Thin Solid Films 621 (2017) 202–206

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Self-assembly of very-low height/width aspect-ratio $Li_3Ni_2NbO_6$ disks embedded in Li_3NbO_4 epitaxial films

Hideyuki Kawasoko [a,*], Ryota Shimizu [b], Yoshitaka Takagi [a], Kuniko Yamamoto [a], Issei Sugiyama [b], Susumu Shiraki [a], Taro Hitosugi [a,b]

[a] Advanced Institute for Material Research (AIMR), Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-8577, Japan
[b] Department of Chemical Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8550, Japan

ARTICLE INFO

Article history:
Received 14 June 2016
Received in revised form 18 November 2016
Accepted 1 December 2016
Available online 07 December 2016

Keywords:
Self-assembled nanostructure
Nanocomposite oxides
Epitaxy
Pulsed laser deposition

ABSTRACT

We here report the self-assembly of $Li_3Ni_2NbO_6$ (LNNO) epitaxial disks with very low height/width aspect ratios. An epitaxial LNNO thin film is obtained at a substrate temperature (T_s) of 400 °C, using a pulsed laser deposition technique, and by increasing the T_s to 600 °C, Li_3NbO_4 epitaxial domains are formed inside the LNNO epitaxial film. Further increasing the T_s to 700 °C leads to the formation of LNNO disks (with diameters of a few micrometers and a typical height of ~100 nm) embedded in a Li_3NbO_4 film. Interestingly, transmission electron microscopy observations reveal that the LNNO disks are separated from the Li_3NbO_4 films by amorphous compounds, indicating the formation of a planar core-shell structure. Understanding of the growth processes of these unique nanostructures pave the way to fabrication of higher hierarchical structures embedded in thin film matrices.

1. Introduction

Self-assembled nanocomposite oxide thin films have attracted considerable attention because of their significant physical properties and potential technical applications, originating from strain or interface effects [1,2,3]. In particular, control of the size, shape, and density of oxide nanostructures embedded in oxide thin films has been an important topic because the physical properties of nanocomposites show strong dependence on those factors, as exemplified in two-phase systems of $YBa_2Cu_3O_{7-x}$-$BaZrO_3$ (superconductivity) [4,5], $BaTiO_3$-Sm_2O_3 (dielectricity) [6,7], and $BiFeO_3$-Sm_2O_3 (magnetism) [8]. Although many studies have focused on self-assembled nanoparticles and nanopillars [2], self-assembled oxide nanostructures with a very low height/width aspect ratio (*i.e.*, disk-like structures) have not been explored. Furthermore, self-assembled nanostructures consisting of three types of compounds, is of great interest for the fabrication of complicated hierarchical structures [9].

A rocksalt-type $Li_3Ni_2NbO_6$ (LNNO) is known as a solid solution of Li_3NbO_4 and NiO. In the LNNO crystal, Li, Ni, and Nb form an ordered structure below 1300 °C [10], while such cations are distributed randomly at higher temperatures. The one end member of the solid solution, Li_3NbO_4, exhibits a photoluminescence effect [11]. In addition, lithium-ion conduction is known to occur in Ni-substituted Li_3NbO_4 [12], suitable for high-performance electrodes in lithium-ion batteries [13]. The other end member, NiO, is widely known as an antiferromagnet [14]. Accordingly, the solid solution LNNO is expected to show intriguing optical, ionic, or magnetic properties. Thus, there is growing interest in the synthesis of LNNO thin films and nanostructures with controlled organization and size; however, there has been no report on the fabrication of LNNO epitaxial films nor self-assembled hierarchical nanostructures.

In this study, we first describe the fabrication of LNNO epitaxial thin films, and then demonstrate the synthesis of very-low aspect ratio self-assembled LNNO epitaxial disks surrounded by amorphous layers, embedded in Li_3NbO_4 thin films on a $MgAl_2O_4$(111) substrate. At a substrate temperature (T_s) of 400 °C, an epitaxial LNNO thin film is obtained, and at T_s = 700 °C, many disks with diameters of a few micrometers are found to self-assemble in the film. Scanning electron microscopy and transmission electron microscopy observations reveal that an amorphous layer separates the LNNO disk and the Li_3NbO_4 film. Furthermore, we discuss the growth processes of the disks accompanying the amorphous layer.

