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## High-quality graphene grown on polycrystalline PtRh<sub>20</sub> alloy foils by low pressure chemical vapor deposition and its electrical transport properties

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High-quality continuous uniform monolayer graphene was grown on polycrystalline PtRh<sub>20</sub> alloy foils by low pressure chemical vapor deposition. The morphology of graphene was investigated by Raman spectroscopy, scanning electron microscopy, and atomic force microscopy. Analysis results confirm that high quality single-layer graphene was fabricated on PtRh<sub>20</sub> foil at 1050 °C using a lower flux of methane under low pressure. Graphene films were transferred onto the SiO<sub>2</sub>/Si substrate by the bubbling transfer method. The mobility of a test field effect transistor made of the graphene grown on PtRh<sub>20</sub> was measured and reckoned at room temperature, showing that the carrier mobility was about 4000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The results indicate that desired quality of single-layer graphene grown on PtRh<sub>20</sub> foils can be obtained by tuning reaction conditions. © 2016 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4941550]

Graphene is a two-dimensional material with honeycomb structure composed of sp<sup>2</sup>-hybridized carbon atoms. Due to its promising applications in electronics, highfrequency devices, photonic detection, sensors, and energy storage,<sup>1-6</sup> graphene has attracted a great deal of interest. In order to obtain high quality single-layer graphene, much effort has been devoted to the synthesis of graphene. Among the various developed techniques, chemical vapor deposition (CVD) has been widely used to grow large-area high-quality graphene.<sup>7,8</sup> Metal catalysts play a crucial role in the preparation of graphene by CVD. In general, polycrystalline transition metals, such as copper and nickel, are employed as catalysts and substrates to grow graphene. Due to the different carbon solubilities, single-layer graphene was obtained on Cu foil based on a self-limited mechanism, while the single-layer and multilayer graphene on Ni foil was obtained based on a segregation-precipitation growth mechanism. Therefore, the quality, uniformity, domain size, and layer count of graphene can be controlled by using different component NiCu bimetal alloys as catalysts and substrates, because their controllable carbon solubility can be tuned by changing the atomic proportions of the two elements.<sup>9–11</sup> Similarly, the transition metals platinum (Pt) and rhodium (Rh) are important catalysts in many foundational research and industry applications.<sup>12–14</sup> Most recently, they were also applied as catalysts to grow graphene.<sup>15–19</sup> On the other hand, carbon solubility in Pt was 1.4 at. % at 1000 °C and the carbon solubility in Rh was lower at 1000 °C (because of 0.4 at. % of carbon dissolved in Rh at 1300 °C). As catalysts, PtRh alloys have better electrochemical activity for alcohol oxidation as well as binary isomorphous system with an fcc crystal structure.<sup>20-22</sup> Therefore, the synergistic effect of PtRh alloys could be used to grow low-dimension nanomaterials. In addition, PtRh binary alloys have high melting points (>1772 °C), which allows the growth of graphene at high reaction temperature and possibly reduced reaction time. Gao *et al.* reported the synthesis of single- and few-layer graphene films using carbon-doped polycrystalline  $Pt_{83}Rh_{17}$  sheet in a high vacuum system. The growth of different layers of graphene was obtained by surface segregation and precipitation.<sup>23</sup> Therefore, PtRh alloy foils might have synergistic behavior for growth of graphene by tuning the atomic ratio of Pt and Rh in bimetals. So PtRh alloy foils might be promising catalysts to grow high quality graphene.

Here, we report our use of PtRh<sub>20</sub> foils as catalyst and substrate to synthesize high quality, large-area monolayer graphene under low fluxes ( $\leq 3$  sccm) of methane by low pressure CVD (LPCVD). The graphene grown on PtRh<sub>20</sub> alloy foils was transferred onto the 300 nm SiO<sub>2</sub>/Si substrate by the bubbling transfer process, so that the PtRh<sub>20</sub> foils can be used repeatedly. The morphology and layering of the graphene were characterized by scanning electron microscopy (SEM), Raman spectroscopy, and atomic force microscopy (AFM). The results indicate that a high-quality, continuous, and uniform single-layer graphene was obtained. Graphene field effect transistor (FET) devices have been fabricated by a standard e-beam lithography technique followed by a liftoff process. The electrical transport properties of the graphene were then measured at room temperature, revealing high mobility ( $\sim 4000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).

