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Electric And Ferro-Electric Behaviour Of Polymer-Coated Graphene-Oxide Thin Film

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Abstract

Graphene oxide (GO) is prepared by the conventional Hummer's method and subsequently coated with polymaleic anhydride-alt-1-octadecene polymer (P-GO). Both GO and P-GO thin films are deposited on silicon substrate by drop-casting followed by air drying. Raman Spectroscopy, voltage - current (I-V) and polarization - electric field (P-E) measurements are used to study the micro-structural, electrical and ferroelectric behaviors of GO and P-GO thin films. The voltage - current (I-V) measurement shows that the synthesized GO and P-GO behaves like semiconducting and conducting materials respectively and are consistence with the results obtained from Raman spectroscopy measurement. The polarization - electric field (P-E) measurements shows that the polarization behavior is similar to lossy capacitor response with the combined effects of capacitor and resistor.

Keywords: Graphene Oxide, Polymer Coated Graphene Oxide, Polarization.

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1. Introduction

In last decades, carbon-based materials have been studied intensively as a potential candidate to overcome the scientific and technological limitations of traditional semiconductor devices [1-3]. After discovery of graphene and graphene oxide, several potential applications for graphene / graphene oxide are under development, and many more have been proposed. These include lightweight, thin, flexible, yet durable display screens, electric circuits, and solar cells, as well as various medical, chemical, and industrial processes enhanced or enabled by the use of new graphene materials. Some of them were proposed the non-volatile memory applications [4-6]. Thus, it would be of great interest if nonvolatile memory can also be realized in graphene so that logic and memory devices can be integrated on a same carbon-based platform because the semiconductor industry has long been seeking a high-density, high-speed, and low power memory technology that retains its data even when the power is interrupted [7]. One challenge, though, is that graphene is so conductive that it's hard to stop current from flowing, and such on-off switching is necessary for any sort of transistor. Graphene oxide (GO) with an ultrathin thickness (~1 nm) is also attractive due to its unique physical-chemical properties. A GO layer can be considered as a graphene sheet with *epoxide, hydroxyl*, and/or *carboxyl* groups attached to both sides. GO can be readily obtained through oxidizing graphite in mixtures of strong oxidants, followed by an exfoliation process. Due to its water solubility, GO can be transferred onto any substrates uniformly using simple methods such as drop-casting, spin coating, Langmuir-Blodgett (LB) deposition and vacuum filtration. The as-deposited GO thin films can be further processed into functional devices using standard lithography processes without degrading the film properties [8,9]. Furthermore, the band structure and electronic properties of GO can be modulated by changing the quantity of chemical functionalities attached to the surface and/or attaching some polymer on the surface of GO. Therefore, GO is potentially useful for microelectronics production.

Based on these facts, we have presented in this work the electric and ferro-electric behaviors of synthesized graphene-oxide (GO) and polymer-coated GO focusing on the fabrication of non-volatile data memory devices in future technological industries.

2. Synthesis Process and Experimental Details

The oxidation of graphite powder was carried out following the modified Hummer's method [10]. In a typical procedure, 200 mg graphite powder, 100 mg sodium nitrate and ~5 mL concentrated H_2SO_4 were mixed and cooled to 0 ^{0}C. Then the solution was kept under vigorous stirring. After 10 min, 600 mg $KMnO_4$ was added to this solution in stepwise manner so that the temperature was < 20 ^{0}C during these $KMnO_4$ addition steps. After the complete addition of $KMnO_4$ the temperature of the solution was slowly raised to 35 ^{0}C and kept in this condition for 30 min. A brownish grey paste was formed. Afterwards, ~10 mL water was added to the whole solution and the solution turned brownish yellow. The temperature of the solution was increased to 98 ^{0}C during water addition and this temperature was maintained for 15 min. The whole solution was then mixed with 28 mL water followed by addition of 500 µL 3 % H_2O_2 that reduces the residual permanganate. The light yellow materials were washed thoroughly with warm water 7–8 times. The solid was air dried and dissolved in ~20 mL distilled water by 15 min sonnication. Then it was centrifuged at 3000 rpm for 30 min. Then the supernatant was collected as graphene oxide (GO) solution. For the preparation of polymer coated GO we have followed our earlier reported method [10, 11]. In brief, 10 mg didodecyl dimethyl ammonium bromide (DDAB) was added to 5 mL of as synthesized GO and sonicated for 7 min. This didodecyl dimethyl ammonium bromide (DDAB) surfactant adsorbed on the surface of GO and make GO hydrophobic. As a result DDAB adsorbed GO are transferred into organic phase. Afterward the pH is adjusted to 8 by adding ~75 mg of Na_2HPO_4 followed by 5 min sonnication. After that, 3 mL of $CHCl_3$ is

