Microstructure of epitaxial $SrRuO_3$ thin films on (001) $SrTiO_3$

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Metallic oxide films of $SrRuO_3$ deposited on (001) $SrTiO_3$ by pulsed laser deposition have been investigated by transmission electron microscopy (TEM) techniques. These films have a single crystalline structure with an extremely smooth surface. A TEM study of cross-sectional samples shows that the film grew epitaxially on the (001) surface of the $SrTiO_3$ substrate. The films grew along the [110] directions with an in-plane orientation relationship of either $SrRuO_3[1\bar{1}0]//SrTiO_3$ [100] and $SrRuO_3[001]//SrTiO_3[010]$, or $SrRuO_3[1\bar{1}0]//SrTiO_3[010]$ and $SrRuO_3[001]//SrTiO_3$ [100]. Domains with a rotation of 90° around $SrRuO_3[110]$ were observed in the dark-field image of plan-view samples. © *1998 American Institute of Physics.* [S0003-6951(98)03308-7]

Heterostructures based on semiconductors, metals, insulators, superconductors, ferroelectrics, and metal oxides are considered as important material systems. This is because they are important in the development of device applications, as well as in fundamental issues such as in interface physics and growth mechanisms of artificial structures.[1–3] Semiconducting heterostructures have been extensively investigated over the past two decades, both theoretically and experimentally, while the study of heterostructures of metal oxides is still in the early stages of development. In the present letter, we report a transmission electron microscopy (TEM) study of the heterostructure of $SrRuO_3$ thin films on a $SrTiO_3$ substrate prepared by pulsed laser ablation.

$SrRuO_3$ belongs to the ternary ruthenium oxide system which includes compounds such as $CaRuO_3$, $BaRuO_3$ and Sr_2RuO_4.[4,5] It is a distorted, pseudo-cubic perovskite[5] and was reported to be an orthorhombic phase of $GdFeO_3$ type.[6] The space group was determined to be Pbnm (No. 62) and lattice parameters $a=5.5670$, $b=5.5304$, and $c=7.8446$ Å.[7] It is paramagnetic and metallic conductive at room temperature[8] and ferromagnetic below ~160 K.[4]

Epitaxial thin films of $SrRuO_3$ have been found useful for electrodes and junctions in microelectronic devices, due to the high resistance to chemical corrosion, outstanding thermal conductivity, and stability. Recently, thin crystalline films of high quality were reported to be successfully grown on different substrate materials by different methods, such as on $SrTiO_3$(100) and $LaAlO_3$(100) by 90° off-axis sputtering technique,[9] on $LaAlO_3$(100)[10] and on $SrTiO_3$(001)[11] by pulsed laser ablation. However, to our knowledge, detailed studies on the structural characteristics of these films have not yet been reported. To examine the quality of the films and to determine their crystallographic structure in order to understand their influence on physical properties, TEM investigations of both cross-sectional and plan-view specimens of the $SrRuO_3$ films have been conducted in the present work.

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$SrRuO_3$ thin films were deposited on (001) $SrTiO_3$ by means of pulsed laser ablation. Details on the growth procedure were described in the literature.[11] Cross-sectional slices were obtained by cutting $SrRuO_3/SrTiO_3$ along the [100] or [010] directions of $SrTiO_3$, and then were glued face to face by joining $SrRuO_3$ surface. Cross-sectional as well as plan-view specimens for TEM observations were prepared by mechanical grinding, polishing, and dimpling, followed by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS™, Model 691, Pleasanton, CA) at 5 kV at an angle of 6°. Electron diffraction patterns and dark-field images were recorded in a Philips EM420 electron microscope operated at 100 kV.

Figure 1 is a low magnification TEM micrograph of a cross-sectional sample, showing the morphology of a $SrRuO_3$ film on $SrTiO_3$. The film has a flat surface and sharp interface and maintains a uniform thickness of 150 nm over the entire specimen. The surface roughness is approximately a few nanometers. It should be noted that Fig. 1 is a dark-field image formed by one of the reflections of the $SrRuO_3$ film. This image shows the existence of two different ''domains'' in the film (see the upper and lower parts of the film). The details of this will be studied in the following.

