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Supporting Information

Direct observation of the work function evolution of graphene-two dimensional metal contacts

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S1: The fabrication of monolayer graphene

The monolayer graphene was synthesized on a 25-um-thick Alfa Aesar 13382 Cu foil by copper-catalyzed chemical vapor deposition method at low pressure in a 2-inch quartz tube [1]. Figure 1(a) shows the schematic diagram of chemical vapor deposition system for graphene on Cu foil. After the Cu foil had been smoothed mechanically, it was cut into about 4 cm^2 pieces. A quartz boat carrying Cu pieces was transferred into the furnace as a platform that supported the copper pieces.

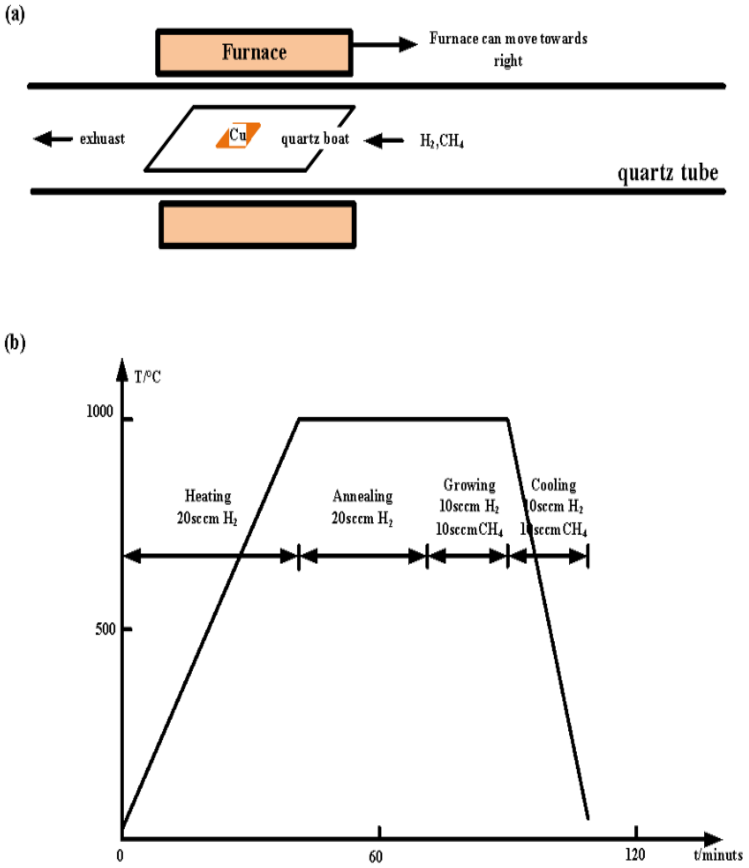

Figure 1. The process of synthesizing graphene with chemical vapor deposition system. (a) The schematic diagram of chemical vapor deposition system for graphene on Cu foil. (b) The main steps of growing graphene on Cu foil.

The pump was started to pull out the air in the quartz tube. In order to purge the air completely, argon had been introduced with a flow rate of 1000 standard cubic centimeter per minute (sccm) for 3 minutes. The temperature in the position of Cu foil rose from 25°C to 1000°C in 40 minutes with a constant flow rate of 20 sccm H_2 that was kept to anneal Cu foil. In the course of heating the tube, the pressure was kept about 45 Pa. When the temperature arrived at 1000°C, it had been kept for 30 minutes to continue to anneal the Cu foil. Native oxide film on the surface of Cu foil can be removed by annealing, and the grain size was also increased to a large scale (~100 um). With a large grain size, high-quality and uniform monolayer graphene was synthesized, for multilayer graphene was generally grown on the graphene boundary [2]. During the annealing process, the surface of Cu foil was also smoothed that was an important factor for growing high-quality graphene film. After annealing, keeping the temperature of 1000°C and the pressure of 45 Pa and only changing the flow rate of H_2 into 10 sccm with introducing 10 sccm CH_4. During this process, CH_4 was decomposed into H and C atoms, and C atoms gathered at the surface of Cu foil and finally grew up into graphene with copper-catalyzed effect. The growth step was maintained for 15 minutes. After the growth step, the heat treatment was closed and furnace was moved away the position of samples. The graphene film was quickly cooled (>30°C) to room temperature with an electric fan blowing the quartz tube, other conditions in the course of cooling were the same as the growth process. When the temperature of the tube reached about 100°C, the flow rate of H2 and CH4 was shut down and displayed zero, and 1000 sccm of Ar was introduced into the quartz tube to purge the remaining H2 and CH4. When the Cu foil was cooled to room temperature, it could be moved away from the tube. The main steps of growing graphene were described in the Figure 1(b).