added and stirred for few seconds and then kept untouched for phase separation. Colorless $CHCl_3$ phase becomes brown leaving the colorless aqueous phase, suggesting that GO was transferred from aqueous to organic phase. The bottom organic phase was collected and mixed with $CHCl_3$ solution of polymaleic anhydride-alt-1-octadecene (40 mg dissolved in 0.5 mL $CHCl_3$) and sonicated for 5 min. Next, a $CHCl_3$ solution of diamine (O, O'-bis (2-aminopropyl) polypropylene glycol-block-polyethylene glycol block-polypropylene glycol) (60 μL dissolved in 500 μL $CHCl_3$) was added in two steps. First, ~100 μL of diamine solution was added and sonnicated for 1 min. The rest of the diamine solution was added after 20 min. After overnight, the $CHCl_3$ was evaporated and brownish precipitate was mixed with 3 mL of water and 5 mg of Na_2CO_3. The whole mixture was sonicated for 5-10 min and left overnight. Optically clear brown solution was obtained, which was used as stock solution. The polymaleic anhydride-alt-1-octadecene polymer-coated GO was further purified from free polymer using acetone induced precipitation of GO. Typically, 1.0 mL of the polymer coated GO solution is mixed with 1.0 mL of acetone and centrifuged at 7000 rpm for 1 min. A brown precipitate was formed, leaving the colorless supernatant. The brown precipitate was collected and dissolved in 200 μL of H_2O. Next, 600 μL acetone was added and again centrifuged at 10000 rpm for 2 min. Brown precipitate was collected, dissolved in 2.5 mL of H_2O and used for further experiments. Due to its water solubility, GO / P-GO can be transferred onto commercial Si-substrates uniformly using simple drop-casting method and dried at room temperature for different measurements. The thicknesses of GO and P-GO are ~100 nm.

Raman measurements were carried out using the LASER excitation wavelengths of 515 nm with the LASER beam spot size ~1 μm and the incident power was ~1mW. In order to measure the electrical properties, Ag-metal top electrodes with a thickness of 200 nm and diameter of 100 μm were deposited at room temperature by electron beam evaporation with an in-situ metal shadow mask. The *I-V* characteristics of Ag/GO/Ag structures were measured at room temperature by Keithley 4200 semiconductor characterization system with voltage sweeping mode. During the measurement, a bias voltage was applied between the top and bottom electrodes with the latter being grounded. The polarization as a function of voltage (P-V or P-E hysteresis loop) is measured using a ferroelectric test system (precision LC Radiant Technology).

3. Results and discussions

Figure 1(a) shows Raman spectra of GO and polymaleic anhydride-alt-1-octadecene polymer coated GO (P-GO) thin films recorded at the visible excitation wavelength of 515 nm in the range 1000–3300 cm^{-1}; where 1st and 2nd order Raman spectra are shown. The 515 nm excitation spectra taken at different points are very similar and they reveal the well known GO Raman spectra. From this data one can conclude that these films are homogeneous in structure and it is built up of relatively large graphene crystallites. The GO's spectral feature shows that the film is highly photo-luminescent and this photoluminescence decreases when GO is coated with polymer (P-GO). When grapheme, a zero-gap semimetal, is oxidized in a manner that produces photoluminescence (PL) for solid, drop-cast GO. Due to removal of π-electrons from GO the fluorescence is decreased in P-GO [12].