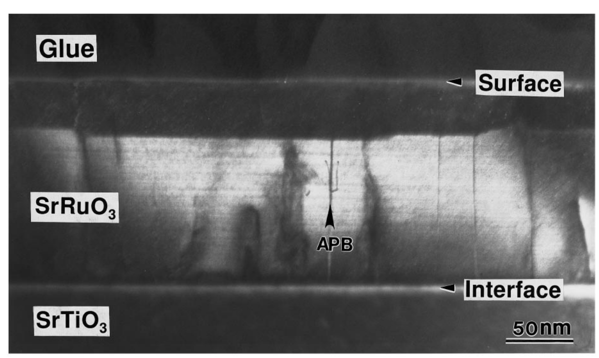

FIG. 1. Dark-field image using the $(\bar{1}11)$ reflection of $SrRuO_3$ showing two types of domain structures (white and black). Dark straight lines (marked by an arrow) within the white regions are antiphase boundaries (APBs).

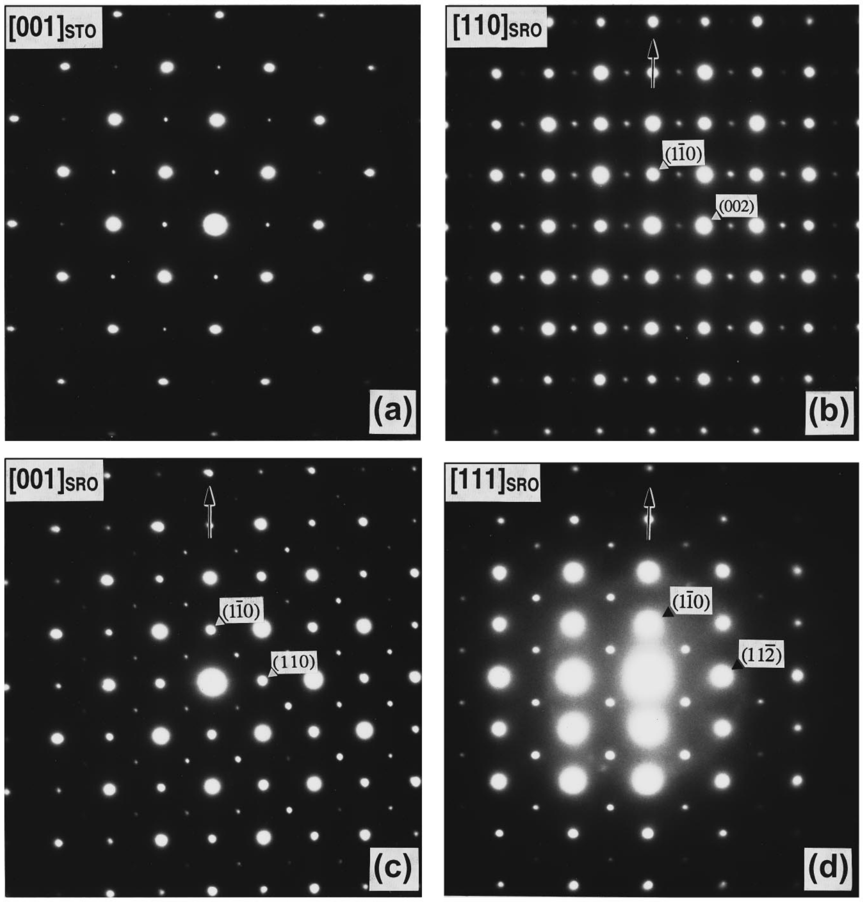

FIG. 2. SAED patterns of the cross-sectional $SrRuO_3/SrTiO_3$. (a) [001] zone of $SrTiO_3$. (b), (c), and (d) are the [110], [001], and [111] zones of the $SrRuO_3$ film, respectively.