PtRh<sub>20</sub> alloy foils (0.1 mm thick, 99.9 wt. %, and the mass ratio of Pt to Rh is 8:2.) were used as both catalyst and substrate, loaded into the center of a quartz tube furnace (KLG-12Y). The furnace system was purged with H<sub>2</sub>/Ar mixed gas (H<sub>2</sub>, 10 vol. %) and evacuated to a vacuum of  $3 \times 10^{-1}$  Pa. The PtRh<sub>20</sub> foil was heated up to  $1050 \,^{\circ}$ C in 200 sccm Ar and 100 sccm 10 vol. % H<sub>2</sub>/Ar mixed gas, and the vacuum was kept at  $10^2$  Pa. Then the sample was annealed at this temperature for 30 min under the same atmosphere. At  $1050 \,^{\circ}$ C, 2–3 sccm flux of CH<sub>4</sub> was flowed to grow graphene under 100 sccm H<sub>2</sub>/Ar at  $10^4$ – $10^5$  Pa for

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FIG. 1. (a) Typical SEM image, (b) AFM height image, and (c) Raman spectrum of graphene grown on PtRh<sub>20</sub> foils at 1050 °C for 30 min under a mixed gas of 100 sccm 10 vol. % H<sub>2</sub>/Ar and 2.5 sccm CH<sub>4</sub>.

10–30 min. Then, the samples were cooled down to room temperature in the furnace under 200 sccm Ar and 100 sccm  $H_2/Ar$ . The bubbling transfer process<sup>24</sup> was used to transfer graphene onto the 300 nm SiO<sub>2</sub>/Si substrate.

The surface morphology of graphene grown on  $PtRh_{20}$  foils was characterized by SEM and AFM. The different domains on the surface of  $PtRh_{20}$  foils, which arise from the polycrystalline structure of the substrate, were observed and are shown in Figure 1(a). The surface of the  $PtRh_{20}$  foil sample had a slightly corrugated structure (Figures 1(a) and

1(b)). The results of AFM indicate that the height of a step of the  $PtRh_{20}$  surface was about 10 nm (Figure 1(b)).

In order to evaluate the quality, defects, and layer count of graphene grown on  $PtRh_{20}$  foils, Raman spectrum was used to analyze the as-grown samples. As shown in Figure 1(c), the typical Raman peaks located at about 1584 and 2698 cm<sup>-1</sup> were found, corresponding to the G band and 2D band of graphene, respectively. The D band located at 1354 cm<sup>-1</sup> was almost invisible, suggesting that high quality graphene was obtained using  $PtRh_{20}$  alloy foil as substrate.



FIG. 2. (a) Optical microscopy image and (b) Raman spectrum of graphene after transferred onto the Si/SiO<sub>2</sub> substrate. Raman maps of (c) full width at half maximum of G bands  $(1584-1590 \text{ cm}^{-1})$ ; (d) full width at half maximum of 2D bands  $(2676-2682 \text{ cm}^{-1})$ ; (e) the intensity ratios of D/G bands; and (f) the intensity ratios of 2D/G bands.

Moreover, the full width at half-maximum (FWHM) of 2D band and the integrated Raman intensity ratios of 2D to G band  $(I_{2D}/I_G)$  in Raman spectra were also used to evaluate the quality and layering of the graphene. For graphene samples prepared on PtRh<sub>20</sub>, the FWHM of 2D band was  $28 \text{ cm}^{-1}$ , typical feature of monolayer graphene.<sup>25,26</sup> The  $I_{2D}/I_G$  of graphene was 3.38 for PtRh<sub>20</sub>. These characteristics further confirm that the graphene prepared on PtRh<sub>20</sub> foils was of high quality and with monolayer structure.

The graphene samples were transferred from the PtRh<sub>20</sub> foils onto the 300 nm SiO<sub>2</sub>/Si substrate using a bubbling transfer method. An optical microscopy (OM) image of the graphene is shown in Figure 2(a). From the OM image of graphene on SiO<sub>2</sub>/Si substrate, we can clearly find that the graphene films showed almost no color change. These results show that large area and continuous graphene film were obtained on PtRh<sub>20</sub> foils. Some wrinkles and tolerable cracks in the graphene films were observed after transference, which occurs very often when using the bubbling transfer method. Raman spectrum of graphene after transfer onto SiO<sub>2</sub>/Si substrate is shown in Figure 2(b). Typical G and 2D bands, located at 1590 and 2692 cm<sup>-1</sup>, respectively, were observed. The FWHM of the symmetric 2D band was

26.5 cm<sup>-1</sup> and intensity ratios of 2D to G band  $(I_{2D}/I_G)$  was 5.3, indicating that the graphene was monolayer. A weak D band located at 1352 cm<sup>-1</sup> was also observed when graphene was transferred onto SiO<sub>2</sub>/Si substrate, derived from wrinkles and cracks. The intensity ratio of D to G bands was very small (~0.2), indicating that the defects in graphene produced with PtRh<sub>20</sub> alloys as substrate are very few. These results indicate that high-quality monolayer graphene was obtained.

