JOURNAL OF APPLIED PHYSICS VOLUME 86, NUMBER 8 15 OCTOBER 1999

Effects of stress relaxation of epitaxial $SrRuO_3$ thin film on microstructures

X. Q. Pan,[a] J. C. Jiang, and W. Tian
Department of Materials Science & Engineering, The University of Michigan, Ann Arbor, Michigan 48109

Q. Gan, R. A. Rao, and C. B. Eom
Department of Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina 27708

(Received 23 February 1999; accepted for publication 13 July 1999)

We report the effect of lattice stress relaxation on the microstructures of epitaxial thin films by domain structure studies of epitaxial $SrRuO_3$ thin films grown on vicinal (001) $SrTiO_3$ substrates. X-ray diffraction analysis revealed that the as-grown films are single domain and have a strained lattice due to the lattice mismatch with the substrate. In contrast, plan-view transmission electron microscopy (TEM) images obtained from the same films showed the coexistence of domains with three different crystallographic orientations. The discrepancy is attributed to the lattice stress relaxation occurring on the TEM specimens as the substrate material is eliminated by ion milling or etching, resulting in the formation of elastic domains with different crystallographic orientations. These studies directly reveal a crucial effect of the lattice strain relaxation on the microstructures and properties of epitaxial thin films when the substrate material is removed. © *1999 American Institute of Physics.* [S0021-8979(99)05220-2]

I. INTRODUCTION

Epitaxial thin films and heterostructures of perovskite oxides have attracted considerable attention, owing to their underlying technologically important properties, such as high-temperature superconductivity, ferromagnetism, ferroelectricity, colossal magnetoresistance, and metallic conductivity. In most heteroepitaxial films, there is an unavoidable microstructural lattice strain in the film, as the thin film is coherently bound to a substrate of different material, i.e., elastic deformation caused by the lattice mismatch between the thin film and the substrate. It is believed that such strain in the epitaxial thin films can have a strong influence on the film properties. For instance, colossal magnetoresistance on the order of 10^6% was observed in epitaxially grown La–Ca–Mn–O thin films on $LaAlO_3$ substrates, while the corresponding bulk crystalline materials showed a low magnetoresistance ratio (~100%) and such a huge difference was attributed to the lattice strain in the thin films.[1]

Epitaxial thin films of $SrRuO_3$ have been intensively studied due to their attractive electrical and magnetic properties that make this material very useful for making devices. Many studies have been focused on the single domain epitaxial thin film fabrication,[2] ferroelectric device fabrications,[3] property measurements,[2,4–7] surface morphology,[8] and microstructure investigations.[3,9,10] In this article, we report the effects of strain relaxation of $SrRuO_3$ thin films on domain structures by transmission electron microscopy (TEM) and x-ray diffraction.

II. EXPERIMENTAL METHODS

$SrRuO_3$ thin films were deposited by 90° off-axis sputtering on exact and miscut (001) $SrTiO_3$ substrates under the conditions described elsewhere.[2] The domain structures of the thin films were studied by x-ray diffraction, selected area electron diffraction (SAED), and electron diffraction contrast imaging within TEM. Cross-sectional as well as plan-view specimens for TEM observations were prepared by mechanical grinding, polishing, and dimpling, followed by Ar ion milling at 4 kV at an angle of 5°. Electron diffraction and dark-field contrast images were carried out within a Philips CM12 electron microscope operated at 120 kV.

III. RESULTS AND DISCUSSION

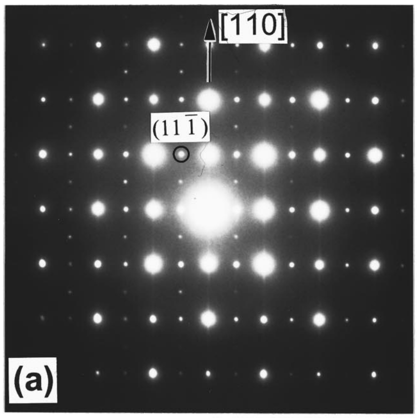
According to the crystallographic features of the $SrRuO_3$ and $SrTiO_3$ structures, the $SrRuO_3$ films can grow on (001) $SrTiO_3$ substrates, with three possible epitaxial arrangements that can be distinguished in the dark-field TEM images: (110) domains with two different in-plane epitaxial arrangements of: (1) *X*-type {$SrRuO_3$ [001]//$SrTiO_3$ [010] and $SrRuO_3$ [110]//$SrTiO_3$ [100]} and (2) *Y*-type {$SrRuO_3$ [110]//$SrTiO_3$ [010] and $SrRuO_3$ [001]//$SrTiO_3$ [100]}, and (3) (001) domains (*Z* type) with in-plane epitaxial arrangements of $SrRuO_3$ [110]//$SrTiO_3$ [010] and $SrRuO_3$ [110]//$SrTiO_3$ [100]. The details have been discussed previously.[10]

The off-axis x-ray azimuthal Φ scans of the $SrRuO_3$ thin film grown epitaxially on a miscut (001) $SrTiO_3$ substrate with miscut angle, $\alpha=2°$ and miscut direction $\beta=5.4°$, revealed a purely single domain (only *X* type) structure.[11] However, the TEM investigations on the same film indicated a multidomain structure.