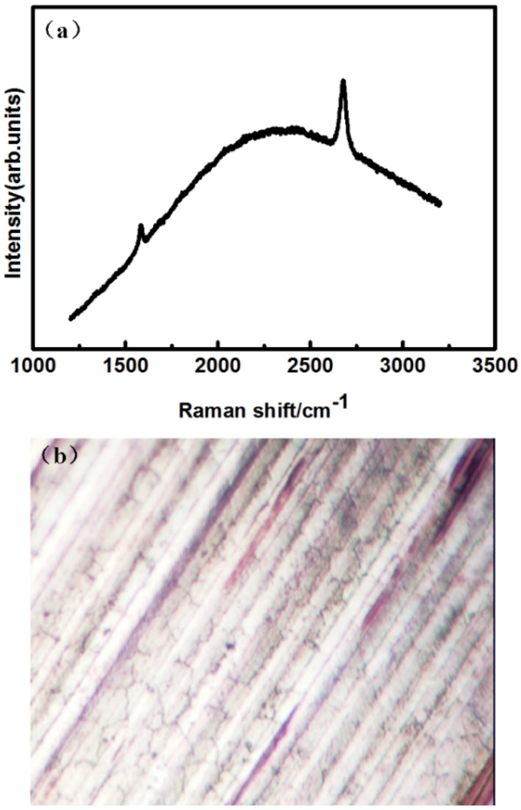

Figure 2. The characterization of growing graphene. (a) Raman spectrum of graphene on Cu foil. (b) The optical picture of graphene on the copper oxidized.

Raman spectroscopy was carried out on the surface of graphene sample with a 514 nm laser, as shown in Figure 2(a). The background showed that the graphene was grown on the Cu foil. The disorder-induced D band (~1338 cm−1) was hardly observed, and The I_{2D}/I_G ratio was much larger than 1, confirming that high-quality monolayer graphene was synthesized. In order to observe the area of graphene, the graphene sample was heated until Cu foil was oxidized by air, which makes the graphene is obvious in the optical microscope. The heating is keeping at the temperature of 120°C for 5 minutes in this work. Figure 2(b) shows the optical picture of graphene on the copper oxidized. Apparently, the monolayer graphene was almost grown on the whole Cu foil.

S2: The calculation obtained from the data:

An important phenomenon was observed where the work function increased from 4.28 eV to 5.00 eV at the graphene-Ni interface, and went up from 4.29 eV to 4.50 eV and then down to 4.29 eV at the graphene-Ti interface when the metal thickness gradually increased from 0.2 nm to 4.2 nm, as shown in Fig. 3(c).

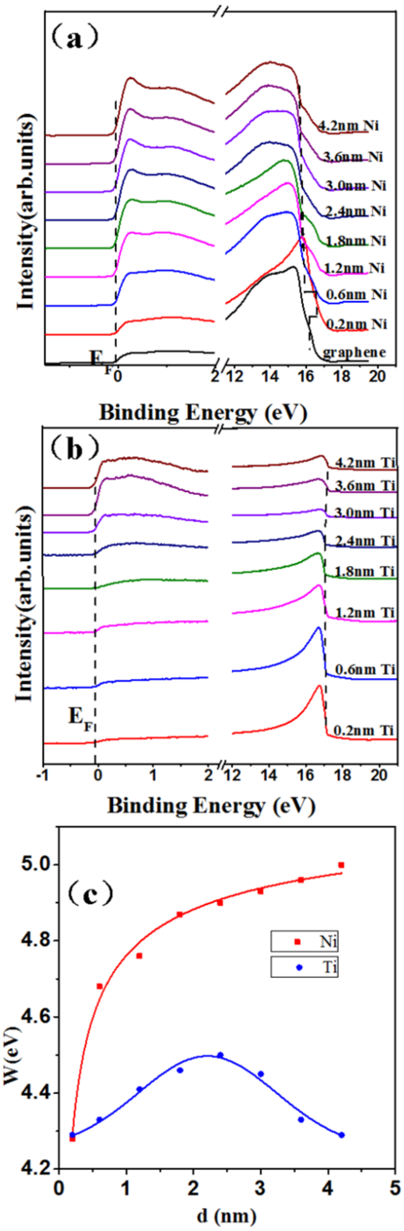

Figure 3. The work function evolution of metal-graphene contact with the metal dimension varying. UPS spectra of the (a) graphene-nickel and (b) graphene-titanium interface as a function of the thickness of metal contact that was deposited on graphene. (c) The work function of the graphene-metal interface as a function of the thickness of the metal contact overlayer.

Here 4.28 eV is the work function with 0.2 nm nickel, which is calculated with the work function (W) equation: $W = h\upsilon - (E_{cutoff} - E_{Fermi})$, where Ecutoff and EFermi are the binding energies of the secondary electron cutoff and the Fermi level, respectively [3-4]. In the UPS spectrum of 0.2 nm nickel, E_{cutoff} is 16.97 eV and E_{Fermi} is 0.03 eV, so $W = h\upsilon - (E_{cutoff} - E_{Fermi}) = 21.22 - (16.97 - 0.03) = 4.28$ eV.