After deconvolution of the 1st order Raman spectra using two Gaussian peaks it shows that the peaks at ~1365 cm^{-1} and ~1586 cm^{-1} are seen in the GO spectrum (Figure 1b) that are well known D-peak and G-peak respectively. The G-peak is due to the doubly degenerate zone center E_{2g} mode [11] and the D-peak rise due to defected graphite [5]. In case of P-GO (Figure 1c) the D-peak is shifted to 1355 cm^{-1}, whereas the G-peak position remains unchanged. Further, their I_D/I_G intensity ratio increases from 1.44 (0.95) to 1.58 (0.97) for the films GO when coated with polymer (P-GO) indicating the formation of more graphitic and/or disorder in structure due to defects. It is worthy to mention that we have used three spectrums in each sample and found that spectral features are similar and intensity ratios are the same.
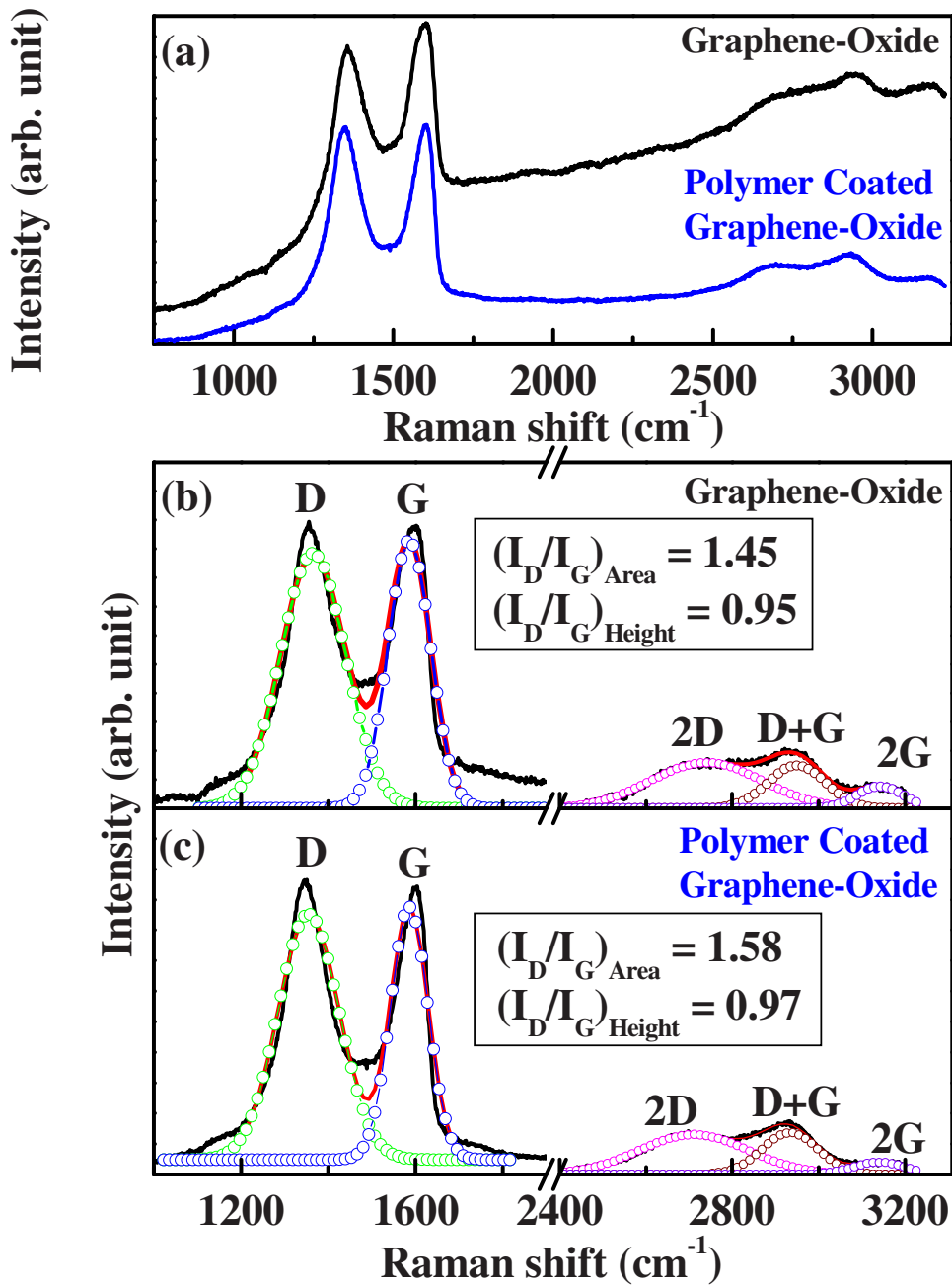
Fig.1 Raman Spectroscopy of (a) GO and P-GO; (b) Deconvoluted 1st and 2nd order Raman spectrum of GO into two and three Gaussian peak respectively; (c) Deconvoluted 1st and 2nd order Raman spectrum of P-GO into two and three Gaussian peak respectively.