2. Experimental details

Thin films were fabricated on $MgAl_2O_4$(111) substrates using a pulsed laser deposition method with a KrF excimer laser

* Corresponding author.
E-mail address: hideyuki.kawasoko.b7@tohoku.ac.jp (H. Kawasoko).

http://dx.doi.org/10.1016/j.tsf.2016.12.006
0040-6090/

(wavelength, 248 nm; laser fluence, 1 J/cm^2; repetition rate, 5 Hz; growth rate, ~130 nm/h). Targets of $Li_4Ni_2NbO_x$ and Li_3NbO_x (Toshima Manufacturing Co.) were used for the growth of LNNO and Li_3NbO_4 thin films, respectively. The amount of Li was enriched for the $Li_4Ni_2NbO_x$ target to compensate for the loss of Li during deposition. In the deposition process, T_s was varied between 400 and 700 °C at an oxygen pressure of 1 mTorr to control the structures of films. The crystal structures of the thin films were evaluated with X-ray diffraction (XRD) measurements, using CuKα radiation (Rigaku, SmartLab). Surface morphology measurements and composition analyses were performed using atomic force microscopy (AFM; Agilent Technologies 5420) and scanning electron microscopy (SEM; JEOL, JSM-7800F) equipped with energy-dispersive X-ray spectroscopy (EDS), respectively. Cross-sectional transmission electron microscopy (TEM; Hitachi, HD-2700), operated at 200 kV, was employed to obtain bright field images, electron diffraction patterns, and EDS mappings.

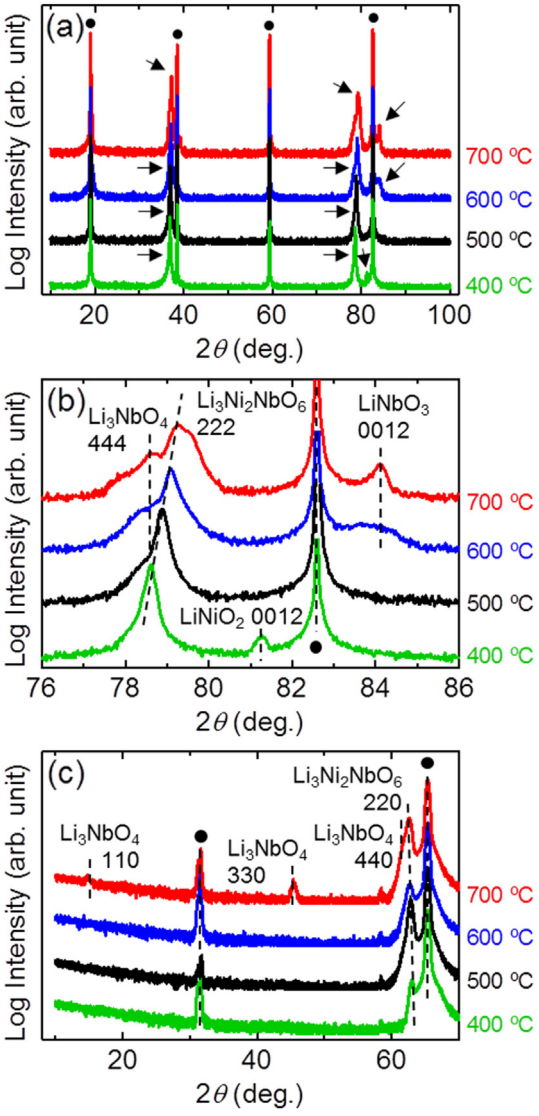

Fig. 1. (a) X-ray diffraction (XRD) patterns of the out-of-plane ω-2θ scan of thin films fabricated at substrate temperatures T_s = 400–700 °C. Arrows indicate the contributions of films. (b) Expanded figure around 2θ = 80°. (c) XRD patterns of the in-plane ω-2θ scan of thin films fabricated at T_s = 400–700 °C. In (a)–(c), black dots indicate the contributions of the $MgAl_2O_4$ (111) substrate.

