Journal Name RSCPublishing

COMMUNICATION

Resistivity peak and magnetic property of an annealed graphene

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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We report on the transport and magnetic properties of graphene annealed at 800 °C under Ar atmosphere. Temperature dependence of resistivity of the annealed graphene shows that the ferromagnetic Curie temperature can be observed from the magnetoimpurity model. The Curie temperature is 220 K for the annealed graphene.

Diluted magnetic semiconductors (DMS) have attracted much attention in spintronic research because future electronic devices will use a spin rather than charge in semiconductors. [1-5] For the application of DMS, maintaining the ferromagnetic ordering at room temperature is very important. Dietl et al. had reported the possibility of room temperature ferromagnetism in semiconductors. [6] Room temperature ferromagnetism has also been shown in carbon-based materials. [7-9] In addition, graphene is a hot issue for future spin electronic devices due to the high mobility and excellent material properties. [10-13] Recently, Palacios et al. predicted an important result that a semiconducting graphene with a density of defects will behave like a DMS. [14] In this study, we report the DMS properties of an annealed graphene.

The graphene film was grown by chemical vapor deposition at 1000 °C, and it was transferred onto silicon substrate. Pristine graphene sample was annealed at 800 °C under Ar atmosphere for 10 min to reconstruct the crystal structure. Superconducting quantum interference devices (SQUID, MPMS Quantum Design) were used to characterize the magnetic properties of the graphene. Raman spectra of the graphene films were measured for excitation of 514.5 nm at room temperature, using a Jobin-Yvon HR800UV spectrometer. The electrical transports were measured in order to confirm the semiconductor properties of graphene film, using Cryostat with He displex (Sumitomo).

Figure 1 shows the results of Raman spectroscopy of graphene films, and we can see the three most prominent peaks, the D peak at ~1350 cm^{-1}, the G peak at ~1580 cm^{-1}, and the 2D peak at ~2680 cm^{-1}. According to Ferrari's famous work, [15] 2D peak of monolayer graphene can be fitted into only a single Lorentzian curve. Whereas 2D peaks of bilayer and few layer graphene can be fitted into several Lorentzian curves. In addition, the ratio of 2D/G is one of the criteria to estimate the number of graphene layers. It is well known that the intensity ratio of the 2D peak to the G peak (I_{2D}/I_G) is higher than 2, and the full width at half maximum (FWHM) of the 2D band is close to 30 cm^{-1} for the single layer graphene. [15-18] In our pristine graphene film, the ratio of I_{2D}/I_G is 2.4, and the FWHM of the single Lorentzian 2D band is 30 cm^{-1}. Notably, our sample is a monolayer, and the annealed graphene shows the optical transformation due to the increased disorder, and the slight shift of 2D peak, because of an unexpected wrinkle formation after annealing. The magnetization versus magnetic field, M-H curves, was measured to investigate the ferromagnetic hysteresis of the graphene films.

Figure 2 shows magnetization curves of the annealed graphene taken at 10 K. It shows clear ferromagnetic hysteresis loops. The annealed graphene has a coercive field (*H*c) of 128 Oe and remanent magnetization of 228 emu/cm^3 at 10 K. Interestingly, the annealed graphene has a ferromagnetic hysteresis, while ferromagnetic property was not observed in our pristine graphene without heat treatment. Recent theoretical works have suggested that graphene materials may show ferromagnetism, due to the existence of various defects or topological structures as spin units. [19, 20]

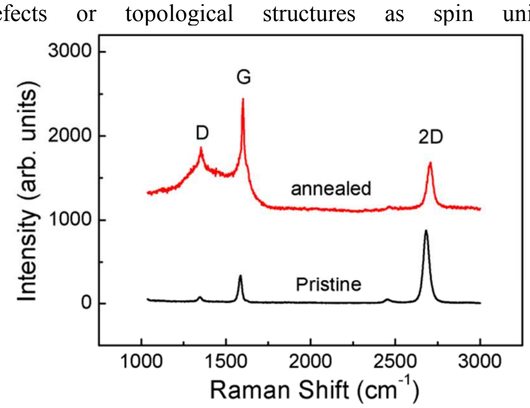

Fig. 1 Raman spectra of graphene films before and after annealing at 800 °C for 10 min.

Experimental results of Wang et al. [21] showed the ferromagnetism of graphene-based materials through the annealing process, and that the observed ferromagnetism originates from the defects in graphene. Its magnetic features have a relation with vacancies in terms of the increased disorder. [22] The presence of the defects breaks the symmetry of the graphene π system, and induces an opening of bandgap in graphene. [23] In addition, Palacios et al. predicted that a semiconducting graphene with a density of defects will behave like a DMS. [14] The long range ferromagnetic order also occurs when the vacancies are all positioned in the same sublattice. [23] Evidently, the Raman spectroscopy of the annealed graphene in figure 1 shows an increased defect concentration and structural modification, because the D peak at ~1350 cm^{-1} is a defect-induced Raman feature observed in the disordered graphene. On the other hand, the graphene edge state study for nanographene shows that the edge state is electronically and magnetically active due to the presence of the non-bonding having a large local density of states with a localized spin. STS (scanning tunneling spectroscopy) and NEXAFS (near edge x-ray absorption fine structure) revealed the presence of the edge state located at the Fermi level and strongly spin polarization. [24, 25] Therefore, nanographene can have discrete band-gaps and show semiconducting properties. It is considered that our defective graphene annealed at 800 °C for 10 min induces the edge state in graphene during producing defects through annealing. However, the temperature dependent-magnetization of the inset of figure 2 does not show a clear phase transition, in which the Curie temperature can be observed exactly. Relatively, transition temperature below 200 K is guessed approximately.

