Magnetoresistance effect in a vertical spin valve fabricated with a dry-transferred CVD graphene and a resist-free process

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Abstract

One of the most prominent and effective applications of graphene in the field of spintronics is its use as a spacer layer between ferromagnetic metals in vertical spin valve devices, which are widely used as magnetic sensors. The magnetoresistance in such devices can be enhanced by a selection of suitable spacer materials and proper fabrication procedures. Here, we report the use of dry-transferred single- and double-layer graphene, grown by chemical vapor deposition (CVD), as the spacer layer and the fabrication procedure in which no photo-resist or electron-beam resists is used. The measured maximum magnetoresistance of NiFe/CVD-Graphene/Co junction is 0.9% for the single- and 1.2% for the double-layer graphene at 30 K. The spin polarization efficiency of the ferromagnetic electrodes is about 6.7% and 8% for the single- and the double-layer graphene, respectively, at the same temperature. The bias-independent magnetoresistance rules out any contamination and oxidation of the interfaces between the ferromagnet and the graphene. The magnetoresistance measured as a function of tilted magnetic field at different angles showed no changes in the maximum value, which implies that the magnetoresistance signal is absent from anisotropic effects.

Introduction

Graphene, a two-dimensional layered semi-metal of densely packed carbon atoms, has attracted much attention in the field of electronics, opto-electronics, and spintronics due to its unique properties. Zero band gap, extremely high carrier mobility, and layer-dependent properties opened a wide range of applications in the field of electronics and opto-electronics [1–6]. Furthermore, a large spin diffusion length due to the weak spin–orbit interactions makes the graphene a promising candidate for the spin transport channel in spintronic devices [7–11]. A spin valve device is one such example, and the spin valve effect can be observed by measuring the magnetoresistance (MR) of the device made of two ferromagnetic (FM) electrodes and a graphene (Gr) channel. Spin-polarized charge carriers are injected from one FM electrode, transport through the Gr channel, and can be detected by the other FM electrode. The MR of the spin valve device results from the relative magnetization alignment between the two FM electrodes creating a parallel and an antiparallel configuration. Generally, spin valve measurement can be done in two ways: one is the lateral spin valve (LSV) and the other is the vertical spin valve (VSV). In the LSV, two FM electrodes are placed laterally adjacent to each other on the Gr channel in a current-in-plane (CIP) configuration [11–14]. In the VSV, the Gr layer is sandwiched between the top and the bottom FM electrodes, which makes a current-perpendicular-to-plane (CPP) configuration [8, 15–20]. Theoretical studies have found that the VSV with FM/Gr/FM structure could provide perfect spin-filtering effects at the interfaces [8, 9, 18]. Thus this configuration is an effective way to study the spin-filtering properties in graphene, although an experimental realization of the spin-filtering is still in question especially for devices adopting transferred graphene.

Until now, the graphene spacer layer in a VSV has been prepared on the bottom FM electrode in different ways such as a transfer of mechanically exfoliated graphene from graphite [21, 22], a direct growth of graphene by chemical vapor deposition (CVD) [18, 23, 24], and a wet transfer of the CVD-Gr [16, 20, 25, 26]. Although the
direct growth of CVD-Gr over the electrode could yield an improved FM/Gr interface and a lattice matching required for spin-filtering effects, there are still questions about the growth mechanisms and the quality of the graphene grown over the ferromagnetic transition metals [27–30] due to a much less MR observed than predicted for a perfect spin-filtering. Adopting transferred graphene, especially CVD-grown one, could still provide useful aspects for the device applications because of its versatility and easiness of fabrication. Despite the several works on VSV with the transfer of either exfoliated or CVD-grown graphene, the oxidation of FM electrodes and the contamination which occurs in FM/Gr/FM interfaces during the fabrication process have been major hurdles. Particularly poly(methyl methacrylate) (PMMA) used for the wet-transfer of graphene and the photo-resists (PR) and electron-beam resists (ER) used during the process contaminates the FM/Gr/FM interfaces and they cannot be removed completely, which eventually degrades the quality of the graphene and the spin valve devices [31–33]. Thus, a VSV device made with CVD-Gr dry-transferred by a non-PMMA agent and PR- and ER-free processes is indispensable to make clean FM/Gr interface and to test for possible improvements in the device characteristics.

In this experiment, we have prepared a VSV device with NiFe/CVD-Gr/Co junctions with a method to minimize the oxidation and contamination of the FM/CVD-Gr/FM interfaces. First, the CVD-Gr was transferred with polydimethylsiloxane (PDMS) as an intermediate agent. Second, the PDMS/CVD-Gr conjugate was fully dried before being transferred onto the bottom FM electrodes. Finally, the FM electrodes were prepared by a shadow mask technique without the use of PR and ER, where a few nm of gold as a capping layer was also used to avoid the oxidation of the FM electrodes. The ohmic current-voltage curve indicates no oxidation at the FM/CVD-Gr/FM interfaces. The MR we obtained is comparable to or higher by a factor of 2 at the most than the values reported previously in devices with transferred graphene. Our study supports that an enhancement can be made in the performance of the VSV devices with transferred graphene even though they cannot yield as high a MR expected for spin-filtering mechanism.