Figure 1(a) shows SAED pattern from a cross section of (110) oriented $SrRuO_3$ film with the electron beam direction parallel to the [010] axis of $SrTiO_3$. This pattern is a superposition of the [110] and [001] zone SAED patterns of the $SrRuO_3$ structure, showing the coexistence of both *X* and *Y*

---

[a] Author to whom correspondence should be addressed; Electronic mail: panx@umich.edu



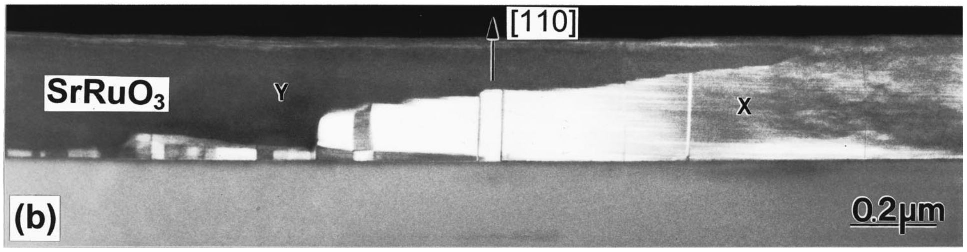


FIG. 1. (a) A SAED pattern taken from a cross-section specimen of a SrRuO$_3$ thin film grown on the vicinal (001) SrTiO$_3$ substrate (α=2°, β=5.4°) showing a superposition of the [110] and [001] zone diffraction patterns of SrRuO$_3$. (b) A dark-field image using weak *111* reflection marked by a circle in (a).

type domains in the film. The morphologies of these domains are shown in Fig. 1(b) which is a dark-field image formed by the weak *111* reflection marked by a circle in Fig. 1(a).

To further confirm the multidomain structure of this SrRuO$_3$ film, TEM studies were carried out on plan-view specimens cut from the same film as studied in Fig. 1. SAED patterns taken from different regions of the specimen show different crystallographic orientations of SrRuO$_3$. Figure 2 shows two electron diffraction patterns [Figs. 2(a) and 2(b)] and a dark-field image [Fig. 2(c)] from a plan-view specimen. Figure 2(a) is a [110] zone diffraction pattern of SrRuO$_3$ from the bright region (*X* domain) in Fig. 2(c), whereas Fig. 2(b) is the [001] zone electron diffraction pattern of the SrRuO$_3$ from the dark region (*Z* domain) in Fig. 2(c). The image in Fig. 2(c) was formed by the 111 reflection in Fig. 2(a). The electron diffraction pattern of the *Y* domain,

