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Continuous composition-spread thin films of transition metal oxides by pulsed-laser deposition

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Abstract

We have designed an improved pulsed-laser deposition–continuous composition-spread (PLD–CCS) system that overcomes the difficulties associated with earlier related techniques. Our new PLD–CCS system is based on a precisely controlled synchronization between the laser firing, target exchange, and substrate translation/rotation, and offers more flexibility and control than earlier PLD-based approaches. Most importantly, the deposition energetics and the film thickness are kept constant across the entire composition range, and the resulting samples are sufficiently large to allow characterization by conventional techniques. We fabricated binary alloy composition-spread films composed of $SrRuO_3$ and $CaRuO_3$. Alternating ablation from two different ceramic targets leads to in situ alloy formation, and the value of x in $Sr_xCa_{x-1}RuO_3$ can be changed linearly from 0 to 1 (or over any arbitrarily smaller range) along one direction of the substrate.

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Keywords: Composition spread; Transition metal oxides; PLD; Epitaxial thin films

1. Introduction

There have been numerous investigations on transition metal oxides (TMO), including cuprates, manganites, and titanates, because of their interesting electric and magnetic properties [1]. In order to more systematically explore TMO alloys with interesting physical properties, we have developed a pulsed-laser deposition–continuous composition-spread (PLD–CCS) approach for fabricating as-grown epitaxial thin films. Composition-spread thin film synthesis can offer an efficient means for the mapping of physical properties. In particular, we concentrate on complex oxides with two or more different metal ions per unit cell. Several growth techniques can be used to grow oxide films with high crystalline quality. A technique based on amorphous precursors has been studied extensively and applied to composition-spread solid-state synthesis by Xiang et al. [2]. In those studies, pulsed-laser deposition (PLD) was used to deposit the precursors. It has been shown, however, that PLD growth at elevated temperatures (leading to crystallization during the growth) has several advantages, which make it the method of choice for growing complex oxide films. The main advantages are accurate stoichiometry control and relative simplicity of the deposition equipment. It is also possible to use PLD to grow structures

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which are not in a thermodynamic equilibrium state, such as superlattices and meta-stable alloys. An earlier implementation [3] uses the flexibility of PLD to facilitate ternary phase spreads and allows to ‘‘zoom in’’ to a portion of the phase diagram. However, thickness and deposition energetics vary as function of position on the substrate, thus several values are convoluted with the composition. Furthermore, the composition is a non-trivial function of position. In this work, we designed a new PLD–CCS apparatus which eliminates the above-mentioned disadvantages, and describe the approach that we have taken to grow composition-spread thin films. We chose the $SrRuO_3$ (orthorhombic perovskite)–$CaRuO_3$ (orthorhombic perovskite) binary alloy for the demonstration of the composition-spread thin-film fabrication. $Sr_xCa_{1-x}RuO_3$ ($x = 0-1$) is known to have metallic conductivity and unusual magnetic properties [1]. $SrRuO_3$ is a ferromagnet with a T_c of about 160 K, whereas the susceptibility of $CaRuO_3$ shows a negative Weiss temperature, suggesting a tendency toward antiferromagnetism.

2. Experimental

As described in more details elsewhere [4], our CCS apparatus is based on a PLD system equipped with a 2 in. diameter substrate heater. This substrate heater unit can be operated at 800 °C in air and can translate (70 mm) and rotate (360°) in synchronization with fully automated target exchange and laser firing. By using the heater translation, precisely controlled by stepping motors, the composition at each position is addressable. Fig. 1 shows schematic illustrations of the PLD–CCS apparatus and the procedure for composition-spread thin-film fabrication. Wedge-type deposition profiles are obtained by translating the substrate behind a slit through which deposition occurs. The laser is fired when the substrate passes predefined positions. Ceramic targets of $SrRuO_3$ and $CaRuO_3$ were alternately ablated by ultraviolet KrF excimer laser pulses ($\lambda = 248$ nm), leading to the deposition of one unit cell (0.4) of film material during each period. The epitaxial composition spread film was grown on $LaAlO_3$(0 0 1) substrates at 675 °C in 80 mTorr of O_2. The value of x in $Sr_xCa_{1-x}RuO_3$ was changed linearly from 0 to 1 along the length of a substrate measuring 10 mm × 45 mm.