Experimental section

Material and device fabrication

Graphene used in this experiment was grown on a Cu foil substrate with low-pressure chemical vapor deposition (LPCVD) with a movable electric furnace. In the LPCVD system, methane(CH₄), hydrogen(H₂), and argon(Ar) gases are connected to the front of a 120 cm-long quartz tube via mass flow controller, and a rotary pump is connected to the rear of the quartz tube for maintaining the vacuum. A Cu foil with 99.8% purity and 25 μm thickness purchased from Alfa-Aesar was loaded into the chamber and then the pressure was lowered to under 10⁻⁶ Torr. The furnace was preheated to 1000 °C behind the sample position with Ar gas flowing in the tube at 100 sccm. After the temperature is stabilized, Ar gas was replaced with H₂ gas (50 sccm) and the furnace is moved to the sample position to perform H₂ annealing of the Cu foil for 30 min. Following the heat treatment for the oxide removal and surface cleaning, graphene was synthesized on Cu surface by flowing CH₄/H₂ gas mixture (10 sccm/50 sccm) for 15 min. Finally, the gas mixture was replaced with Ar gas (100 sccm) to stop the graphene growth and the sample was rapidly cooled by removing the hot furnace.

The step-by-step dry-transfer process of the CVD-Gr and the device fabrication procedure is shown in figure 1(a). The typical size of the CVD-Gr used was 5 mm × 5 mm. First, the unwanted graphene on one side of the Cu foil was etched by O₂-plasma since the graphene was inevitably grown on both sides and the one on the Cu surface facing downward during the growth has an inferior quality. This surface is marked as ‘rear’ in step 1. After that, a PDMS stamp was attached to the graphene on the ‘front’ side. The PDMS/graphene/Cu foil was then attached to a glass slab and dipped into a 0.15 M ammonium persulfate (APS) solution to etch the Cu foil. After Cu etching, the PDMS/graphene conjugate was rinsed several times with deionized water and dried with nitrogen gas. Using a desiccator, moisture on the graphene was completely removed before the subsequent steps. The dry graphene on the PDMS stamp was then attached to the target substrate containing the bottom electrode. Finally, by slowly peeling off the PDMS stamp, the graphene was left behind on top of the bottom electrode, as shown in step 7. Figure 1(b) shows the optical image after the transfer.

We now describe the whole device fabrication procedure. A silicon substrate of 1 cm × 1 cm size and 0.5 mm thickness covered with 100 nm insulating SiO₂ layer was cleaned using a hot acetone bath and washed with methanol followed by a blow dry with nitrogen gas. A 40 nm-thick and 6 mm-long bottom NiFe electrode was directly deposited on the substrate using a shadow mask with 2 nm Au as a capping layer via e-beam evaporation under the base pressure of 10⁻⁶ Torr. Then a single layer (SL) CVD-Gr was dry-transferred on top of the bottom FM electrode as explained above. The dry-transfer process was repeated for a double layer (DL) device. After the graphene transfer, it was placed on a hot plate (100 °C) inside a high vacuum (10⁻⁶ Torr) to make better FM/CVD-Gr adhesion. Finally, 80 nm-thick and 4 mm-long top Co electrode with 5 nm Au capping layer was deposited by using the shadow mask to make NiFe/CVD-Gr/Co junctions as shown in...
figure 1(a), step 8. The unwanted part of the graphene which sticks outside the top electrode was removed by O$_2$-plasma etching while the graphene under the top electrode was protected by the electrode itself. This makes the transport occur through the junction only. The final image of the device is shown in figure 1(c).

Characterization and measurement

Raman spectrometer was used to characterize the dry-transferred CVD graphene layer on the bottom FM electrode. Figure 2(a) shows the Raman spectral peaks with the laser excitation energy of 2.41 eV. The intensity ratio between 2D and G peaks for the black curve is found about 2.6, which is large enough to confirm a SL graphene, whereas the ratio is reduced to 1.7 for the red curve and warrants a DL graphene [34, 35]. Furthermore, figure 2(b) represents the single Lorentzian fitting for the 2D peak of SL graphene, whereas figure 2(c) shows the broad 2D band of DL graphene, which is fitted with four Lorentzian curves [34, 36, 37]. Moreover, the low intensity of D peaks indicates a good quality of CVD-Gr since the D peak is related to the amount of disorder [36, 38].