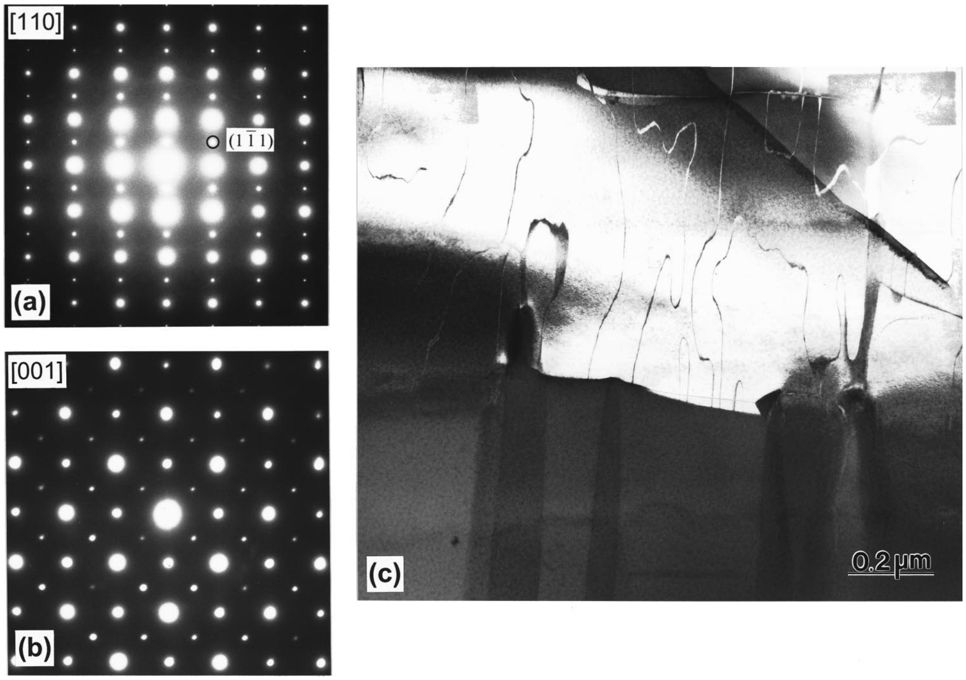


FIG. 2. (a) and (b) SAED patterns taken from a plan-view specimen of the same SrRuO$_3$ film as in Fig. 1, showing the [110] and [001] zone electron diffraction patterns of SrRuO$_3$, respectively. (c) A dark-field image formed by the weak *111* reflection in (a).

which is rotated by 90° around the [110] axis with respect to that of the *X* domain, was also frequently observed. These results reveal that the $SrRuO_3$ film is composed of orientation domains of all three (*X*, *Y*, and *Z*) types, although the x-ray diffraction studies showed a single domain structure as mentioned previously. A similar discrepancy between the x-ray and TEM results was observed on $SrRuO_3$ films grown on exact (001) and different miscut (001) $SrTiO_3$ substrates: (i) $\alpha=4.5°$, $\beta=0.7°$; (ii) $\alpha=0.9°$, $\beta=5.7°$.

From the above results, it can be seen that the results from x-ray diffraction and TEM studies on the same $SrRuO_3$ thin film sample are not consistent with each other. Furthermore, the results from cross-sectional and plan-view TEM studies are also not in agreement with each other. This difference cannot be ascribed to an accidental cutting of TEM specimens from different regions of the film, since similar results were obtained in many specimens prepared from different regions of each $SrRuO_3$ film studied. Therefore, the reason for the multidomain structure observed in TEM should be understood with other mechanisms.

$SrRuO_3$ is a $GdFeO_3$ type pseudocubic perovskite with a slight orthorhombic distortion and a bulk lattice parameters of: $a_{\mathrm{SRO}}=0.393$ nm.[12,13] $SrTiO_3$ has a cubic perovskite structure with lattice constant of $a_{\mathrm{STO}}=0.3905$ nm. X-ray diffraction studies of $SrRuO_3$ thin films deposited on $SrTiO_3$ substrates show that the in-plane lattice parameter of the film ($\sim$0.390 nm) is the same as that of the substrate, resulting in biaxial compressive stress in the plane.[2] This results in a tensile strain normal to the film and an expanded lattice parameter (0.396 nm). Thus, the as-grown $SrRuO_3$ thin films are in a strained state due to the coherent growth.

To conduct plan-view TEM studies, the specimens are thinned from the substrate side. The regions which are used for TEM observations are so thin that the substrate material is completely removed by ion milling. Due to the absence of the substrate material in these regions, the residual stress in the film can be reduced by the formation of domains that may have different orientation relationships with respect to the substrate. As a result, multidomain structures consisting of all three possible (*X*, *Y*, and *Z* type) domains can be observed in the plan-view TEM specimens, although the as-grown film was determined to be single domain according to the x-ray diffraction analysis.

To prepare cross-sectional TEM samples both the film and the substrate material are thinned simultaneously by ion milling. Thus, the film is still bound to the substrate, although the specimen thickness is small. However, the bonding strength between the film and the substrate becomes weak if the specimen thickness is small, especially if it is much smaller than the thickness of the $SrRuO_3$ film. All $SrRuO_3$ films studied in this work have a thickness of $\sim$300 nm, while typical thickness of oxide specimens, which is suitable for conventional TEM observations (at 120 kV), is about 50 nm. Because of the reduced influence of the substrate on the film, the residual stress existing in the film may be partially released by the formation of domains with different orientations. The nucleation of these domains may begin near the film surface, where the substrate has a smaller effect on the film compared to the region close to the interface. These domains will then grow into the film, but usually do not extend up to the film/substrate interface, as shown in Fig. 1(b), where the *Y*-type domain is separated from the substrate by the original *X*-type domain (i.e., the original orientation of the as-grown film). The schematic diagrams in Fig. 3 show a possible process of domain nucleation and growth in a cross-sectional TEM specimen.

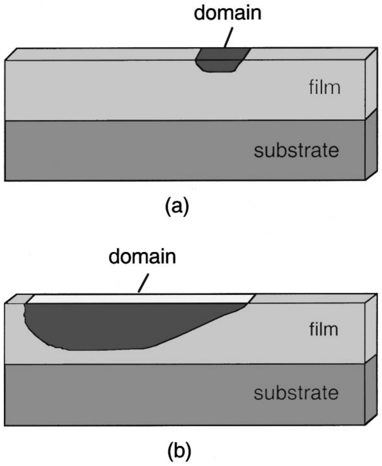


FIG. 3. Schematic diagrams showing the possible process of the nucleation and growth of orientation domain.

