Growth and Morphological Evolution of $\text{Co}_3-x\text{Mn}_x\text{O}_4$ ($x = 1, 2$) Thin Films

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We grew epitaxial $\text{CoMn}_2\text{O}_4$ and $\text{Co}_2\text{MnO}_4$ thin films on Nb-doped (0.1 wt.%) SrTiO$_3$ (100) single-crystal substrates by using pulsed laser deposition and studied how the growth temperature affected their crystal structures and surface morphologies. For $\text{Co}_2\text{MnO}_4$, increasing the growth temperature induced no significant changes except for an enlarged grain size. In contrast, for $\text{CoMn}_2\text{O}_4$, increasing the growth temperature caused its surface morphology to evolve from spherical grains to rectangular nanorods; additionally, X-ray diffraction showed that these rectangular nanorod grains scattered to domains with different crystal orientations. We attribute this rectangular nanorod pattern to self-assembled domains originating from Jahn-Teller distortions and film-substrate lattice mismatch.

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I. INTRODUCTION

Transition-metal oxides have been intensively studied because of their interesting physical properties caused by the strong correlation between their spin, charge, and lattice structure [1, 2]. Among the transition-metal oxides, spinel oxides generally take an $\text{AB}_2\text{O}_4$ structure, where A and B represent cations occupying tetrahedral and octahedral sites, respectively [3]. Because the valence states of these cations can vary widely, spinel oxides can have complicated chemical and physical properties [3-5]. Researchers have taken particular interest in cobalt manganese ($\text{Co}_3-x\text{Mn}_x\text{O}_4$ [$0 \leq x \leq 3$]), a spinel oxide whose properties change based on site occupancy and valence [6-10]. $\text{CoMn}_2\text{O}_4$ (i.e., when divalent $\text{Co}^{2+}$ and trivalent $\text{Mn}^{3+}$ ions occupy this material’s tetrahedral and octahedral sites, respectively) is considered a “normal-type spinel” [11-13]. Contrary to other normal-type spinel compounds with cubic unit cells, $\text{CoMn}_2\text{O}_4$ has a tetragonal crystal structure with a distortion parameter of $c/(a,b) = 1.14$ ($a = b = \sim 8.1$ Å, $c = \sim 9.29$ Å) caused by cooperative Jahn-Teller distortion of $\text{Mn}^{3+}$ ($3d^4$) ions. In contrast, $\text{Co}_2\text{MnO}_4$ (i.e., when the octahedral site is equally occupied by $\text{Co}^{3+}$ and $\text{Mn}^{3+}$ ions while the tetrahedral site is still occupied by $\text{Co}^{2+}$) has a cubic structure ($a = b = c = \sim 8.26$ Å) [14].

In this work, we report on the growth of $\text{Co}_2\text{MnO}_4$ and $\text{CoMn}_2\text{O}_4$. In particular, we focus on the relationship between the surface morphology and the growth temperature. For the $\text{CoMn}_2\text{O}_4$ thin film, increasing the growth temperature caused its round domains to evolve into rectangular nanorod domains; in contrast, for the $\text{Co}_2\text{MnO}_4$ thin film its round domains remained even as the growth temperature was increased. We also found that post-growth annealing induced the square domains to evolve into rectangular nanorod domains. Additionally, the rectangular nanorod domain boundaries formed deep valleys. This rectangular nanorod morphology may allow cobalt manganese spinel thin films to be used in solid-state gas detection with high efficiency because of their increased surface areas [15].

II. SAMPLE SYNTHESIS AND EXPERIMENTAL METHODS

$\text{Co}_2\text{MnO}_4$ and $\text{CoMn}_2\text{O}_4$ thin films were grown on Nb-doped (0.1 wt.%) SrTiO$_3$ (Nb-STO)(100) substrates with cubic crystal structure ($a = b = c = 3.905$ Å) at growth temperatures ($T_g$) ranging from 720 °C to 820 °C.
Fig. 1. (a) RHEED patterns taken from (a) the Nb-STO(100) substrate and during the growth of (b), (c), (d) CoMn$_2$O$_4$ and (e), (f), (g) Co$_2$MnO$_4$ thin films with a [100] azimuth. The growth temperatures shown are (b), (e) 720 °C, (c), (f) 770 °C, and (d), (g) 820 °C.

Fig. 2. θ-2θ XRD scans of the cobalt manganese oxide thin films near the (002) reflection from the Nb-STO substrate for various growth temperatures. For CoMn$_2$O$_4$, we plotted the data from all $T_g$ because they change considerably. In contrast, for Co$_2$MnO$_4$, we plotted only the representative data from $T_g = 720$ °C. (b) and (c) are θ-rocking curves for the (004) reflections from the CoMn$_2$O$_4$ and the Co$_2$MnO$_4$ thin films, respectively, grown at $T_g = 720$ °C.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the RHEED patterns for the Nb-STO(100) substrate, which exhibits a bright specular spot, due to reflections from the atomically-flat surface. However, during growths at $T_g = 720$ °C and 770 °C of CoMn$_2$O$_4$ [Figs. 1(b) and (c)] and Co$_2$MnO$_4$ [Figs. 1(e) and (f)], spotty patterns emerged as the bright specular spot disappeared indicating island growth. However, there are differences in the RHEED patterns between the CoMn$_2$O$_4$ and the Co$_2$MnO$_4$ thin films. The spots in the CoMn$_2$O$_4$ pattern are streaky compared with those in the Co$_2$MnO$_4$ pattern, implying that CoMn$_2$O$_4$ has a flatter surface. For CoMn$_2$O$_4$ grown at 820 °C [Fig. 1(d)], upon increasing $T_g$ to 820 °C the spots shown in Figs. 1(b) and (c) disappear and a streaky spot emerges at the position of the specular spot shown in Fig. 1(a). For Co$_2$MnO$_4$ grown at 820 °C [Fig. 1(g)], a streaky spot emerges superimposed onto the patterns shown in Figs. 1(e) and (f). Even with these differences in detail, the streaky spot emerging at $T_g = 820$ °C verifies that these samples have atomically-flat surfaces.