5.00 eV is the work function with 4.2 nm nickel, $W = h\upsilon - (E_{cutoff} - E_{Fermi}) = 21.22 - (16.25 - 0.03) = 5.00$ eV

The work function with 0.2 nm titanium is 4.29 eV, $W = h\upsilon - (E_{cutoff} - E_{Fermi}) = 21.22 - (16.96 - 0.03) = 4.29$eV

The work function with 2.4 nm titanium is 4.50 eV, $W = h\upsilon - (E_{cutoff} - E_{Fermi}) = 21.22 - (16.75 - 0.03) = 4.50$ eV

The work function with 4.2 nm titanium is 4.29 eV, $W = h\upsilon - (E_{cutoff} - E_{Fermi}) = 21.22 - (16.96 - 0.03) = 4.29$ eV

In Fig. 4(a)-(d), ΔV is the difference in the work function between metal and graphene. $\Delta V = W_{metal} - W_G$, where W_{metal} and W_G are the work functions of metal and graphene, respectively.

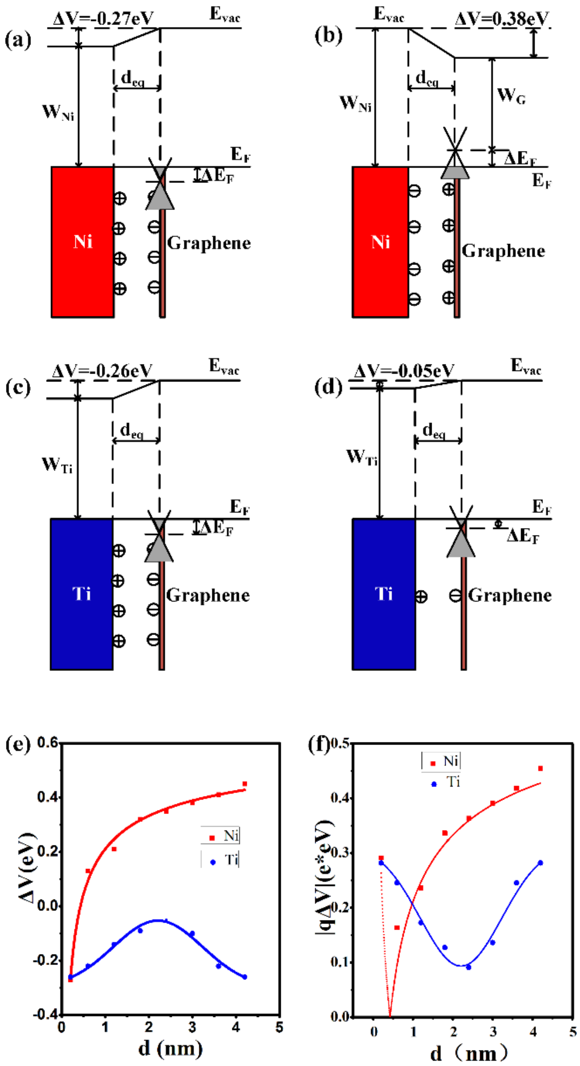

Figure 4. The analysis of metal-graphene contact as to two dimensional and bulk metal. Interfacial energy diagrams of (a) 0.2 nm and (b) 3.0 nm thick nickel, (c) 0.2 nm and (d) 2.4 nm thick titanium overlayers on graphene at the graphene-metal interface. (e) The difference in the work function between metal and graphene (ΔV) as a function of the thickness of the metal overlayer. (f) The energy barrier of metal/graphene as a function of the thickness of the metal. The vacuum energy level (E_{vac}), ΔV, the equilibrium interfacial distance (d_{eq}), the Fermi level (E_F), the difference in the energy levels between the Dirac point and Fermi level of graphene (ΔE_F), the work function of nickel (W_{Ni}), the work function of nickel (W_{Ti}), the work function of graphene (W_G) and the thickness of the metal overlayer (d) are shown in Fig 4(a)–(f).

In Fig. 4(a), ΔV is -0.27 eV with 0.2 nm nickel, W_{metal} is 4.28 eV and W_G is 4.55 eV, $\Delta V = W_{metal} - W_G = 4.28 - 4.55 = -0.27$ eV.

In Fig. 4(b), ΔV is 0.38 eV with 3.0 nm nickel, $W_{metal} = h\upsilon - (E_{cutoff} - E_{Fermi}) = 21.22 - (16.32 - 0.03) = 4.93$ eV, WG is 4.55 eV, $\Delta V = W_{metal} - W_G = 4.93 - 4.55 = 0.38$ eV.

In Fig. 4(c), ΔV is -0.26 eV with 0.2 nm titanium, $\Delta V = W_{metal} - W_G = 4.29 - 4.55 = -0.26$ eV.

In Fig. 4(a), ΔV is -0.05 eV with 2.4 nm titanium, $\Delta V = W_{metal} - W_G = 4.50 - 4.55 = -0.05$ eV.

ΔV with different metal thicknesses were calculated, as shown in Fig. 4(e).

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