Effect of Superparamagnetic Fe₃O₄ Nanoparticles on Schottky Barriers of Graphene

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We demonstrated the effect of superparamagnetic Fe₃O₄ nanoparticles on the Schottky barriers of graphene, in which the Fe₃O₄ nanoparticles were fabricated by a hydrothermal method, and the single-layer graphene sheets were mechanically exfoliated from Kish graphite. The Fe₃O₄ nanoparticles were superparamagnetic with the saturation magnetic moment of ∼32 emu/g at room temperature. We have found that the Fe₃O₄ nanoparticles decorated on the graphene surface can dramatically modify the Schottky barriers of the whole devices possibly due to the magnetic stray field from the Fe₃O₄ nanoparticles in proximity to graphene. The Schottky barrier could be further tuned by the quantity of Fe₃O₄ nanoparticles.

Index Terms—Fe₃O₄ nanoparticles, graphene, Schottky barrier, superparamagnetism.

I. INTRODUCTION

HALF-METAL magnetite (Fe₃O₄) is a widely studied material as it presents unique properties such as the theoretically 100% spin polarization at the Fermi level [1], the metal–insulator transition (Verwey transition) at 120 K [2], [3], the ferromagnetic nature with a Curie temperature of 858 K, the largely unquenched orbital moment [4], and the multiferroicity at low temperatures [5]. The merits of magnetite offer unique opportunities for both material science and engineering [6]. At room temperature, Fe₃O₄ is a conductor [conductivity is ∼2.5 × 10⁴ (Ω·cm)⁻¹] [7], and its conductivity decreases with decreasing temperature. The good conductivity of magnetic Fe₃O₄ thin film above Verwey transition temperature will interfere the electrical research of heterostructures with other conductor. However, the uniformly dispersed superparamagnetic Fe₃O₄ nanoparticles are insulating because of the interspace among the Fe₃O₄ nanoparticles. For every individual Fe₃O₄ nanoparticles, it has a net magnetic moment, which will contribute to a local stray field, in spite of total superparamagnetism for large quantity nanoparticles [8]. Accordingly, Fe₃O₄ nanoparticles have uniquely superiority in studying the electrical and magnetic transport properties for Fe₃O₄/graphene composite structure.

Graphene is a single layer of carbon atoms arranged in 2-D hexagonal honeycomb lattice, and has attracted lots of interests due to its unique chiral Dirac electronic spectrum [9], [10]. A crucial challenge for graphene-based spintronics is to develop magnetic order or even long-range ferromagnetic order in graphene [11]. Graphene possesses large phase coherence length of up to ∼8 µm for spin injection [12], [13], holding great potential for spintronic applications. The surface decoration of graphene offers huge opportunities, because graphene is a fully open system [14], [15]. Functional defects, p–n-type doping, and additional spin-orbit interactions can be introduced when atoms are intimately absorbed from an external source [16]–[25]. One has even considered to induce topologically nontrivial gaps inside the Dirac cone. It has been suggested that magnetic attachments that break the time reversal symmetry of graphene can induce pseudospin organization, which would result in topologically nontrivial states [22], [26]. Adatom adsorptions (In, Ti, and Pb) are believed to generate a gap within the Dirac cone, thereby introducing the quantum spin Hall effect in graphene sheets [16], Zhang et al. [27] theoretically calculated the Ir and W (5d) atom attachments that can mediate a quantum anomalous Hall state induced by large spin-orbit interaction of the 5d metals. Hong et al. [21] have experimentally shown that spin-flip scattering can be introduced by fluorine doping. Han et al. [20] achieved tunneling spin injection from Co into single-layer graphene, and observed a nonlocal magnetoresistance of 130 Ω at room temperature, which is the largest value at that time. Qin et al. [28] confirmed that Pd deposition on graphene can enhance quantum coherence. Furthermore, magnetic decoration of graphene is more fascinating because of proximity-induced ferromagnetism in graphene, and thus, one can obtain the ferromagnetic graphene without sacrificing its excellent transport properties [29], [30].

Magnetic Fe₃O₄ nanoparticles/graphene composite structures are interesting spintronic systems for the study of novel electrical and magnetic transport properties. However, up to now, most studies have focused on enhancing lithium storage rate [31]. The effect of electrical and magnetic transport properties of graphene by the attachment/decoration of Fe₃O₄ nanoparticles has still remained unknown. In this paper, we report the fabrication and characterization of Fe₃O₄ nanoparticles and graphene composite structures. The tunable Schottky barriers of graphene by Fe₃O₄ nanoparticles were observed for the first time.
Fe₃O₄ nanoparticles were baking for 5 min at 50 °C.