In case of 2nd order Raman spectra of GO, after deconvolution into three peaks; we have observed that the 2741 cm^{-1} (2D), 3143 cm^{-1} (2G) and 2950 cm^{-1} (D+G) peaks respectively that are assigned as the overtone of D-peak, G-Peak and combination of D+G peaks respectively. In case of P-GO all these peaks are shifted towards lower band energy and are at ~ 2711 cm^{-1} (2D), ~2934 cm^{-1} (D+G) and ~3140 cm^{-1} (2G) peaks. The 2D peak is shifted from 2741 cm^{-1} to 2711 cm^{-1} and their peak width is reduced (see table 1a) indicating the reduction of graphene layer number. The $2(I_D/I_G)$ intensity ratios also increase from ~5(2.1) to ~7(3.3) for the GO when coated with polymer (P-GO) thin films. It is noted that the intensity ratio are considered as an area as well as height in D-peak (2D-peak) and G-Peak (2G-peak) respectively that shows similar trends. The results obtained from the Raman spectra are tabulated in table 1 and the results are well agreed with the formation of more graphitic in nature when GO is coated with polymer.

The *I-V* (current-voltage) characteristics of the Ag/GO/Ag memory cell are studied by dc voltage sweep measurements to evaluate the memory effects of the obtained devices. Figure 2(a-b) plots show a typical *I-V* curve within the range 0-3V with a sweeping step of 0.01 V of a Cu/GO/Ag cell and Cu/P-GO/Ag cell respectively. This curve clearly shows that the GO is semi-conducting in nature whereas P-GO is conducting in nature that are consistence with the Raman spectra results where we have observed the P-GO is more graphitic in nature than GO. During polymer grafting stage we have used Na_2CO_3 base. It is reported in earlier report that base can partially convert GO to graphene. We have also noticed that in polymer coating stage light yellow color of GO turns into brown/black [11]. This fact also indicated particle conversion of GO to graphene.

