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Epitaxial composition-graded perovskite films grown by a dual-beam pulsed laser deposition method

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ABSTRACT

We prepared $SrTiO_3$ (STO) to $Ba_{0.6}Sr_{0.4}TiO_3$ (BST06) out-of-plane composition-graded films on STO (100) substrates by means of a dual-beam dual-target pulsed laser deposition technique. In the deposition system, a sliding mirror divides one KrF excimer laser beam into two, realizing the dual-beam of controlled intensity ratio. X-ray diffraction reciprocal space mapping has revealed that the graded films deposited under oxygen pressure at or lower than 1×10^{-3} mbar were coherently strained with the same in-plane lattice parameter as the substrate. Their composition gradient along the growth direction was confirmed by Rutherford backscattering analysis to be uniform. We deposited BST06 top layers of various thickness on epitaxial composition-graded (ECG) buffer layers and examined their coherency and crystallinity. In comparison with the cases of STO homoepitaxial buffer layers, ECG buffer layers achieved better crystallinity of top BST06 layers, suggesting that the crystallinity of a heteroepitaxially-grown film is affected not only by the in-plane lattice matching but also by the out-of-plane lattice continuity with the substrate. ECG films that bridge compositions of substrate and top layer materials can be useful buffer layers for epitaxial growth of lattice-mismatched oxide films.

1. Introduction

The researches on functionally graded materials (FGM), originating in development of structures for minimizing thermal residual stress, have widely spread their application fields including surface hardening, energy hervesting, electronic devices, and biomechanics [1]. Out-of-plane composition-graded films, a category of FGM, have been studied to obtain graded band gap semiconductors [2], but only with their lattices relaxed. In the present work, we attempted to prepare a type of FGM films that achieves both coherent epitaxy (i.e. the in-plane lattice parameter pinned to that of the substrate) and linear composition gradient, namely epitaxial composition graded (ECG) films.

We expect that such ECG films would be a promising materials for the strain engineering techniques. It is well known that physical properties of solid crystalline materials can be significantly modified by a lattice strain. As well as conventional pressure application to bulk materials, coherent heteroepitaxial growth of thin films has become a popular method to induce huge strain into the lattice. Actually, coherent growth on a single-crystalline substrate with larger (smaller) in-plane lattice parameter would cause a tensile (compressive) strain to the film material, being equivalent to uni- (bi-)axial pressure application. A lattice mismatch of 2.1%, which is the case of a $La_{1-x}Sr_xMnO_3$ film on a $LaAlO_3$ substrate, brings the film a change of c/a ratio from 1 to 1.06 that corresponds to +11 GPa of biaxial pressure [3]. The successful results on strain-induced modification of the physical properties of thin films by coherent heteroepitaxy include enhancement of the electrons mobility in Si films on relaxed Si–Ge layers [4], enhancement of the superconducting critical temperature in $La_{1.85}Sr_{0.15}CuO_4$ films on $SrLaAlO_4$ substrates [5], transition of a ferromagnetic metal $La_{1-x}Sr_xMnO_3$ ($0.3 \le x \le 0.5$) into an antiferromagnetic insulator by growing on $LaAlO_3$ substrates [3], and transition of $EuTiO_3$ from a paraelectric antiferromagnet into ferroelectric ferromagnet by growing on $DyScO_3$ substrates [6]. In general, however, a large mismatch would cause difficulty in realizing excellent crystallinity of heteroepitaxial layers, due to appearance of dislocations [7]. Insertion of a graded buffer layer has been reported to be effective in reducing dislocation densities in Si–Ge system [8]. Thus we expected that this structure would improve the crystallinity of a coherently strained film, opening up the practical application of strongly correlated electron material films with physical properties modified by strain.

Several types of pulsed laser deposition (PLD) techniques have been demonstrated to grow composition graded oxide films. A multiple-target single-beam PLD technique was attempted for $Ba_xSr_{1-x}TiO_3$ (BST; x=0.75, 0.8, 0.9, and 1.0) graded multilayers,

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exchanging the targets one after another [9]. Alternative ablation from two targets by a single beam has been effectively used for in-plane composition graded films using an automatic-controlled shadowing mask [10,11]. PLD and rf magnetron sputtering methods with dual-beam have also been proposed as useful techniques for material synthesis. An example of dual-beam dual-target PLD work is to shoot laser beams at YBa_2O_δ and CuO targets simultaneously for obtaining high-quality superconducting $YBaCuO_{7-\delta}$ films [12]. For BST films, $SrTiO_3$ (STO) and $BaTiO_3$ targets were rf sputtered simultaneously with various plasma power ratio, resulting in a series of BST films of $0 \leq x \leq 1$ with an x-step of 0.1 [13]. A trial of preparing graded films by dual-beam dual-target PLD has been also done with $Nd:Gd_3Ga_5O_{12}$ and $Y_3Sc_2Ga_3O_{12}$ targets [14]. In this case two laser equipments were used, varying the pulse repetition rate of each laser independently to modulate the composition of layers.