II. EXPERIMENT

Alcohol-soluble Fe₃O₄ nanoparticles were synthesized by hydrothermal method. In brief, FeCl₃·6H₂O (0.8109 g) and NaHCO₃ (0.756 g) were dissolved in deionized water (30 mL) with the aid of magnetic stirring. Meanwhile, L-ascorbic acid (0.088 g) was separately dissolved in deionized water (10 mL) by stirring. After 30 min, two solutions were mixed and the stirring continued for another 20 min. Finally, the solution was transferred into a 125 mL teflon-lined stainless-steel autoclave, and heated at ∼150 °C for 6 h in a furnace. The as-obtained nanoparticles were collected by centrifuge and washed by alcohol and deionized water several times. Finally, the particles were dispersed in alcohol solution in view of its effumability.

Single-layer graphene sheets were exfoliated from Kish graphite flakes and on a silicon wafer with 300 nm thick silicon dioxide layer. Devices were fabricated using a standard electron-beam lithography and Au (60 nm thickness) electron-beam evaporation. There are four device samples, denoted as S1, S2, S3, and S4. In order to accelerate the evaporation of alcohol, before measuring the current–voltage (I–V) curves, the devices dripping with alcohol or alcohol-soluble Fe₃O₄ nanoparticles were baking for 5 min at 50 °C.

The morphology and magnetic properties of Fe₃O₄ nanoparticles were characterized by a scanning electron microscope (SEM, JEOL, JSM-7100F), transmission electron microscope (TEM, JEM-200CX), atomic force microscopy (AFM), and vibrating sample magnetometer (VSM). Graphene sheets were confirmed as single layer by a laser Raman spectrometer (JY HR800). Electrical curves were measured by Keithley 4200-SCS electrometer.

III. RESULTS AND DISCUSSION

Fig. 1 shows the magnetic hysteresis loop of Fe₃O₄ nanoparticles, clearly indicating superparamagnetism of large quantity Fe₃O₄ nanoparticles. Experimental (black solid rectangle) and calculated (red solid line) data represent the best fit for the Langevin function. Insets: SEM (left top) and TEM (left bottom) images. Inset: photograph before and after magnet attraction (right bottom), denoting ferromagnetism of each individual Fe₃O₄ nanoparticle.

For superparamagnetic particles, the true magnetic moment at a particular temperature can be calculated using the Langevin function [32]

$$M = M_S \left( \coth \left( \frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right)$$

where \(\mu(=M_S \pi D^3/6)\) is the true magnetic moment of each particle, \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, \(D\) is the mean diameter of each particles, and \(M_S\) is the saturation magnetization. The red solid line in Fig. 1 shows the best fit for the Langevin function in (1). From this data fitting, the mean diameter of each particles is 12.32 nm, which is corresponding to the value from SEM and TEM.

Left top and bottom insets are the SEM and TEM images of Fe₃O₄ nanoparticles, respectively, indicating the granular and uniform morphologies of the Fe₃O₄ nanoparticles. SEM and TEM results also show that the diameter of Fe₃O₄ nanoparticles is ∼10 nm with a standard deviation of 5 nm based on the estimation from 100 nanoparticles. Right bottom inset is the photograph before and after the magnet attraction. It shows that Fe₃O₄ nanoparticles can be attracted by magnet after several minutes. Although the total magnetic moment of large quantity Fe₃O₄ nanoparticles is zero revealed by superparamagnetism in macroscopy, each individual Fe₃O₄ nanoparticle has magnetic moment, because the particles can be attracted by magnet, as shown in Fig. 1 (right bottom inset). Namely, it has no magnetic influence on graphene in macroscopy, but each individual Fe₃O₄ nanoparticle will be a magnetic source forming a stray field to graphene and then affecting the properties of graphene, as discussed below.

Raman scattering spectroscopy was performed to confirm that graphene is single layer, as shown in Fig. 2. We can see both the characteristic \(G\) (∼1580 cm⁻¹) and 2D (∼2700 cm⁻¹) peaks of the single-layer graphene. The 2D peak (full-width at half-maximum is 31.2 cm⁻¹) and 2D/G ratio indicate that the sample is a single-layer graphene sheet, and D peak (∼1350 cm⁻¹) associated with defects is...
not observed. Left inset is the optical micrograph of single-layer graphene. The dashed lines show the edges of the single-layer graphene sheet. Only 2.3% incident light is absorbed by single-layer graphene [33]. Thus, the contrast of graphene on silicon oxide wafer is not distinct. Appreciable contrast of the single-layer graphene with bottom adjacent triangular purple multilayer graphene region was observed (see the left inset). Right inset shows an AFM image of the graphene sheet with Fe$_3$O$_4$ nanoparticles. The Fe$_3$O$_4$ nanoparticles appear to be granular and discrete. AFM image reveals that Fe$_3$O$_4$ nanoparticles are dispersed on the graphene surface with a very low coverage of $<5\%$.

