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Oriented film growth using two-dimensional metal oxide nanosheet as seed layer

Tatsuo Shibata, Katsutoshi Fukuda, Yasuo Ebina, Takayoshi Sasaki*
NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Introduction

It is of crucial importance to develop techniques for the design and orientation control of crystal films. Since the film growth of crystals is strongly dominated by the surface structure of the substrate, one effective and feasible way to control the crystal growth is to use seed layers to introduce atomic regularity to the surface. Recently, so-called nanosheets have been synthesized via delamination of various layered compounds. Nanosheets have notably high two-dimensional anisotropy with an ultrathin thickness of around 1 nm and a lateral size of up to several tens of micrometers. They inherit high crystallinity from layered precursors, and an individual nanosheet can be considered as a two-dimensional single crystal. Using this unique two-dimensional material, novel method to control the film orientation has been developed. [1]

In this report, we have demonstrated oriented film growth of $SrTiO_3$ with a well-known perovskite structure promoted by ultimately thin seed layer of unilamellar metal oxide nanosheets. The nanosheet seed layer and $SrTiO_3$ films deposited on it were characterized by in-plane XRD technique.

Experimental

The $Ca_2Nb_3O_{10}$ nanosheet was prepared by delaminating a layered niobate, $KCa_2Nb_3O_{10}$, into colloidal single sheets. The resulting two-dimensional crystallites had a molecular level thickness of ~1.5 nm, and consisted of perovskite-related structure. A monolayer film of niobate nanosheet was deposited by Langmuir-Blodgett method onto glass substrate. A source of $SrTiO_3$ film was deposited by spin coating a precursor sol onto the substrate, which was heated at 550 °C for 1 h to crystallize $SrTiO_3$. In-plane XRD measurements were carried out using synchrotron radiation X-rays with a constant incident angle of 0.19° at BL-6C (KEK-PF).

Results & Discussions

Fig. 1 schematically illustrates the cross-sectional structure of the deposited film. $SrTiO_3$ crystal was grown on a glass substrate modified by a monolayer of $Ca_2Nb_3O_{10}$ nanosheets as the seed layer.

In-plane diffraction is useful technique for providing structural information of this ultrathin two-dimensional crystal. Fig.2 shows in-plane XRD patterns for the monolayer film of the nanosheet and deposited $SrTiO_3$ films. The nanosheet exhibits six diffraction peaks, which are indexable to its two-dimensional square unit cell (0.386×0.386 nm^2). The $SrTiO_3$ film grown on the nanosheet seed layer exhibited only several sharp diffraction peaks, which can be indexed as 100, 110, 200, 220, and 310 (i.e. only *hk0* reflections), respectively. The absence of general *hkl* peaks strongly suggests a uniaxial (001) orientation of the film. On the other hand, the film directly prepared on the glass substrate showed all peaks of $SrTiO_3$, suggesting randomly oriented crystal growth. Close structural similarities and lattice constants between $Ca_2Nb_3O_{10}$ nanosheet and $SrTiO_3$ (100) face (0.390×0.390 nm^2) could lead to an epitaxial relationship between them. Since all the nanosheets were tiled randomly in the azimuthal direction on the substrate, the grown film has macroscopically uniaxial orientation. The results clearly suggest that unilamellar nanosheets with a molecular-level thickness can promote oriented film growth on their surfaces.

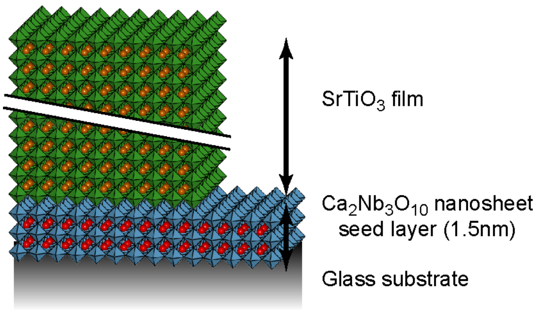

Fig.1: Schematic illustration of the deposited film structure.

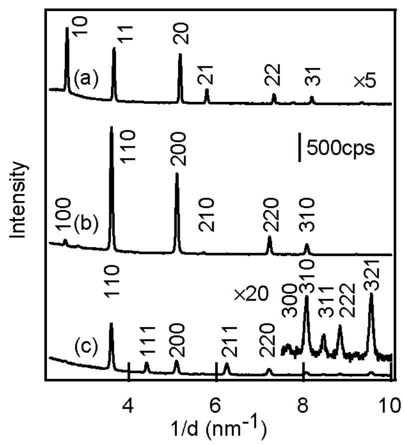

Fig.2: In-plane XRD patterns for (a) monolayer film of $Ca_2Nb_3O_{10}$ nanosheet and SrTiO3 thin films (b) with and (c) without nanosheet seed layer.

Reference

[1] T. Shibata et al., Adv. Mater. 20, 231 (2008).

* Sasaki.Takayoshi@nims.go.jp