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The controllable growth of Co–$BaTiO_3$ nanocomposite epitaxial film by laser molecular beam epitaxy

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A B S T R A C T

Co–$BaTiO_3$ epitaxial films were successfully deposited on (0 0 1) $SrTiO_3$ substrates using the laser molecular beam epitaxy deposition. The growth behaviors were well controlled and monitored *in situ* by reflection high energy electron diffraction. Both the *ex situ* characterizations with high resolution transmission electron microscopy and X-ray dispersive analysis revealed that the Co nanocrystals in the face-center cubic structure dispersed well in the single $BaTiO_3$ matrix. Our controllable process might provide an efficient way to engineer Co–$BaTiO_3$ nanocomposite films with desired qualities.

1. Introduction

Nanocomposite thin films formed by embedding metallic nanocrystals (MNCs) in dielectric matrices exhibit extraordinary optical, electrical and magnetic properties and have great potential in many applications [1,2]. For instance, magnetic MNCs (such as Fe, Co, Ni, etc.) embedded in $BaTiO_3$ can greatly enhance the third order nonlinear susceptibility $\chi^{(3)}$ than that of pure dielectric material [3,4]. Moreover, such $BaTiO_3$ nanocomposite films would show multifunction with the coexistence of the ferroelectric and ferromagnetic orders [5,6]. During the past few years, a variety of preparation methods, including sol–gel [7], atom beam sputtering [8], and pulsed-laser deposition (PLD) [9–11], have been carried out to incorporate MNCs into dielectric to fabricate such composite films. Nevertheless, efficient control of the growth of such nanostructures is still challenging with above-mentioned methods. The laser molecular beam expitaxy (L-MBE), combining the advantages of both PLD and MBE, shows great potential in the implementation of embedding MNCs in complex oxide. With the *in situ* monitoring of the reflection high-energy electron diffraction (RHEED) [12–16], both matrix and MNCs can be precisely engineered with desired qualities by regulating the growth conditions.

Although the Co NCs were embedded successfully in BTO matrix in our previous study [11], further work needs to be done to scrutinize the growth process as well as the relevant controlling method. In this paper, the growth process of epitaxial Co:$BaTiO_3$ films on $SrTiO_3$ (1 0 0) substrates was carefully investigated using L-MBE. We show that the metallic Co NCs formed in the $BaTiO_3$ matrix is with the Stranski–Krastanov (S–K) growth mode, and the $BaTiO_3$ matrix keeps layer-by-layer growth even after the interruption of Co S–K growth. Our studies show that the controllable growth of magnetic metal nanocomposite film is significant not only for fundamental research but also for applications.

2. Experiment

The experimental parameters were listed in Table 1. The Co–$BaTiO_3$ nanocomposite films were grown by L-MBE, where a KrF excimer laser was alternately focused on the $BaTiO_3$ target and on the Co metallic target. Typically, certain number of pulses are first deposited on the Co target and consequently followed by another fixed number of pulses on the $BaTiO_3$ target to form the layer. The thickness of each $BaTiO_3$ layer was evaluated from the RHEED intensity oscillation period (here ~20 nm). The procedure was repeated up to 9 times until a 200 nm-thick Co:$BaTiO_3$ composite film was grown. Once the deposition of the $BaTiO_3$ layer was accomplished, the sample was annealed about 30 min

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in an oxygen ambient with a pressure of 10 Pa. The Co concentration in the films was adjusted by changing the number of laser pulses on the Co target. Four film samples with the number of pulses 0, 150, 300, 600 per layer on the Co target were prepared and characterized (here, the samples are denoted as sample 0, sample 1, sample 2, and sample 3, respectively).

During the deposition process, the *in situ* RHEED diagnosis was performed in anti-Bray condition using a 25 keV electron beam under a grazing incidence of 1–3° toward the surface. For (0 0 1) surface, the in-plane lattice constants are obtained by computing the streak spacing. The out-of-plane lattice constants are determined by the distance between spots in the vertical direction arising from the bulk diffraction [16]. The morphologies and the microstructures of the Co–$BaTiO_3$ nanocomposite films were investigated by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), and atomic force microscopy (AFM) (operating at trapping mode). Energy dispersive analysis of X-ray (EDX) equipped in HRTEM system was used to analyze the compositions.

3. Results and discussion

The single-crystal $SrTiO_3$ substrate was first annealed at 650° C in the ultra-high vacuum (UHV) environment for 3 h. The RHEED pattern of the annealed substrate was shown in Fig. 1(a), giving the information about the surface (note that a smooth surface is critical to support the epitaxial growth). The RHEED patterns of the $BaTiO_3$ surface deposited on the $SrTiO_3$ surface are shown in Fig. 1(b). It demonstrated that the $BaTiO_3$ film grew heteroepitaxially on the $SrTiO_3$ substrate in the layer-by-layer mode. We also see that the streaks become brighter and narrower

Table 1
The experimental parameters for the Co-$BaTiO_3$ film fabrication.