In this paper, we report on the scheme of our novel dual-beam dual-target PLD system, which requires only one laser equipment. The laser beam is divided by a mirror into two parts that irradiate two targets separately. Therefore the ablation occurs simultaneously on both, enabling mixing of species from two targets before reaching the substrate surface. Atomic level mixing in the gas phase, as well as continuous composition evolution of film composition, should be an advantage over alternative ablation or pulse number modulation techniques. We also demonstrate, as an example, the preparation of ECG films, choosing the composition from STO to BST ($x = 0.6$; denoted as BST06 hereafter) on STO (001) single crystal substrates. It is known that bulk BSTs of $0 \leq x \leq 0.6$ are of cubic structure at RT with their lattice parameter increasing proportionally to x [15], making themselves convenient as buffer layers whose unit cell volume can be tuned [16]. As the lattice parameters of cubic STO and BST06 are 0.3905 and 0.3965 nm, respectively, a coherently strained BST06 film on a STO (001) substrate is supposed to have c-axis length of 0.4088 nm and c/a ratio of 1.047, on the assumption of unchanged unit cell volume [see Fig. 2(a)]. Finally, coherency and crystallinity of BST06 top layers deposited on STO–BST06 ECG buffer layers were examined. It was confirmed that their crystallinity was enhanced by inserting an ECG buffer layer, suggesting that the crystallinity of a heteroepitaxially-grown film is affected not only by the in-plane lattice matching but also by the out-of-plane lattice continuity with the substrate.

2. Experimental details

The schematic of the deposition system is shown in Fig. 1. STO and BST06 targets were placed in the vacuum chamber, both facing the substrate with target-substrate distance of 50 mm. The substrate is heated by a silicon carbide resistive heater (DCA Instruments, DCA-SM01-SIC). A mirror placed in front of a KrF excimer laser (Lambda Physik, COMPex 102) can be slid to change the fraction of reflected photons from 0 to 100%. The reflected photons reach the STO target surface after being focused, while the unreflected part passes aside to reach the BST06 target. Thus simultaneous ablation occurs on two targets, resulting in mixture on the film composition, which should be controlled by the mirror position h. During the preparation of the present manuscript, we have learned a recent report by Cho et al. concerning a one-laser, dual-beam PLD setup, which is quite similar to ours but equipped with an attenuator in each of two beam paths to control the deposition rate [17]. The advantages of the sliding mirror scheme over the attenuators scheme include the constant laser fluence on the target surface for any incident energy and full usage of the original laser power.

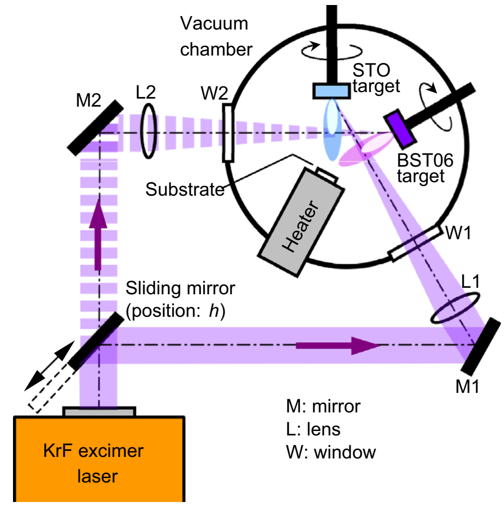

Fig. 1. Schematic diagram of the dual-beam dual-target PLD system. The laser path with the mirror in (out) is indicated with a continuous (dashed) band.

The common deposition conditions are as following; the laser fluence of 1.0 J cm^{-2}, the repetition rate of 5 Hz, and the substrate temperature of 873 K, followed by the cooling at −15 K min^{-1} in O_2 ambient of 267 mbar. During the deposition of a graded film, the energy ratio between two laser beams for (STO, BST06) targets was gradually changed from (100:0) to (0:100) by sliding the mirror, according to a sequence of mirror-position h versus time t (h–t). To design the h–t sequences, it is essential to know h dependence of deposition rate and composition of BST films. We prepared in advance several test samples of BST monolayered films on thermally oxidized Si substrates at fixed h under an oxygen ambient pressure (p_{O_2}) of 1×10^{-5} mbar, and examined their thickness and composition by a profilometer and energy-dispersive X-ray spectroscopy, respectively.

Graded films were deposited under various oxygen pressure (p_{O_2}), keeping other deposition conditions and the h–t sequence fixed. The coherency and crystallinity of each film was examined by observing a reciprocal space map (RSM) of X-ray diffraction (XRD) using a diffractometer (Bruker, D8) with Cu $K\alpha_1$ radiation (0.15406 nm). The depth profiles of composition in graded films were investigated by Rutherford backscattering (RBS) measurements using the Van de Graaff accelerator of CEMHTI. The incident energy of He^+ ions and the detector angle was 2 MeV and 165°, respectively. Fitting to RBS profiles was performed by using SIMNRA software [18] to extract the depth profile of each element, except the oxygen one.

3. Results and discussion

As was expected, the laser energy for each target shows linear dependence on h, as shown in Fig. 2(b). The h dependence of deposition rate, which is shown in Fig. 2(c), was not flat but formed a valley. This is because the deposition rate has non-linear dependency on the spot size at constant fluence in general PLD techniques [19]. Composition analysis has revealed that Ba content among A-site ions also has a strong h-dependence, due to the same reason, while Ti content among A and B-site ions is almost independent of h [Fig. 2(d)]. On these basis, we designed a h–t sequence shown in Fig. 2(e), aiming at a constant change of composition along the depth.

Fig. 3(a–c) show RSMs around (103) reflection of graded films deposited under p_{O_2} of 1×10^{-2}–1×10^{-5} mbar. An ECG film (with a-axis length identical with that of the substrate, and c-axis