Figure 2(a) shows a [001] zone axis selected-area electron diffraction (SAED) pattern of the $SrTiO_3$ substrate from the same cross-sectional specimen. Figures 2(b) and 2(c) are the SAED patterns taken from two different regions of the $SrRuO_3$ film, for which the electron beam direction is the same as for Fig. 2(a). Electron diffraction patterns of the $SrRuO_3$ films show that the film consists of small domains with two different orientations [Figs. 2(b) and 2(c)] with respect to the substrate. Figure 2(b) is identified to be the [110] zone electron diffraction pattern of the $SrRuO_3$ structure, in which the [110] direction is parallel to the normal of the as-grown film surface, i.e., the growth direction, while the [001] direction is located in the film plane. Figure 2(c) is the [001] electron diffraction pattern of the $SrRuO_3$ structure. Again, Fig. 2(c) shows that the growth direction of the film is along the [110] direction instead of the [001] direction proposed previously.[11] Tilt experiments were also conducted to further confirm this conclusion. Figure 2(d) shows a [111] zone SAED pattern of the $SrRuO_3$ structure, which was obtained by tilting the specimen around the growth direction, starting from Fig. 2(b), by either $+45°$ or $-45°$. Similarly, if the specimen is tilted along the growth direction by $\pm 45°$, starting from Fig. 2(c), the same electron diffraction pattern as shown in Fig. 2(d) will be obtained. In other words, if the specimen is tilted around the growth direction from the [110] zone SAED [Fig. 2(b)] by 90°, the [001] zone electron diffraction pattern shown in Fig. 2(c) will be obtained, and vice versa.

From the above results it can be concluded that the $SrRuO_3$ thin film grew along the [110] direction and consists of two types of domain structures which can be clearly seen from the dark-field image. An example is given in Fig. 1 which was taken under nearly two-beam conditions using the (111) reflection in Fig. 2(b). White and black regions correspond to the electron diffraction patterns of Figs. 2(b) and 2(c), respectively. Both types of domains are epitaxially grown on the (001) $SrTiO_3$ surface, and each type of domain has a definite orientation relationship to the substrate. Over the entire film, $SrRuO_3$[110]//$SrTiO_3$[001]. Moreover, if one assumes that one type of domain has an in-plane orientation relationship with $SrRuO_3$[110]//$SrTiO_3$[100] and $SrRuO_3$[001]//$SrTiO_3$[010], then the other type of domain will have an in-plane orientation relationship of $SrRuO_3$[110]//$SrTiO_3$[010] and $SrRuO_3$[001]//$SrTiO_3$ [100]. This means that the two types of domains are rotated around the growth direction with respect to each other by 90°.

The 90° rotational domain structures in $SrRuO_3$ films were also observed in the plan-view samples. Figure 3(a) shows a SAED pattern taken from a plan-view specimen from the same film studied by cross-sectional TEM. It shows different features from the [001] zone electron diffraction [shown in Fig. 2(c)]. It is a superposition of two [110] zone SAED patterns that are rotated around the zone axis with respect to each other by 90°. Reflections located in the center of the square, formed by strong reflections, result from double diffraction between the two types of 90° rotational