Background vacuum	$\sim 3\times10^{-6}$ Pa
Working vacuum	$\sim 5\times10^{-5}$ Pa
Substrate	$SrTiO_3$ (0 0 1)
Substrate temperature	~650 °C
Target	$BaTiO_3$ purity > 99.9%, Co purity > 99.9%
Annealing condition	650 °C, 10 Pa O_2 pressure, 30 min
Typical laser energy density	2–3 J/cm^2
Laser pulse frequency	1 Hz for $BaTiO_3$ deposition, 2 Hz for Co deposition

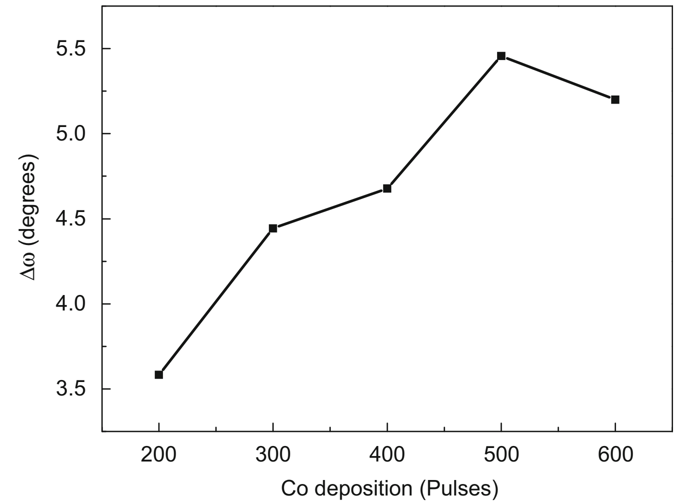

Fig. 2. Out-of-plane $\Delta\omega$ orientation distributions of the Co grains as a function of Co deposition pulse measured using RHEED.

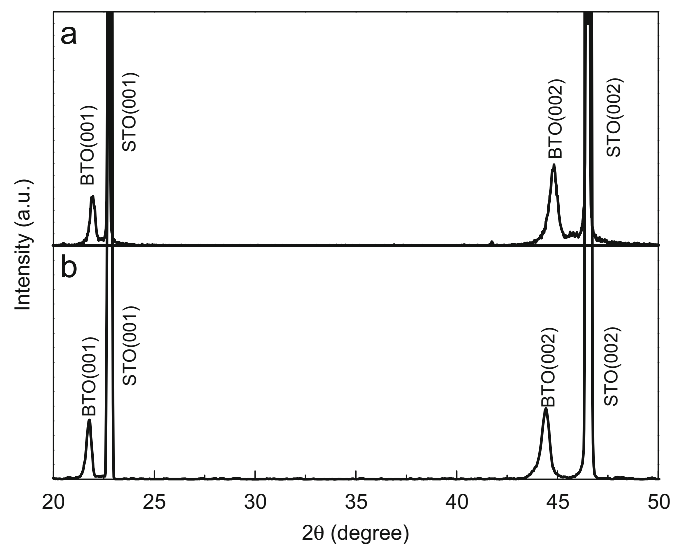

Fig. 3. XRD θ–2θ scans of $BaTiO_3$ film: (a) pure $BaTiO_3$ film and (b) Co:$BaTiO_3$ nanocomposite film.

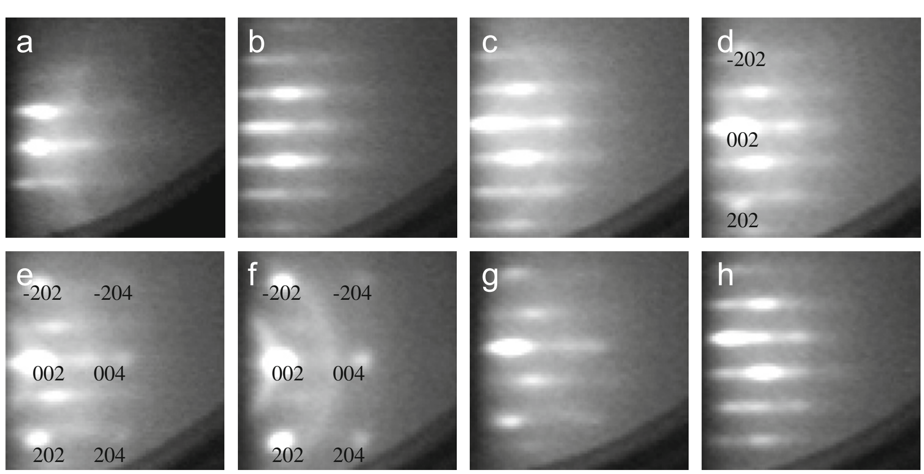

Fig. 1. Evolution of RHEED patterns along the ⟨0 1 0⟩ azimuth during the Co–$BaTiO_3$ nanocomposite film fabrication: (a) annealed $SrTiO_3$ substrate, (b) $BaTiO_3$ surface, (c) 100 pulses for Co deposition, (d) 200 pulses for Co deposition, (e) 300 pulses for Co deposition, (f) 600 pulses for Co deposition, (g) 30 pulses for $BaTiO_3$ deposition, and (h) 180 pulses for $BaTiO_3$ deposition. The numbers in figures (d), (e), and (f) denote the Bragg spots.