To obtain the transport properties, we performed the temperature dependence of resistivity. Figure 3 shows the resistivity versus temperature from the annealed graphene. The temperature-dependent resistivity was measured in the temperature range from 150 to 300 K. The resistivity of the annealed graphene decreases with increasing temperature like a usual semiconductor, and then has an abrupt peak at the high temperature region. According to magnetoimpurity model, [26, 27] the resistivity has a close relation with the Curie temperature in DMS. The main important property of magnetic semiconductors is a resistivity peak that displays in the vicinity of the Curie temperature. As the carrier scattering increases due to magnetic impurity in a maximum near the Curie point, the interaction between carrier and impurity becomes maximum. [26, 27] From the above theory, the Curie temperature is approximately 220 K for the annealed graphene. In addition, Ugeda et al. reported the Curie point of the disordered graphene due to vacancy distribution. The predicted Curie point for the vacancy concentration, $n_v \sim 3$ □ 10^{11} cm^{-2}, is known to be 200 K. [22] From the Raman spectroscopy of figure 1, the defect density (cm^{-2}) of the annealed graphene can be investigated and defined as [28] $n_D = \{1.8 \times 10^{22}/\lambda_{laser}^4\}(I_D/I_G)$, where λ is the laser wavelength, and I_D/I_G is the ratio of the peak intensity of the D peak to that of the G peak. The calculated defect density, 7.5×10^{13} cm^{-2}, is two orders magnitude higher than Ugeda's result. After all, our Curie temperature increased approximately up to 220 K. We also performed the time-dependent annealing for the graphene for 10, 20, and 30 min at 700°C. We obtained a modulation of electrical properties by thermal annealing (unpublished). In this result, we had two kinds of electrical properties, semiconductor and metal-insulator transition. Furthermore, high temperature and longer annealing time induce much more defects in graphene. Resistivity peak was shown in graphene annealed at 800°C for 10 min. However, we could not obtain the conductive graphene layer after annealing for 30 min at 800°C. Therefore, we could not measure the electrical and magnetic property.

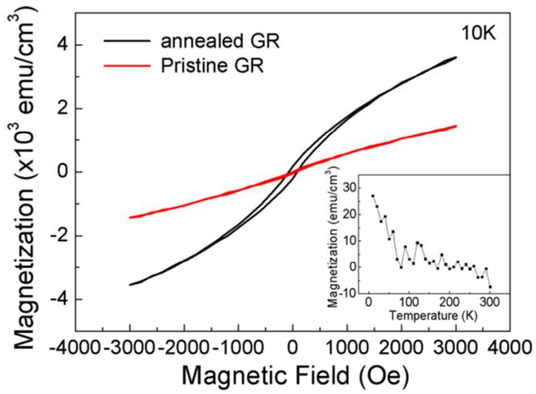

Fig. 2 Magnetization vs magnetic field (M-H) curves of the annealed graphene film at 10 K. The inset shows magnetization vs temperature of the annealed graphene film.

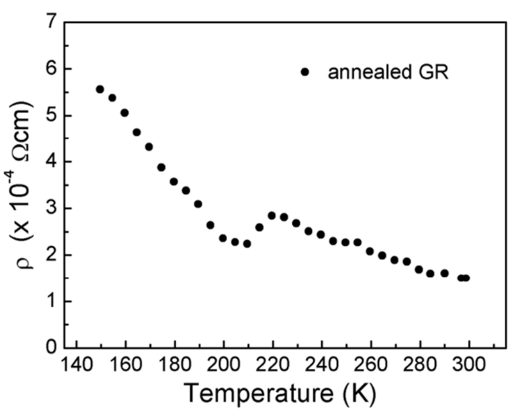

Fig.3 Temperature dependent resistivity of the graphene film annealed at 800 °C for 10 min.

Conclusions

In conclusion, ferromagnetism was well observed for the annealed graphene, and the transport measurement indicates that the Curie temperature is 220 K for the annealed sample from the magnetoimpurity model. The temperature-dependent resistivity showed a DMS property with a resistivity peak. The study of ferromagnetic property will make graphene a powerful candidate for spin-related electronic structures.

This work was supported by the Leading Foreign Research Institute Recruitment Program (No.2012-00109), and the Basic Science Research Program (NRF-2013R1A1A2008875, NRF-2014R1A2A2A01007718), through the National Research Foundation of Korea, funded by the Ministry of Education and a Korea University Grant. EKK acknowledges the financial support of the Mid-career Researcher Program through a grant from the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT & Future Planning (NRF-2013R1A2A2A01015824).

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