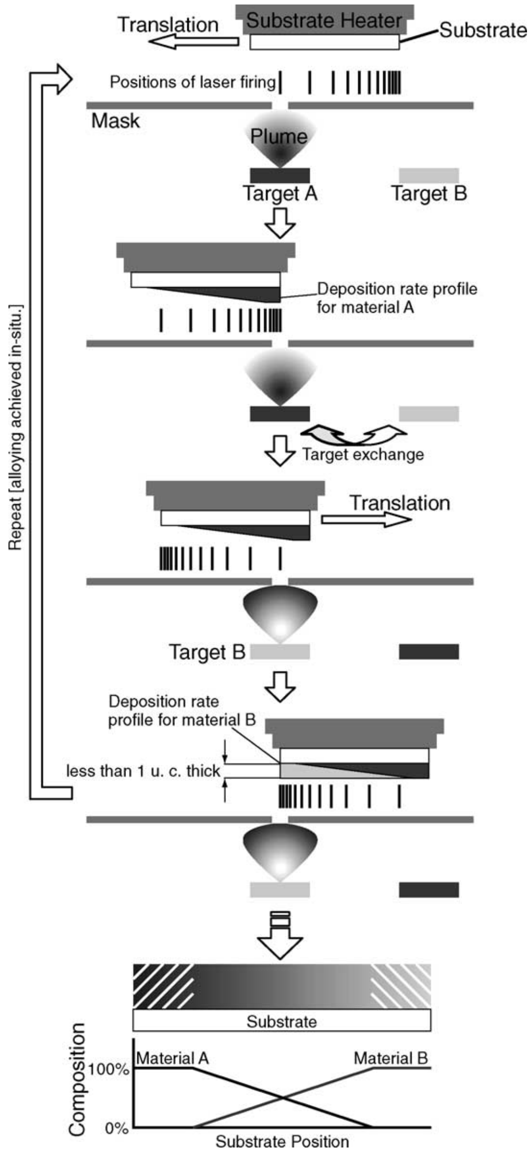

Fig. 1. Schematic illustrations of the PLD–CCS apparatus and the procedure for a typical composition-spread thin-film fabrication.

3. Results and discussion

The composition profile of a $Sr_xCa_{1-x}RuO_3$ composition spread as determined by energy dispersive

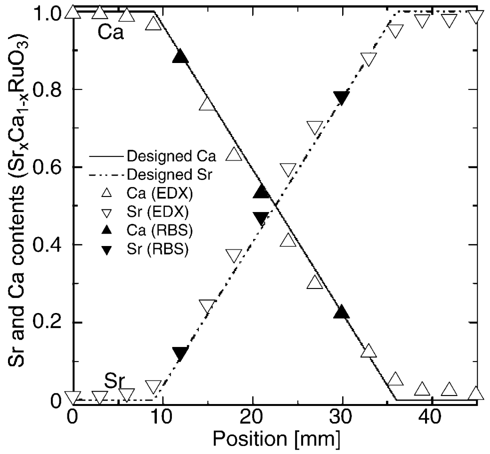

Fig. 2. Sr and Ca compositions of a $Sr_xCa_{1-x}RuO_3$ composition-spread thin film plotted as a function of substrate position. Compositions at each position were determined by EDX and RBS.

X-ray spectrometry (EDX) and Rutherford backscattering spectrometry (RBS) are shown in Fig. 2. The measured compositions at each position are in good agreement with the designed values, and the compositions determined by EDX corresponded well with the RBS results.

X-ray diffraction patterns of $Sr_xCa_{1-x}RuO_3$ individual and composition-spread thin films are depicted in Fig. 3. As is the case for all CCS approaches, each sample of finite size bears a compositional variation; in the case of this particular $Sr_xCa_{1-x}RuO_3$ composition-spread thin film, the composition varies from 0.07 to 0.13 within the 2.5 mm sample width. All XRD patterns of composition-spread thin films show a single peak, indicating the correct formation of the alloy and no phase separation into $SrRuO_3$ and $CaRuO_3$. Since the 2-theta position for the individual $Sr_xCa_{1-x}RuO_3$ film and the sample from the composition spread are almost identical, we conclude that the out-of-plane lattice constants of both thin films are similar. The full width of half maximum (FWHM) of the composition-spread thin films were larger than those of individual thin films due to the lateral composition variations in the former samples. Out-of-plane lattice constants (pseudo-cubic) of these films are slightly larger than those of bulk polycrystals; however, the dependence of the lattice parameter on the strontium-to-calcium ratio is very similar to that observed for bulk polycrystalline samples [5].

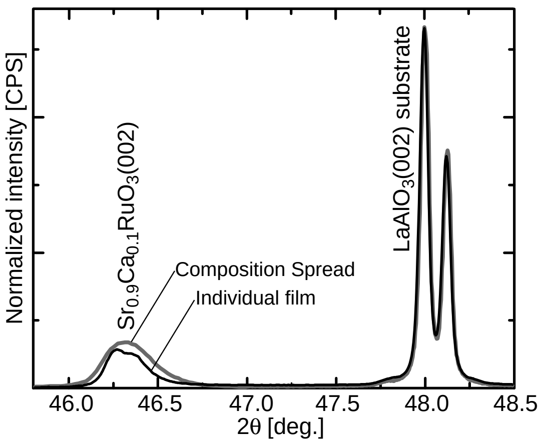

Fig. 3. XRD patterns of individual and composition-spread $Sr_xCa_{1-x}RuO_3$ ($x = 0.9$) thin films. Broadening of the peak for the composition-spread sample is attributed to the fact that for this sample the composition varies from 0.07 to 0.13 across its 2.5 mm width.

4. Conclusion

We have designed and developed a continuous composition-spread PLD apparatus and successfully applied it to the fabrication of as-grown epitaxial $Sr_xCa_{1-x}RuO_3$ ($0 \leq x \leq 1$) composition-spread thin films on 45-mm-long substrates. The compositions at each position of the composition-spread films (as determined by EDX and RBS) are in agreement with the designed values. The approach overcomes difficulties associated with an earlier PLD–CCS method, namely the non-uniformity in film thickness and deposition energetics across the composition spread. Nevertheless, the sample sizes obtained by this technique allow us to use standard characterization techniques, such as SQUID magnetometry, resistivity measurements, ellipsometry, etc.

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