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Toward van der Waals Epitaxy of Transferable Ferroelectric $BaTiO_3$ Thin Films on Graphene

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Abstract

The trend of "Internet of Things" requires transferable ferroelectric thin films for functional devices like actuators and sensors. We report here the growth of a typical ferroelectric perovskite compound, $BaTiO_3$, on a graphene monolayer which remains intact during the oxide growth process at high temperatures and at elevated oxygen pressure. The growth of $BaTiO_3$ on the graphene monolayer follows the Volmer-Weber growth mode at the initial growth stage. The crystallization of $BaTiO_3$ films are facilitated by graphene, and the $BaTiO_3$ thin film is highly (001)-oriented. The $BaTiO_3$ thin film on graphene can be easily exfoliated using a metal stressor layer. The graphene monolayer "stick" to the exfoliated $BaTiO_3$ film which demonstrate good piezoelectric properties. These results not only demonstrate the possibility to fabricate high quality crystalline ferroelectric films via a graphene monolayer, but also open the pathway to realize van der Waals epitaxy ferroelectric films which can be transferred onto arbitrary substrates, particularly onto flexible substrates for wearable devices applications.

1. Introduction

$BaTiO_3$ is the material with excellent dielectric and piezo-(ferro-)electric properties which can be used to fabricated various functional devices, such as sensors, actuators, memories, micro-electro-mechanical-systems *etc*. For more application scene, we need to integrate the $BaTiO_3$ thin films onto Si or flexible substrates, however the task is quite difficult because the oxidization of Si and the melting of flexible substrates. Therefore, it is necessary to develop a method to fabricate BaTiO3 thin films that can be easily transferred onto arbitrary substrates. There have been some reports on the (quasi-)van der Waals epitaxy of 2 or 3-dimensional materials on graphene, which is an ideal superlative substrate for the subsequent transfer of the films onto an arbitrary substrate.[1–4] Lee *et al.* reported that highly oriented perovskite dielectric $SrTiO_3$ thin films could be grown on graphene/SiO_2/Si substrates. However, the exfoliation and transfer of oxide films on graphene have rarely been examined and the ferroelectric and piezoelectric properties need to be further explored. In this work, we show that (001)-oriented crystalline $BaTiO_3$ (BTO) films could be grown on monolayer graphene covered SiO_2/Si substrates by careful control of growth conditions, and the BTO film could be easily released from the substrate using a stressor layer. The graphene turns out to be stable pretreatment. The growth dynamics, particularly the growth mode at the initial growth stage. The exfoliated BTO films show good ferroelectric properties. These results demonstrate the possibility to achieve functional oxide thin films with high crystalline quality on arbitrary substrates via a graphene monolayer.

2. Experiments

The film growth was carried out using a PLD system (SKY Co., Ltd) with a base pressure of 10^{-4} Pa in the chamber and an excitation laser wavelength of 248 nm. A commercial graphene/SiO_2/Si (001) substrate was used. The crystallization of the film has been examined by X-ray diffraction (XRD) using a Rigaku diffractometer. Transmission electron microscope (TEM, JEOL JEM-F200) was used to investigate the interface and the crystalline properties of the film. To release the film, a Cr stressor was sputtered on the film surface and a tape was adhered to the Cr stressor as a handle. The morphology and piezoelectricity of the BTO films were characterized by using a Bruker piezoresponse force microscopy (PFM) system (Dimension Icon).

3.Resulets and discussion

As shown in Fig. 1, the surface of the graphene is flat and intact after pretreatment which means that the graphene is not damaged. The Raman spectra shows the G and 2D peak which indicate the graphene is not oxidized. The XPS results also indicate the graphene is not oxidized.

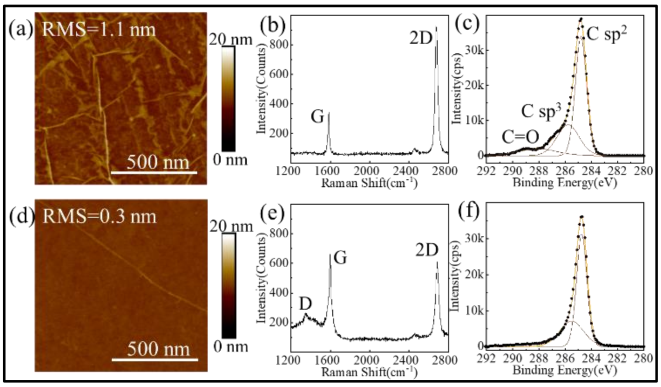

Figure 1 Pretreatment of graphene. (a, d) AFM image of the graphene before and after pretreatment. (b, e) Raman spectra of the graphene before and after pretreatment. (c, f) XPS C1s peak and fitting of the graphene before and after pretreatment.