The inset in Fig. 3(a) shows the photograph of the device (S1) fabricated by the electron-beam lithography and Au electron-beam evaporation, in which the electrodes and the channels are both 2 $\mu$m wide. The dashed lines show the edges of the single-layer graphene sheet. All of our devices were measured with a two-probe method. There are two kinds of contact from our pure graphene measurement, namely, Ohmic contact and Schottky contact, as shown in Fig. 3(a) and (b), respectively. Different contact types of pure graphene may come from the process of devices fabrication.

From black rectangle solid and red circle solid straight lines in Fig. 3(a), it can be seen that S1 (pure graphene) is ohmic contact, and the resistance is $\sim$1000 $\Omega$. However, when we measured S1 of graphene with baking for 5 min at 50 $^\circ$C after dripping 0.05 mL solution with alcohol-soluble Fe$_3$O$_4$ nanoparticles, it becomes Schottky contact, as shown in Fig. 3(a) (right bottom inset). In order to eliminate the influence of alcohol to the graphene, we measured the graphene with 0.05 mL alcohol without Fe$_3$O$_4$ nanoparticles (S2). Before measurement, we also baked the device for 5 min at 50 $^\circ$C to accelerate the alcohol evaporation without damaging the device. The red circle solid straight line in Fig. 3(a) shows that it is still Ohmic contact and the resistance is $\sim$857 $\Omega$, which is slightly reduced possibly due to the extra conductivity contributed by residual alcohol.

Fig. 3(b) and inset of Fig. 3(b) show the $I$–$V$ curves of S3 and S4. In which, Fig. 3(b) is the $I$–$V$ curves of S3 (graphene decorated with different volumes of Fe$_3$O$_4$ nanoparticles). Inset of Fig. 3(b) is the $I$–$V$ curves of S4 measured at larger voltage. From the $I$–$V$ curves, we can see that the devices show Schottky contact no matter pure graphene and graphene decorated with Fe$_3$O$_4$ nanoparticles. After decorated with Fe$_3$O$_4$ nanoparticles, the Schottky barrier becomes larger, and the Schottky barrier can be tuned by the quantity of Fe$_3$O$_4$ nanoparticles. In other words, the resistance of device decreases because of the decoration of Fe$_3$O$_4$ nanoparticles.

Using the thermionic emission theory, our devices can be seen as Au/graphene/Au junction, and the current densities in a metal-semiconductor/metal junction is written as [34]

$$J_{1(T)} = A^* T^2 \exp \left( -\frac{q \Phi_{B1}}{k_B T} \right) \times \left[ \exp \left( -\frac{q V_1}{k_B T} \right) - 1 \right]$$  \hspace{1cm} (2)

$$J_{2(T)} = -A^* T^2 \exp \left( -\frac{q \Phi_{B2}}{k_B T} \right) \times \left[ \exp \left( -\frac{q V_2}{k_B T} \right) - 1 \right]$$  \hspace{1cm} (3)

where $A^*$ is the Richardson constant, $\Phi_{B1}$ and $\Phi_{B2}$ are the Schottky barrier heights, and the other symbols have their usual meanings. Obviously, the voltage saturates in both directions, but maybe at different values, just like the $I$–$V$ curve in Fig. 3(a) (right bottom inset). The larger
Based on the double thermionic emission model and considering the spin-split in the conduction band, the spin-dependent current density is given by [35]

\[
J_{\text{1(1)(1)}}(T) = \frac{1}{2} A^{*}T^{2}\exp\left(-\frac{q\Phi_{B1}}{k_{B}T} - (+)\frac{\Delta p_{s}}{k_{B}T} - (+)\mu_{B}B\right) \\
\times \left[\exp\left(-\frac{qV_{1}}{k_{B}T}\right) - 1\right]
\]

(4)

From (4), we can see that current density \(J\) decreases compared with (2) when there is an external field. This explains that the resistance of the device decreases while compared with (2) when there is an external field. This is due to the fact that the resistance of the device decreases while compared with (2) when there is an external field.

**IV. CONCLUSION**

We have demonstrated the influence of superparamagnetic Fe\textsubscript{3}O\textsubscript{4} nanoparticles on the Schottky barriers of graphene, in which the Fe\textsubscript{3}O\textsubscript{4} nanoparticles were synthesized by a hydrothermal method, and the single-layer graphene sheets were mechanically exfoliated from Kish graphite. SEM, TEM, and AFM images reveal the morphology of Fe\textsubscript{3}O\textsubscript{4} nanoparticles. The stray field in proximity to graphene coming from each individual Fe\textsubscript{3}O\textsubscript{4} nanoparticle is the primary influence on Schottky barriers of the devices, and Schottky barrier can be tuned by the quantity of Fe\textsubscript{3}O\textsubscript{4} nanoparticles. This paper provides a reference basis in tailoring the electrical properties of graphene by superparamagnetic Fe\textsubscript{3}O\textsubscript{4} nanoparticles, and paves a way to further study the magnetic transport properties of graphene decorated with Fe\textsubscript{3}O\textsubscript{4} nanoparticles.

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**REFERENCES**