Figure 2(c-d) shows the same *I-V* curve, where the voltage is swept in a sequence of 0 V→+3 V→0 V→ – 3 V→ 0 V→+3 V with a sweeping step of 0.01 V. The I-V curve of the GO shows hysteresis loop that indicates the bipolar resistive switching effect and is higher than P-GO. The GO layer can be considered as a graphene sheet with epoxide, hydroxyl, and/or carboxyl groups attached to both sides, and physical properties of GO can be modulated by those chemical functionalities on the surface. When there are significant amount of epoxide, hydroxyl, and carboxyl groups on the GO surface, the conductance of GO is assumed to be low due to sp^3 bonding feature. As a negative voltage bias is applied, some oxygen-related functional groups inside the GO layers are shifted, resulting in an increase of sp^2 bonds. The conductance of GO becomes higher due to an increase in the concentration of interlayer π electrons. While sweeping the voltage to certain positive values, the oxygen-related groups diffuse toward GO sheets and attach to them again. Correspondingly, the sample returns to the high resistance state. Therefore, desorption and absorption of the oxygen-related functional groups on the GO sheets corresponds to the low and high resistive states, respectively. However, I-V curve shows a hysteresis loop in GO that indicates the formation of the ferroelectric materials and could be very useful for non-volatile memory cell device. These effects are comparatively lower in case of P-GO than GO due to attachment of polymeric atoms and formation of more conducting materials as observed in figure 2(b). Again, figure 2(e-f), presented the I-V semi-log curve; where current – voltage characteristics device clearly exhibits very interesting bistable electrical behavior of GO [13] and P-GO [14] as shown in figure 2(e) and 2(f) respectively. Polymer is nonconducting in nature and its adsorption lowers the conductance. However, GO is partially converted to graphene during polymer coating. This conversion increases the conductivity of P-GO.
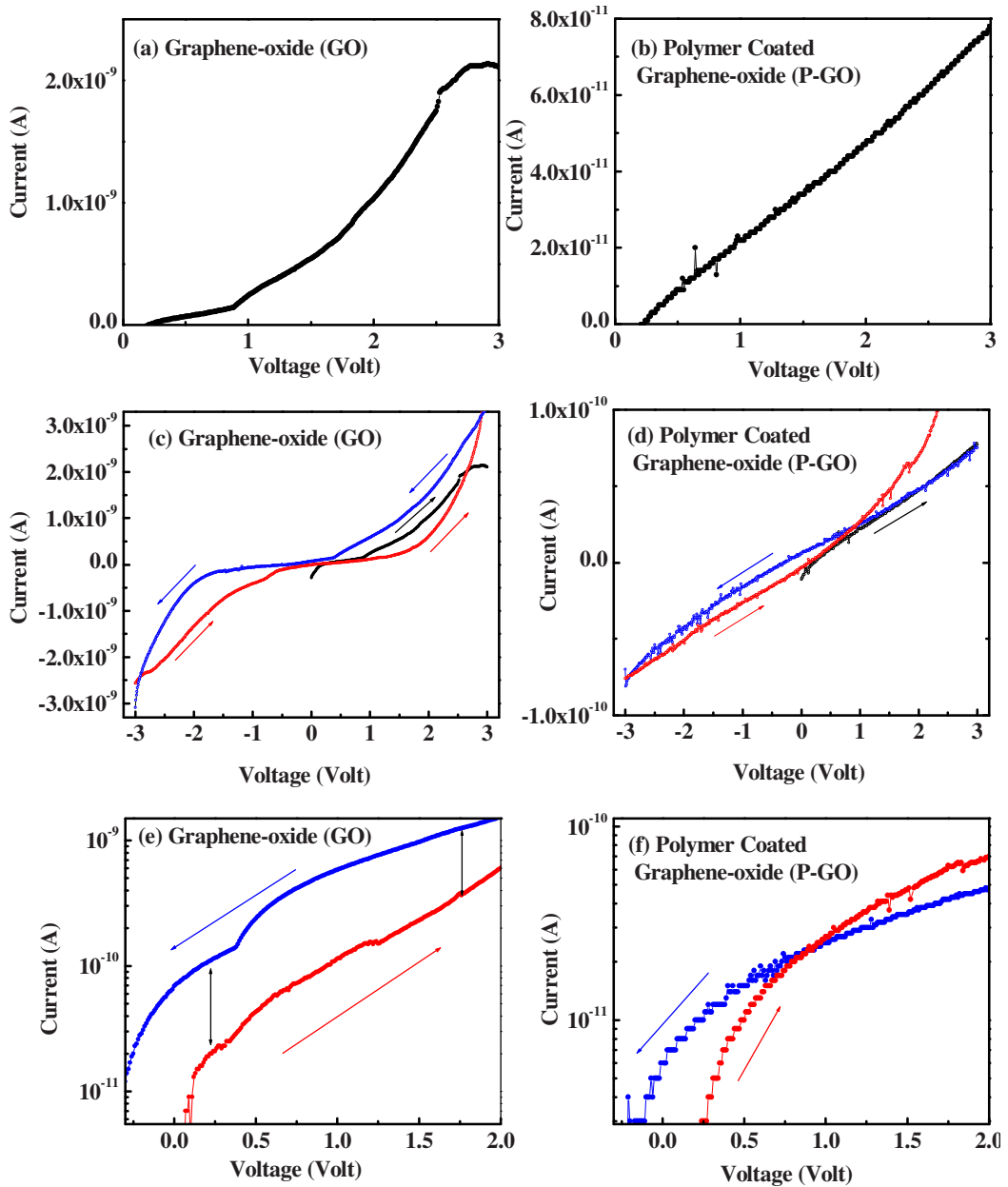
Fig. 2. Voltage (V) and Current (I) relationship of GO and P-GO within the range 0-3V (a-b); 0→+3V→0→-3V→0→+3V (c-d) and semi-log Voltage (V) and Current (I) relationship of GO and P-GO (e-f).

