman spectroscopy is known to be a useful tool for studying the properties of doped graphene, since doping can shift the G band and greatly influence the intensity of the D band [31,32]. In Figure 2d, the G band, which corresponds to the stretching vibration of the carbon-carbon bond, is shifted to a higher frequency of 1589 cm^{-1} from the G band of the intrinsic graphene (1580 cm^{-1}). This can be attributed to the tensile strain effect induced by boron doping [33]. The I_D/I_G value of the BGE film is 0.08, much lower than those of the BGO, BGH, and BGC films, which suggests that electropolishing can effectively reduce the concentration of structure defects on the surface of the copper foils and in the boron-doped graphene. Raman mapping was conducted to investigate the homogeneity of the boron-doped graphene. In Figure 2e,f, the I_{2D}/I_G value ranges from 1.7 to 2.3, while the I_D/I_G value varies from 0.06 to 0.16. The Raman mapping results indicate that the boron-doped graphene film maintains the single-layer feature and a low defect density in an area of $20 \times 20\text{ }\mu\text{m}^2$.

Figure 2. (a) The optical image of the surface of the electropolished copper foil. (b) The TEM image of the boron-doped graphene on the copper grid. (c) The SEM image of the boron-doped graphene on the silicon substrate with a 300-nm oxide layer. (d) The Raman spectrum of the boron-doped graphene on the silicon substrate with a 300-nm oxide layer. The Raman mapping of the I_{2D}/I_G value (e) and I_D/I_G value (f) of the boron-doped graphene grown on the electropolished copper foil in an area of $20 \times 20 \mu\text{m}^2$.

Figure 3a displays the transmittance of the boron-doped graphene grown on the electropolished copper foil. The transmittance of the boron-doped graphene at 550 nm is 97.4%. Figure 3b shows the XPS spectra of C1s of the boron-doped graphene grown on the electropolished copper foil. Through multipeak analysis, four components can be identified: A peak related to sp² carbon at 283.9 eV, a peak related to sp³ carbon at 284.8 eV, and two lower peaks at 285.9 and 287.9 eV associated to oxidized C species. The presence of C–O bonding is normally attributed to the oxidation of graphene edges and defects [34,35]. Figure 3d shows the XPS spectra of B1s of the boron-doped graphene grown on the electropolished copper foil. The peak of B1s with a binding energy of 190.2 eV is associated to sp² C–B bonds in graphene, which is significantly broadened and shifted to high energy, compared with the B element (187.1 eV) and BC₄ (186.7 eV) [36]. The higher binding energy suggests that the B element was substitutional doped into the graphene film. The B/C atomic ratio was estimated to be 1.8% through fitting analysis. The growth temperature of the boron-doped graphene was found to greatly influence the doping concentration of boron. With a high growth temperature of more than 1020 °C, the boron concentration decreased below the detection limit of XPS. Thus, a low growth temperature of 980 °C was chosen.

Figure 3. The transmittance (a) and Hall resistance (c) of the boron-doped graphene grown on the electropolished copper foil. The XPS spectra of C1s (b) and B1s (d) of the boron-doped graphene grown on the electropolished copper foil.

To estimate the carrier concentration of the boron-doped graphene, the Hall resistance of the boron-doped graphene grown on the electropolished copper foil was measured at room temperature. In Figure 3c, the Hall resistance shows a linear dependence on the magnetic induction intensity of the applied magnetic field. For two-dimensional materials, the Hall resistance:

$$R_{xy} = R_H B \quad (1)$$

where R_H is the Hall coefficient, and B is the magnetic induction intensity. The hole-doped feature of the BGE films was clearly demonstrated by the positive value of the slope of the Hall resistance. From the slope of the Hall resistance, the carrier concentration of the BGE films was calculated to be $2.31 \times 10^{12} \text{ cm}^{-2}$.

Furthermore, we conducted the measurements of the sheet resistance (R_s) of the BGE films on the silicon substrate with a 300-nm oxide layer. The R_s value of the BGE films is $2.35 \pm 0.32 \text{ k}\Omega/\square$, while the R_s value of the BGO films is $3.13 \pm 0.39 \text{ k}\Omega/\square$. As a two-dimensional material, the carrier mobility of graphene can be obtained using the formula [36]:

$$\mu = \frac{1}{R_s n q} \quad (2)$$

where μ is the carrier mobility, R_s is the sheet resistance, n is the carrier concentration, and q is the elementary charge. The carrier mobility of the BGE film was deduced to be $1.15 \times 10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. The carrier concentration of the BGO film obtained from Hall measurements was $3.65 \times 10^{12} \text{ cm}^{-2}$, which led to a carrier mobility of $5.46 \times 10^2 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$. The low carrier mobility can be associated to the high defects density of the BGO film, compared to the BGE film. For further comparison, we also measured the electrical properties of the pristine graphene grown on the electropolished copper foil. The sheet resistance and carrier concentration of the pristine graphene were $1.58 \pm 0.13 \text{ k}\Omega/\square$ and $1.14 \times 10^{12} \text{ cm}^{-2}$, respectively. The carrier mobility can be calculated to be $3.47 \times 10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ consequently. The relatively high carrier concentration of the pristine graphene can be attributed to molecules adsorption from the atmosphere [9]. Since boron doping induces substitutional defects in graphene, the decreased carrier mobility of the BGE film is still higher than previous reports [8,9]. High carrier mobility of the BGE films is greatly required for appli-

cation in microelectronics [15,37], and also suggests that the electrochemical polishing of copper foil can significantly improve the quality and uniformity of boron-doped graphene.

4. Discussion

Boron-doped graphene grown on an original copper surface is defective, with a high sheet resistance and low carrier mobility due to the high surface roughness and impurities. In this study, three methods of surface engineering of the copper catalyst were introduced to obtain high-quality boron-doped graphene. Ethylic acid treatment showed a more pronounced effect in removing surface impurities than hydrochloric acid treatment. However, the BGH films showed poor uniformity with the partial multilayer region, while the BGC films still contained a considerable number of structural defects. For further improvement, electrochemical polishing was introduced and displayed the best performance of smoothing the surface of the copper catalyst as well as removing impurities in all the methods. The boron-doped graphene with high uniformity and few structural defects can be synthesized on the electropolished copper foil. The B/C atomic ratio was estimated to be 1.8% through XPS analysis. The carrier concentration and carrier mobility of the single-layer boron-doped graphene film on the electropolished copper foil was $2.31 \times 10^{12} \text{ cm}^{-2}$ and $1.15 \times 10^3 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature, respectively. Our results suggest that the boron-doped graphene grown on the electropolished copper catalyst has few structural defects and a high carrier mobility, which makes it a potential candidate for the applications in electronics and optoelectronics.

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