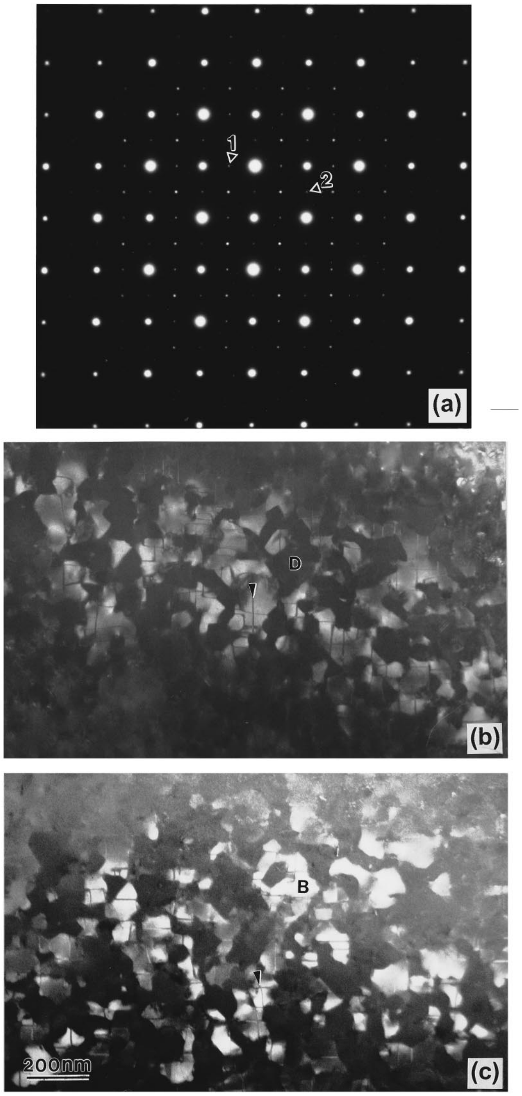

FIG. 3. (a) A SAED pattern taken from a plan-view specimen showing the superposition of two 90° rotational [110] zone SAED patterns. (b) and (c) are dark-field images obtained by using weak reflections 1 and 2 from (a), respectively. Fine dark straight lines (marked by arrows) in (b) and (c) are APBs.

domain structures, which can be clearly distinguished by carrying out dark-field imaging. Figures 3(b) and 3(c) are dark-field images using weak reflections ''1'' and ''2,'' respectively [Fig. 3(a)], which belong to two different [110] electron diffraction patterns, for which the crystal lattice is rotated by 90° around [110]. The black and white contrast in images [Figs. 3(b) and 3(c)] represent two different types of domain structures. The contrasts in these two images are reversed, which indicate that the $SrRuO_3$ thin films consist of only these two 90° rotational domain structures. Additionally, fine dark straight lines [marked by arrows in Figs. 3(b) and 3(c)] within each domain are APBs, similar to those shown in Fig. 1.

At first, the growth of $SrRuO_3$ films along the [110] direction seems illogical. However, if we consider the possible interfacial structure model of $SrRuO_3/SrTiO_3$, we find that this is reasonable. Let us assume that the $SrRuO_3$ films grow with their *c* axes normal to the $SrTiO_3$ (001) surface. Then the in-plane orientation relationship is: $SrRuO_3$[100]//$SrTiO_3$[110] and $SrRuO_3$[010]//$SrTiO_3$[$1\bar{1}0$]. The lattice mismatches along the $SrRuO_3$ [100] and [010] directions are equal to 0.14% and 0.81%, respectively, which was calculated using the formula given in the literature.[11] Similarly, if the $SrRuO_3$ films grow with the [110] axis normal to the $SrTiO_3$ (001) surface, then the in-plane orientation relationship is: $SrRuO_3$[110]//$SrTiO_3$[100] and $SrRuO_3$[001]//$SrTiO_3$[010]. The lattice mismatches along the $SrRuO_3$ [110] and [001] directions are then 0.44% and 0.47%, respectively. By comparing these two possible models, we find that the strain field from the lattice mismatch is more isotropic for the latter case than for the former case. Therefore, it is likely that the growth of $SrRuO_3$ films along the [110] axis is more favorable.

The mechanism for the formation of a 90° rotational domain structure is not yet clear. There are some results in the literature[12] which indicate that the misorientation of the substrate is responsible for the formation of the single crystalline films. It can be predicted that surface properties, such as orientation of the substrate, roughness, steps, kinks, and even surface reconstruction may play an important role in growing single crystal films. Detailed studies of $SrRuO_3$ thin films grown on the $SrTiO_3$ substrates with different degrees of misorientations from the (001) planes are in progress.

In conclusion, we have determined that metallic oxide thin films of $SrRuO_3$, produced by pulsed laser deposition, were epitaxially grown on (001) $SrTiO_3$ along the [110] directions and rather well lattice matched to the substrate. The films are composed of two types of 90° rotational domain structures. Each type of domain has an in-plane orientation relationship with respect to the substrate of either $SrRuO_3$ [110]//$SrTiO_3$[100] and $SrRuO_3$[001]//$SrTiO_3$[010], or $SrRuO_3$[110]//$SrTiO_3$[010] and $SrRuO_3$[001]//$SrTiO_3$[100]. Antiphase boundaries were observed within each domain structure.

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