To understand the non-volatile memory cell of both GO and P-GO films, we have measured the polarization (P) as a function of electric field (V) i.e. *P-E hysteresis curve* as shown in figure 3(a-b) and their semi-log curve is shown in Figure 3(c-d). A P-E loop for a device is a plot of the charge or polarization (P) developed, against the field applied to that device (E) at a given frequency. The significance of this measurement can be more easily understood by examining the P-E loops for some simple linear devices. The

P-E loop for an ideal linear capacitor is a straight line whose gradient is proportional to the capacitance and for an ideal resistor the current and voltage are in phase and so the P-E loop is a circle with the centre at the origin. If these two components (capacitor & resistor) are combined in parallel we get the P-E loop, which is in effect a lossy capacitor, where the area within the loop is proportional to the loss tangent of the device, and the slope proportional to the capacitance. In our case the P-E loop as shown in figure 3(a-b) is the combination of ideal linear capacitor and resistor i.e lossy capacitor [15]. It is observed that the gap of the hysteresis loop in GO is obviously larger when applied voltages (V) are increases; whereas in case of P-GO the trends is opposite in nature. The results show that the remanant polarizations increases with applied voltage in case of GO; whereas it decreases in P-GO films. All polarization parameter obtained from the P-E hysteresis loops are tabulated in table 2. Inclusion of polymer (hydro-carbon) in GO degradation would be characterized by a decrease in remanent polarization and an increase in leakage current. The P-E semi-log curve shows a perfect hysteresis loop in the 1st quadrant in the graph; while it is not fully understood how this happens. However, the polarization is very poor and could be improved by adding some ferromagnetic metal or else for making perfect ferroelectric material that could be useful for the non-volatile memory cell devices.
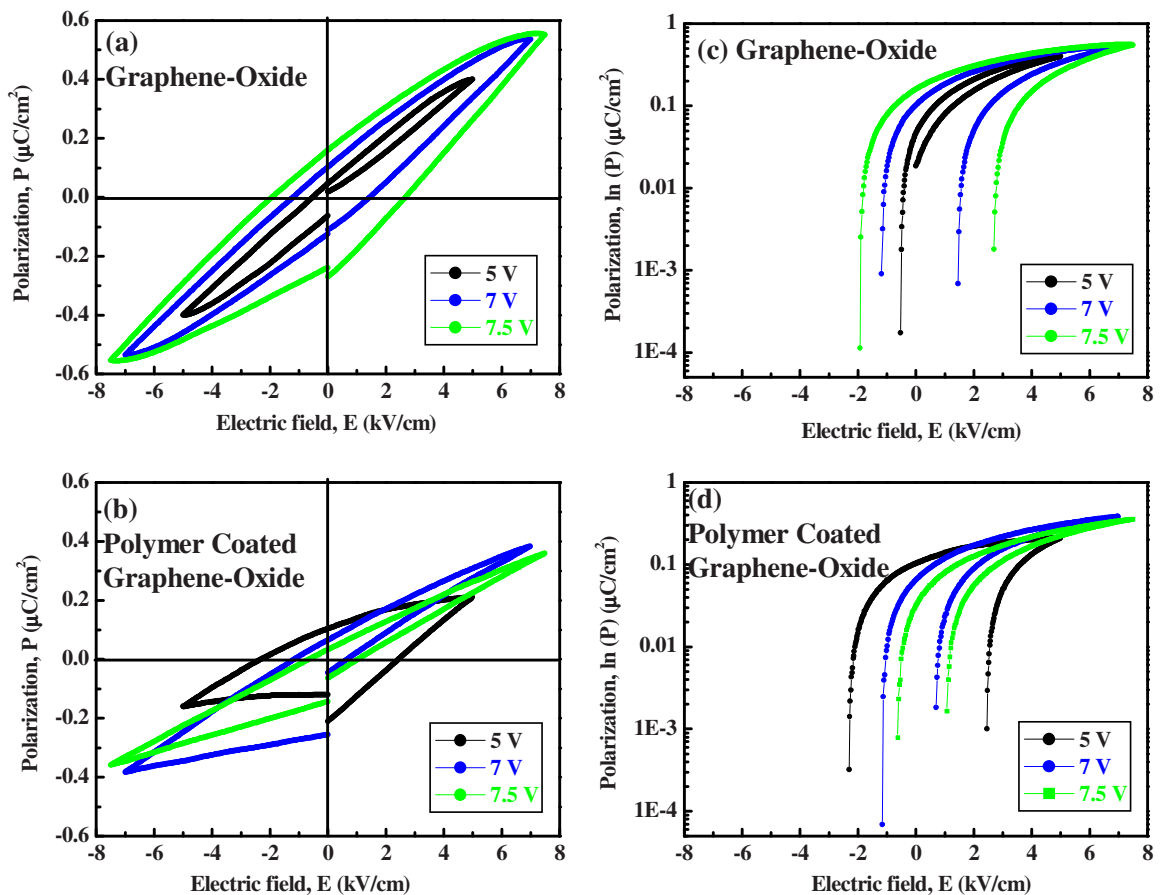

