Monoclinic phase transition in stress-induced BiFeO$_3$ epitaxial films

Yen-Chin Huang 1, Hsin-Hua Lee 1, Yi-Chun Chen 1, Ching Cheng 1, Kuang-I Lin 1, Jenn-Shyong Hwang 1, Wen-I Liang 1, Hsiang-Jung Chen 1, and Ying-Hau Chung 2

1Department of Physics, National Cheng Kung University, Tainan, Taiwan
2Department of Material Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan

Material system near morphotropic phase boundary usually attracts a lot of attention due to their unique physical properties. The key issue of the mechanism is to reveal the coupling between the multiple phases or the intermediate states during phase transformation. Recently, highly-strained multiferroic BiFeO$_3$ (BFO) films have been reported to possess a partial isomeric boundary between tetragonal(T) and rhombohedral(R) phases. In this study, we investigated the as-grown state of mixed-phase BFO and the evolution of phases under external stimulus. Through first-principle study and Raman measurement, we found the mixed phase BFO films at room temperature included two monoclinic phases, R-like $M_r$ (P1) and T-like $M_t$ (Pm). $M_t$ phase transformed gradually to T-like $M_t$ phase when the temperature was increased to about 448 K. The R-like phase disappeared at about 450 °C. However, the T-like phase lasted to higher temperatures. This result showed the possible path of transition near the morphotropic phase boundary.

INTRODUCTION

BFO is rhombohedrally distorted perovskite. It is the multiferroisom material that exhibits ferroelectricity ($T_c$=1100 K) and G-type antiferromagnetism ($T_N$=643 K) at room temperature. When growing on the substrate of compressive stress, the BFO structure coexists tetragonal-like and rhombohedral-like phase. (a) The mix phases are also showed in the topography. (b)(c)Through the RSM, these two phases belong to the monoclinic $M_r$ and $M_t$ phases respectively.

EXPERIMENTAL METHOD

Schematic diagram of the (a) Piezo- response force microscopy and (b) Raman instrument. (c) By rotating the sample, the orientation of distinct polarization is directly obtained by analyzing the in-plane signal with different contrast.

RESULTS AND DISCUSSION

(a) Topography with thickness :

(b) Thickness-dependent Raman spectra :

(c) In-plane PFM :

(d) Simulated structures of T-like (Pm) and R-like (P1) phases :

Fig. (a)(b) The T-like phase sample transformed to the mixed (T-like and R-like) phase sample when increasing thickness. (c) PFM also showed at least two phases with in-plane polarization along [100] and [110], which may correspond to the $M_r$ and $M_t$ phases, separately. (b)(d) Raman spectrum and the first principle calculation showed the T-like and R-like phases belonged to Pm and P1 symmetry. The ratio of P1 to Pm phase increased with thickness. The in-plane polarization of Pm phase paralleled to the [100], and the P1 phase along [110].

CONCLUSIONS

• Piezo-response microscopy showed at least two phases with in-plane polarization along [100] and [110] direction in the strained BFO films. This result corresponded with the $M_r$ and $M_t$ phases shown in X-ray data.
• Raman and first principle simulation results suggested the two phases in mixed-phase BFO were of Pm (T-like) and P1 (R-like) symmetry.
• The in-plane polarization of T-like phase (Pm) rotated from [100] to [110] at about 175 °C.
• The ratio of the R-like (P1) phase decreased with increasing temperature, and totally disappeared at about 450 °C.

This work was supported by National Science Council through project NSC 96-2112-M-006-018-MY3.