3. Results and discussion

Fig. 1(a) and (b) show the XRD patterns of out-of-plane scans, and Fig. 1(c) shows an in-plane scan along $MgAl_2O_4$ [110] for the thin films deposited at T_s = 400–700 °C. In the out-of-plane scans, the film deposited at T_s = 400 °C exhibits two strong peaks, at 2θ = 36.9° and 78.7°, corresponding to LNNO 111 and LNNO 222, respectively. The full width at half-maximum (FWHM) of the rocking curve of LNNO 111 is 0.055°, indicating the high crystallinity of the film. In spite of the presence of a small amount of $LiNiO_2$ 0012 (2θ = 81.3°, Fig. 1(b)), the LNNO film deposited at T_s = 400 °C was epitaxially grown on the substrate, as confirmed from the in-plane scan (Fig. 1(c)); only the LNNO 220 peak is clearly visible at 2θ = 62.6°.

With increasing T_s above 500 °C, the $LiNiO_2$ 0012 peak disappears and Li_3NbO_4 is formed in the film. The original peak at 2θ = 78.7° (LNNO 222) shifts to a higher angle, and another peak at 2θ ~ 78.5° evolves with increasing T_s (Fig. 1(b)). The film deposited at T_s = 700 °C clearly shows two peaks, at 2θ = 78.5° and 79.3°, which can be assigned to Li_3NbO_4 444 and LNNO 222, respectively. We further notice that, in the films deposited at T_s = 600 and 700 °C, an additional peak appears near 2θ = 84.1°, possibly indicating $LiNbO_3$ 0012.

The observed Li_3NbO_4 thin films are also epitaxially formed, as confirmed from the in-plane scan (Fig. 1(c)). In addition to the peak of LNNO 220 (2θ = 62.6°), the film fabricated at T_s = 700 °C shows three peaks, at 2θ = 14.8°, 45.4°, and 62.2°, originating from Li_3NbO_4 110, 330, and 440, respectively. Along with the observation of the Li_3NbO_4 444 peak in the out-of-plane scan (Fig. 1(b)), we conclude that both the LNNO and Li_3NbO_4 films are epitaxially grown on $MgAl_2O_4$ (111) substrates (T_s = 700 °C).

To characterize the spatial distribution of LNNO and Li_3NbO_4, the surface morphology of the films was observed using AFM. As shown in Fig. 2(a)–(d), the surface structures strongly depend on T_s; groove structures develop on the film surface with increasing T_s. The film deposited at T_s = 400 °C does not display any nanostructures on its flat surface (Fig. 2(a)); the root-mean-square roughness of the surface was 0.18 nm, evaluated within the white square in Fig. 2(a) (2 μm × 2 μm). In contrast, sharp groove structures are present in the films deposited at T_s = 500 and 600 °C (Fig. 2(b) and (c), respectively). For the film deposited at T_s = 700 °C, isolated islands with the size of a few micrometers are observed, and the surface on the islands exhibits rim structures with a height of ~30 nm. With increasing T_s from 500 to 700 °C, the height of the islands, measured from the bottom of the groove, increases monotonically from ~30 nm to ~50 nm. We hereafter call these very-low height/width aspect-ratio island structures "disks". In the T_s range forming groove structures (500–700 °C), XRD patterns suggest that the amount of Li_3NbO_4 and $LiNbO_3$ increase at higher T_s. Accordingly, we speculate that the disks and groove structures are related to LNNO and other Li-Nb oxides.

To elucidate the origin of the structural evolution and the composition of disks, we employed SEM-EDS mappings (Fig. 2(e)) and TEM observations (Fig. 3). The SEM-EDS mappings of the film deposited at T_s = 700 °C reveal that Ni resides exclusively on disks, while Nb and O are distributed uniformly over the film. Because only the LNNO contains Ni, the SEM-EDS and XRD results suggest that the disks consist of LNNO. However, because of the large probing depth of EDS with the order of a few micrometers, it is unclear whether the disks are on top of the Nb-oxide layer or they are embedded in the Nb-oxide layer; thus, we next used TEM to investigate the cross-sectional structures.