Fig. 3. Polarization (P) as a function of electric fields (E) hysteresis loops of GO and P-GO: (a-b) linear P-E loops and (c-d) semi log P-E loops.

Table 1: Summary results of Raman measurements.

Peaks of Raman spectra		Samples							
		GO				P-GO			
Order	Identified Peaks	Position (cm^{-1})	Width (cm^{-1})	(I_D/I_G) ratio		Position (cm^{-1})	Width (cm^{-1})	(I_D/I_G) / 2(I_D/I_G) ratio	
				Area	Height			Area	Height
1st order Raman	D-Peak	1365.3	148.8			1355.1	140.5		
	G-Peak	1586.2	98.1	1.44	0.95	1586.3	86.4	1.58	0.97
2nd order Raman	2D-Peak	2740.6	257.4			2711.4	251.0		
	2G - Peak	3142.6	106.8	4.99	2.07	3139.9	117.5	7.04	3.30
	(D+G) - Peak	2950.0	132.2		--	2934.2	129.2		--

Table 2: Summary results of polarization measurements. GO and P-GO are measured using PMF1011-278 ferroelectric tester with standard bipolar system (Precision LC Radiant Technology) keeping measurement parameters remains same. [Area = 10^{-4} cm^2; Thickness = 1.5 µm; Hysteresis Period = 10 ms; Preset delay = 10^3 ms)].

Sample	Polarization Parameter							
	Applied Voltage / Electric field		$C_{Max-Eff}$ (nF)	$\pm V_C$ (Volt)		Offset (µC/cm^2)	Polarization (µC/cm^2)		
	(Volts)	(kV/cm)		$+V_C$	$-V_C$		P_{max}	$+P_r$	$-P_r$
GO	5	33.34	0.0080	0	-0.528	-0.019	0.400	0.046	-0.063
	7	46.67	0.0077	1.443	-1.193	0.113	0.536	0.102	-0.125
	7.5	50	0.0073	2.682	-1.923	0.276	0.552	0.160	-0.239
P-GO	5	33.34	0.0042	2.439	-2.309	0.217	0.211	0.103	-0.121
	7	46.67	0.0055	0.671	-1.152	0.052	0.383	0.065	-0.256
	7.5	50	0.0048	1.047	-0.647	0.068	0.359	0.032	-0.145

