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Mechanisms of Polarization Switching in Graphene Oxide and Poly(vinylidene fluoride)-Graphene Oxide films

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Abstract

Polarization switching in graphene oxides (GO) and polyvinylidene fluoride (PVDF)-GO nanocomposite is investigated by piezoelectric force microscopy (PFM). The dynamical switching results reveal that GO films exhibit ferroelectric and piezoelectric properties with two-dimensional characteristics. Abnormal polarization switching is observed in PVDF-GO films, which is promising for electronic applications.

1. Introduction

Ferroelectrics are important electronic materials since they are used for nonvolatile random access memories, data storage and field-effect devices. In the past decade, low-dimensional ferroelectric materials used for those devices are of much interest because of the rapid advance in movable personal electronics, where compact and high-performance electronic components are in high demand. Recently, applications of graphene-related two-dimensional (2D) materials in electronics have attracted much attention. However, there is still a lack in using those two-dimensional materials as ferroelectrics for electronic applications. In this work, we will investigate the ferroelectric and piezoelectric properties of graphene oxides (GOs) and ferroelectric polymer-graphene oxide nanocomposites. For the sake of understanding the polarization switching mechanisms of these film structures, switching spectroscopic piezoelectric force microscopy (SS-PFM) [1] is employed.

2. Experiments and discussion

A modified Hummers method was used to prepare the graphene oxides from natural graphite. GO films in a thickness of about 1-2 μm were prepared on the indium-tin-oxide (ITO) glass substrate. Gold electrodes with a diameter of 0.1 mm were deposited on the film surface via the magnetron sputtering. The P-E polarization hysteresis loops at different temperatures are shown Fig.1, revealing the ferroelectricity and pyro-electricity of GO films. Fig.2(a) shows the hysteresis of piezoelectric phase switches measured by SS-PFM at different frequencies f of the applied DC bias fields (no AC bias is applied).

The imprint bias or the critical applied DC bias where the polarization switching occurs is denoted as E_c and is measured by the average of the forward and reverse coercive fields. Fig.2(b) shows the log-log plots of E_c versus f, demonstrating that a power-law relation $E_c \sim f^{\beta}$ can be used to characterize well the dynamical switching mechanisms with a dynamical scaling exponent β=0.25. The dynamical switching is also characterized using a high-frequency AC bias field overlaid with the applied DC field. Fig.2(b) shows the imprint bias of dynamical switching in the GO films at different frequencies f of the applied DC bias when a 30-KHz AC bias field is applied at the on-state ('ON') or off-state ('OFF') of the DC bias field. When the AC bias is applied at the 'OFF' of the DC bias, the exponent β=0.59 is significantly different with that when there is no AC bias applied during the switching.

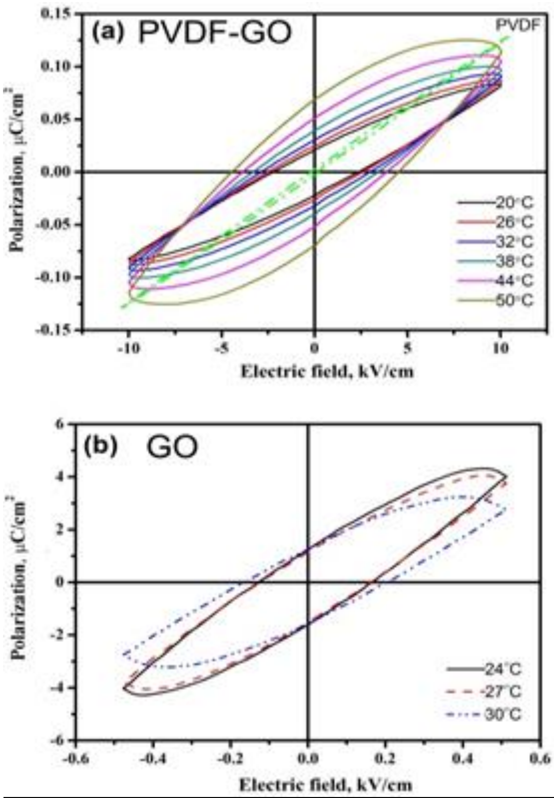

Fig.1 P-E hysteresis loops of PVDF-GO (a) and GOs (b) at different temperatures.