Further Raman mapping analysis of graphene is shown in Figures 2(c)–2(f). For Raman mapping of graphene film which were randomly chosen from continuous regions, the length of one step was 0.5  $\mu$ m and the area of the whole scan was 5  $\mu$ m × 5  $\mu$ m. As shown in Figures 2(c) and 2(d), G bands (1584–1590 cm<sup>-1</sup>) and 2D bands (2676–2682 cm<sup>-1</sup>) had full widths at half maximum of about 16 and 26 cm<sup>-1</sup>, respectively. The very low intensity ratios of D/G bands (Figure 2(e)) demonstrated that graphene has only few defects. From Figure 2(f), the intensity ratios of 2D/G bands were found to be between 4.5 and 6. All these Raman mapping results indicated that high-quality continuous singlelayer graphene was obtained under the optimized growth conditions.



FIG. 3. (a) Sketch of a graphene back-gate field effect transistor (FET) (thicknesses of SiO<sub>2</sub>, Cr, and Au are 300 nm, 5 nm, and 100 nm, respectively). (b) Optical microscopy image of FET devices in the Hall configuration. 0–5 name the corresponding electrode ends ( $W_{00} = 2 \mu m$ ;  $L_{00} = 8.5 \mu m$  (by design, will be smaller in reality)). (c) AFM phase image of a part of the FET device. (d) Voltage-current relation between two face to face electrode ends. (e) Source-drain current I<sub>sd</sub> vs. backgate voltage V<sub>g</sub> between 00 electrode ends at RT. ( $V_{sd} = 10 \text{ mV}$ ).

The electrical transport properties of graphene grown on PtRh<sub>20</sub> foils using CVD were studied at room temperature. We chose the uniform monolayer graphene films after being transferred onto p-type Si wafers covered with 300 nm SiO<sub>2</sub> on top as samples, which were characterized by SEM and Raman spectroscopy. The graphene FET was fabricated by a standard two step electron beam lithography (EBL) process. Cr (5 nm thick) and Au (100 nm thick) were successively deposited as both source and drain electrodes using a thermal evaporation (TE) system for thin film deposition. Figures 3(a)and 3(b) show a schematic of typical backgate FET and an OM image of FET devices in the Hall configuration, respectively. Figure 3(c) gives an AFM phase image of a part of the FET device. For the sample of graphene used as channel layer material, the length is L, the width is W, the thickness is D, the area S = LW, and the sectional area A = WD; the dielectric SiO<sub>2</sub> layer is sandwiched between graphene and Si substrate with gate capacitance of Cg

$$C_g = \varepsilon \varepsilon_0 / d = 11.505 \,\mathrm{nF/cm^2},\tag{1}$$

where  $\varepsilon_0$  is permittivity of vacuum,  $8.85 \times 10^{-12}$  F/m;  $\varepsilon$  is the relative dielectric constant of SiO<sub>2</sub>, 3.9; and d is the thickness of oxide layer (SiO<sub>2</sub>), 300 nm

Transconductance 
$$g_m \equiv \partial I_{sd} / \partial V_g$$
.

FET mobility

$$\mu_{FE} = \frac{g_m}{V_{sd}} \cdot \frac{L}{W} \cdot \frac{1}{C_g},\tag{2}$$

where  $V_{sd}$  is source-drain voltage.

Voltage-current measurements were taken between source and drain electrodes. The linear V-I curves indicate Ohmic contact between Cr/Au electrodes and graphene (Figure 3(d)), and the resistances between 00 electrodes of the sample prepared on PtRh<sub>20</sub> substrates was about 2 k $\Omega$ . Figure 3(e) shows source-drain current I<sub>sd</sub> as a function of backgate voltage V<sub>g</sub>. By using the formula (2), the FET carrier mobilities of graphene grown on PtRh<sub>20</sub> alloy foils were reckoned to be about 4236 cm<sup>2</sup>/V s (electron) and 3753 cm<sup>2</sup>/V s (hole). Compared with the intrinsic Dirac point of graphene, the current minimum was shifted toward positive V<sub>g</sub> side, indicating p-type doping behavior. The positive shift was obtained at about 12.0 V, which might be due to the interaction with substrate.<sup>27</sup> The mobility of graphene is high in the recent reports of preparation of graphene using CVD method.<sup>28–30</sup>

In summary, large-scale, continuous, uniform monolayer graphene films were prepared on polycrystalline PtRh<sub>20</sub> alloy foils by thermal LPCVD. The quality, morphology, and structure were analyzed using SEM, AFM, Raman spectroscopy, and maps. The analysis results confirm that high quality monolayer graphene was fabricated on PtRh<sub>20</sub> foil through controllable reaction conditions (flow rate of CH<sub>4</sub> and reaction pressure). Graphene films were transferred onto the SiO<sub>2</sub>/Si substrate by a bubbling transfer method, and in this way, the PtRh<sub>20</sub> alloy foils can be used repeatedly. The FET mobility at room temperature of graphene grown on PtRh<sub>20</sub> was measured and reckoned, and it presents a p-type behavior. The results indicate that the quality of graphene grown on  $PtRh_{20}$  foils by LPCVD is comparatively good and can be applied to graphene based nanoelectronic devices.

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