4. Conclusion

Reliable and reproducible hysteresis and polarization behaviors are observed in GO/P-GO thin films. Ferroelectric behaviors show the combination of capacitor and resistor and have very poor polarization. The ferroelectric loop of GO increases with increase of applied voltage/electric field, indicating the electric field inside the bulk GO is the controlling factor of the forming. The resistances of the high and low resistance states also show dependence on the GO and P-GO thin films, demonstrating that the resistance occurs in a

certain region. Based on the experimental results, the possible physical mechanisms of combined capacitive and resistive polarization behaviors in GO/P-GO thin films can be understood by considering the desorption/absorption of oxygen-related groups and/or polymer-related groups on the GO sheets.

Acknowledgement

References

[1] Avouris, P., Chen, Z.H., Perebeinos, V., 2007. Carbon-based electronics, Nature Nanotech. 2/10, p. 605.
[2] Novoselov, K.S., Geim, A. K,. Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I.V., Firsov, A.A., 2004. Electric field effect in atomically thin carbon films, Science 306/5696, p. 666.
[3] Rueckes, T., Kim, K., Joselevich, E., Tseng, G.Y., Cheung, C.L., Lieber, C.M., 2000. Carbon Nanotube-Based Nonvolatile Random Access Memory for Molecular Computing, Science 289/5476, p. 94.
[4] Doh, Y.-J., Yi, G.-C., 2010. Non-volatile memory devices based on few-layer graphene films, Nanotechnology 21, p. 105204
[5] Liu, J., Yin, Z., Cao, X., Zhao, F., Wang, L., Huang, W., Zhang, H., 2013. A flexible, all reduced graphene oxide non-volatile memory device, Adv. Mater. 25, p. 233.
[6] Jeong, H.Y., Kim, J.Y., Kim, J.W., Hwang, J.Ok., Kim, J.-E., Lee, J.Y.,Yoon, T. H., Cho, B. J., Kim, S.O., Ruoff, R.S., Choi, S.-Y., 2010. Graphene Oxide Thin Films for Flexible Nonvolatile Memory Applications, NanoLett. 10, p. 4381.
[7] Meijer, G.I., 2008. Who Wins the Non-volatile Memory Race? Science 319/5870, p. 1625
[8] Eda, G., Fanchini, G., Chhowalla, M., 2008. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, Nature Nanotech. 3/5, p. 270.
[9] Cote, L.J., Kim, F., Huang, J., 2009. Langmuir-Blodgett assembly of graphite oxide single layers, J. Am. Chem. Soc. 131/3, p. 1043.
[10] Hummers, W., Offeman, R., 1958. Preparation of graphitic oxide, J. Am. Chem. Soc. 80/6, p. 1339.
[11] Bhunia, S. K., Jana, N. R., 2011. Peptide-Functionalized Colloidal Graphene via Interdigited Bilayer Coating and Fluorescence Turn-on Detection of Enzyme, ACS Appl. Mater & Interfaces. 3, p. 3335
[12] Luo, Z., Vora, P., Mele, E. J., Johnson, A. T. C. Jr., Kikkawaa, J. M., 2009. Photoluminescence and Band Gap Modulation in Graphene Oxide, Appl. Phys. Lett. 94, p. 111909
[13] Tuinstra, F., Koenig, J., 1970. Raman Spectrum of Graphite, J. Chem. Phys. 53, p. 1126
[14] Zhuge, F., Hu, B., He, C., Zhou, X., Liu, Z., Li, R.-W., 2011. Mechanism of nonvolatile resistive switching in graphene oxide thin film, Carbon, 49, p. 3796
[15] Stewart, M., Cain, M.G., 1999. NPL Report CMMT (A) 152 "Ferroelectric Hysteresis Measurement & Analysis" Centre for Materials Measurement and Technology National Physical Laboratory and University of Manchester, UK.