The vertical magneto-transport measurement was carried out at room as well as cryogenic temperatures by using ac lock-in technique with the bias current (I) ranging from 40 to 80 $\mu$A. The external magnetic field (B) was applied along the top electrode by an electromagnet. The schematic measurement configuration of the VSV...
device is shown in figure 3(a). Spin-polarized current is injected from the top Co electrode (FM1) to the bottom NiFe electrode (FM2) through the CVD-Gr, whereas the voltage (V) is measured between FM1 and FM2 with other contacts as a 4-probe method. The VSV effect was studied by analyzing the MR at different temperatures for SL and DL devices. The MR is calculated by using the formula $MR = \frac{(R - R_P)}{R_P} \times 100$. $R$ is the resistance at each value of $B$ and $R_P$ corresponds to the resistance when the magnetization of both electrodes are parallel. Figures 3(b) and (c) show the MR of SL and DL devices as a function of $B$ at different temperatures. The maximum MR, which is the difference between the highest resistance at anti-parallel state and the lowest resistance at parallel state of the electrode magnetization, is 0.9% for SL device and that of DL device is 1.2% at 30 K. The maximum MR decreases to 0.18% for SL and 0.22% for DL devices, respectively, at room temperature. The decrease in MR at higher temperature is mainly due to the spin scattering and thermal smearing effects [39–41].

The maximum MR we obtained for DL device is higher than SL device as shown in figure 4(a). Similar behavior was observed in other studies, although its interpretation as the enhanced spin-filtering effects with increasing number of graphene layers as predicted by the theory is still under debate [8, 9]. The maximum MR we reported here are comparable to [16, 23, 27] or higher by a factor of 2 than those values reported before in devices with transferred graphene [24–26, 42, 43]. This increase in MR is attributed to the fabrication process we adopted, as it excludes any possible contamination and oxidation in the VSV devices. Furthermore, no sign inversion in the spin valve signal (negative MR) is observed suggesting FM/CVD-Gr/FM interfaces are free from any residue and oxidation. Experimentally it was found that an oxidized interface can invert the MR signal by changing the spin-polarization at the Fermi level [12]. Figure 4(b) shows the spin-polarization efficiency (P) of the FM electrodes at different temperatures. The value of P was determined by using Julliere’s formula [41] by excluding the spin-flip process, which is given by $MR = 2P_1P_2/(1 - P_1P_2)$. We assumed the same value of P for NiFe and Co. The values of P are about 6.7% and 8% at 30 K for SL and DL devices, respectively. This indicates that the spin-polarization rate of FM electrode in DL device is larger than SL device, which is also the reason behind the large MR of DL device.
Figures 5 (a) and (b) show the I–V curve of SL and DL CVD-Gr VSV devices measured at different temperatures. The observed linear I-V characteristics indicate that SL and DL CVD-Gr sandwiched between FM electrodes do not act as a tunneling barrier, suggesting a perfect ohmic junction. Some of the articles reported that SL graphene in VSV device acted as a tunneling barrier showing a non-linear behavior \[15, 44\], which may be due to the oxidation and contamination produced at the FM/Gr/FM junction. Figure 5 (c) shows the maximum MR of SL and DL CVD-Gr VSV devices as a function of bias current at different temperatures. A bias-dependent MR is predicted to exist.
when the electrons tunnel through the barrier as in the case of magnetic tunneling junction due to the excitation of magnons or the existence of trap states \[41, 45\]. The bias-independence observed in our experiment indicates that no such phenomena are present in our devices and further confirms that the transport through the junction is ohmic and not tunneling.

Finally, we have measured the MR under a tilted magnetic field by a mechanical rotation of the electromagnet. The MR of the DL device measured as a function of the tilted magnetic field at room temperature is shown in figure 6(a). The angle indicated is that between the magnetic field and the sample plane. The angle-dependent measurement helps to verify that the MR is not due to a spurious signal that could mix with the VSV signal. The maximum MR as shown in figure 6(b) has no significant change with the angle, which excludes the contribution from the anisotropic magnetoresistance (AMR) since the AMR should depend on the angle between the current flow and the magnetization direction of the FM electrodes \[41, 45–47\]. Here we have detected a pure spin valve signal with the dry-transferred CVD-Gr as the spacer layer in the VSV device, prepared without using PR and ER. Figure 6(c) demonstrates the variation of the width of the peaks in figure 6(a) with the angle. It is related to the change of coercive field (\(H_c\)) of the electrodes. The width increases as the angle increases to 90° then decreases with a following cyclic order as we analyze it up to 250°. The maximum we obtained at 90° (perpendicular to the sample plane) is due to the highest energy required to align the magnetization of FM electrodes since the perpendicular direction is the hard axis of the FM layers.

**Conclusion**

We fabricated a VSV device with a dry-transferred CVD-Gr as a spacer layer without using any PR and ER throughout the fabrication process, thereby making it oxidation- and contamination-free at the FM/Gr/FM interfaces. The maximum MR and spin-polarization efficiency we obtained are about 1.2% and 8% for DL and 0.9% and 6.7% for SL CVD-Gr at 30 K, which drops about 80% at room temperature. These values are generally higher than the previous results in VSV device using transferred graphene as the spacer layer, and are attributed to the fabrication process we adopted. The linear I-V curve with bias-independent nature of the maximum MR and no sign reversal of MR signal further support that it was not affected by any spurious effects caused by doping, oxidation, and contamination. Finally, the spin valve measurement under the tilted magnetic field...
verifies that the obtained MR signal is free from AMR contribution. This fabrication technique can open a new perspective towards the VSV with CVD-Gr and provide a way to improve its performance given that the VSV with directly grown graphene does not necessarily show good spin-filtering phenomena.

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