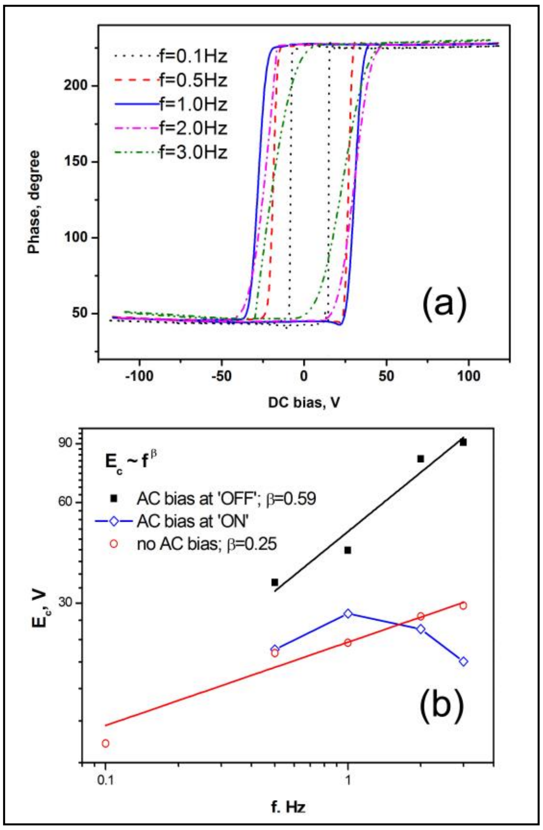

Fig.2 (a) Dynamical hysteresis of PFM phase signals without AC bias in GO films (b) The power-law scaling for imprint bias E_c with respect to f in GO films under dynamical switching.

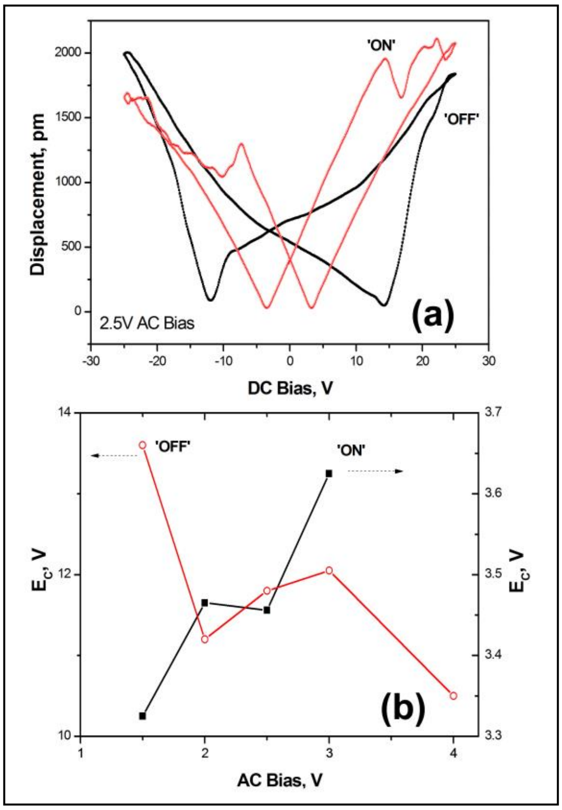

Fig.3 (a) Butterfly curves of piezoelectric response; and (b) AC bias related imprint bias of switching in PVDF-GO films.

It is noted that from previous well-investigated hysteresis models [2,3], the dynamical exponents are β=0.33 and 0.66 for 2D and three-dimensional (3D) systems, respectively. It is thus suggested that GO sheets are typical 2D piezoelectric systems likely resulting from the functional groups at their edges. The AC bias field could activate other functional groups and the electro-mechanical response of the whole system is thus three dimensional.

Polarization switching in polyvinylidene fluoride (PVDF)-GO nanocomposites is investigated to further explore the role of GOs in enhancing the ferroelectric and piezoelectric properties of ferroelectric polymer PVDF. PVDF-GO nanocomposite films were prepared by tape casting of GO and PVDF mixtures in DMF organic solvent.

The effects of AC bias on the electro-mechanical coupling in PVDF-GO film is found to be consistent with those of polarization switching in conventional ferroelectric films [4] when the AC bias is applied at the 'OFF' state, as shown in Fig.3. However, the dynamical polarization switching is abnormal since the E_c is found to increase with increasing AC bias applied at the 'ON' state, as shown in Fig. 3(b). The results suggest that PVDF-GO nanocomposites have unique polarization switching mechanisms due to the tight bonding of PVDF main chains with GO nanosheets.

3. Conclusions

SS-PFM analyses demonstrate that GO films could possess 2D ferroelectric and piezoelectric properties. PVDF-GO films show polarization switching behaviors that have not been observed in other conventional ferroelectrics. It is suggested that GO nanosheets and PVDF-GO nanocomposites are promising ferroelectric and piezoelectric materials for modern electronic applications.

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