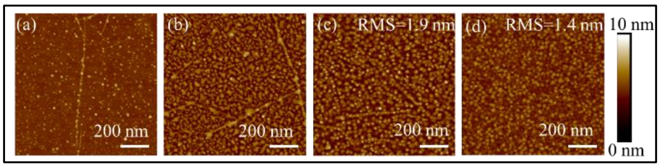

Figure 2 AFM images (1 μm×1 μm) of BTO films grown with different laser pulse numbers (equivalent thicknesses, 0.03 nm/pulse): (a) 10 pulses; (b) 100 pulses; (c) 1000 pulses and (d) 3000 pulses. The RMS values of the coalesced films were marked in (c) and (d).

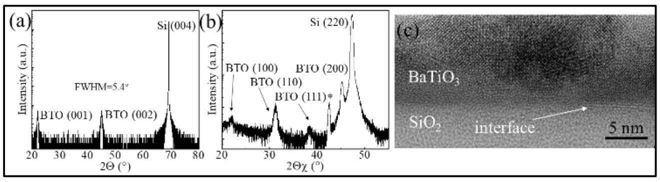

Figure 3 Crystallinity and interface characterization of the BTO film grown on graphene/SiO_2/Si. (a) XRD pattern of specular 2Θ scan around Si (004) Bragg conditions. (b) XRD pattern of an in-plane scan around Si (220) Bragg conditions of the same sample. (e) HRTEM cross-sectional image of the sample at the BTO/graphene/SiO_2 interface.

Fig.2 shows the surface of the BTO films with different thickness. At beginning, there are islands form on the graphene especially near to the wrinkle of the graphene. That indicate the growth mode of BTO on graphene is Volmer-Weber growth. The coalesced BTO thin films is flat, the root mean square roughness is 1.4 nm.

Fig. 3 shows the crystalline and the interface of the sample. The XRD results in Fig. 3a and b indicate the BTO films are (001)-orientated textured. In fig. 3 c, a cross-section TEM image shows a clear interface between the SiO_2/Si substrate and the BTO thin films.

Fig.4 a shows the process of the exfoliation of the BTO films. and Fig.4 b is the photo of the exfoliated film. As the Raman spectra shown in Fig.4 c, the graphene is “stick” to the BTO thin film. Fig. 4 d-f show the PFM results of the exfoliated BTO thin films, that results indicate the BTO films are ferroelectric.

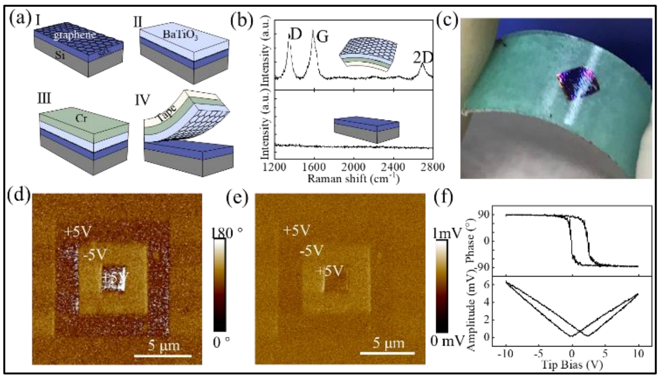

Figure 4 (a) Schematic illustrations for the film growth and exfoliation process. (b) Raman spectra on the surface of the exfoliated film (upper) and on the SiO_2/Si substrate surface (lower). (c) Photo of the exfoliated BTO thin film. (d) Piezoresponse phase of the exfoliated BTO film, the pattern was read out 1 hour after being written. (e) The phase (upper) and amplitude (lower) responses measured using a piezoresponse force microscope on a single location of the exfoliated BTO film on the Cr foil as a function of the sweeping tips bias.

4. Conclusions

(001)-oriented textured crystalline BTO films have been successfully grown on graphene by using the PLD approach. Graphene is flat and intact during the pretreatment. The growth mode of the BTO film on graphene is Volmer-Weber growth. By optimizing the growth conditions, the BTO film shows good crystallinity piezoelectric properties. BTO films can be easily exfoliated from the SiO_2/Si substrate using a Cr stressor. These results open a pathway to obtain high quality functional oxide films on an arbitrary substrate, which is of great interest for the applications of wearable electronic devices. In the future, our research will focus on the possible vdW epitaxial growth (or remote epitaxy) of oxides on graphene supported by crystalline substrates like Ge and $SrTiO_3$.

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