According to the TEM observations, the *Z*-type domain is not likely to be formed in cross-sectional specimens. This is due to the coherent (although weak) bonding at the film/substrate interface, which results in a partial strain relaxation only in the upper parts of the film. The reduction of the residual stress in the film through the formation of the *Z*-type domain may not be enough to accommodate the free energy increase by the introduction of domain walls. It should be pointed out that multiple domains are not likely to be formed in the cross-sectional TEM specimen prepared from a single-crystalline film with *small* film thickness ($\leqslant$100 nm) because the substrate will have a strong effect on the film through the interfacial bonding. This is why a single-domain structure was observed in the epitaxial $SrRuO_3$ thin films (with a thickness of 100 nm) grown on the vicinal (001) $SrTiO_3$ substrate, which is consistent with the x-ray analysis.[11]

In order to verify the effect of strain relaxation on the formation of multidomain structures in $SrRuO_3$ thin films, we have studied the domain structure of both as-grown and lift-off thin films epitaxially grown on 2° miscut (001) $SrTiO_3$ substrates using x-ray diffraction analysis. The lift-off thin films were prepared by selective chemical etching of $SrTiO_3$ in a $HF{:}HNO_3{:}H_2O$ solution, and their strains are fully relaxed as evidenced by their bulklike in-plane and out-of-plane lattice parameter (0.393 nm).[14] Figure 4(a) shows the off-axis Φ scan of the $SrRuO_3$ *221* reflection corresponding to (110) oriented domains from the as-grown film. Two peaks which are 180° apart were observed in the Φ scan for the (110) oriented domain, suggesting the existence of only one (110) domain (*X* type). In contrast, the Φ scan for (001) domains does not show any significant peak, which indicates that the as-grown film was single domain. However, a striking difference is observed in the off-axis Φ scans of *221*

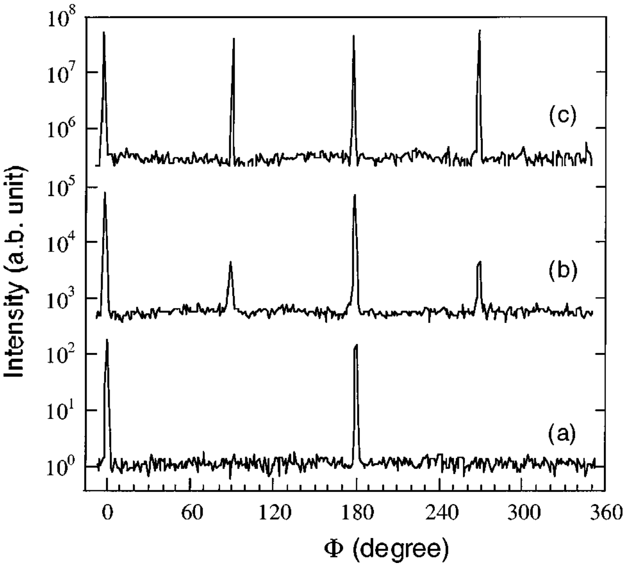


FIG. 4. (a) X-ray off-axis Φ scans of $SrRuO_3$ *221* reflection for (110) oriented domain for as-grown thin film on miscut (001) $SrTiO_3$ substrate, (b) and (c) for (110) and (001) oriented domains for lift-off thin film prepared from the same film as in (a).

reflection for the lift-off film. Four peaks are observed in the Φ scan for (110) domain [see Fig. 4(b)], indicating the coexistence of both *X*- and *Y*-type domains. We also observe four peaks in the *221* reflection scan for the (001) domain as shown in Fig. 4(c), which indicates the formation of *Z*-type domain in the lift-off films. From the integral peak intensity we estimate that the amount of *X*-type domain and *Z*-type domain in the lift-off $SrRuO_3$ film is almost the same, while the amount of *Y*-type domain is slightly less. Furthermore, TEM examinations of the lift-off film used for the x-ray diffraction analysis showed the same domain structure as that in the previous studies (Fig. 2). Therefore, the x-ray diffraction results support our findings in the TEM studies, and the amount of different domains formed is probably dependent on how much strain is relaxed.

Very recently, stress effects on magnetic and electrical properties of the epitaxial $SrRuO_3$ thin films were studied.[14] It was found that the strain-free lift-off $SrRuO_3$ thin films show a Curie temperature of 160 K and a saturated magnetic moment of 1.45 μ_B/Ru atom. These values are different from those of the stressed as-grown $SrRuO_3$ thin film, but the same as those of the corresponding *bulk* single crystals. According to the present study of lattice strain relaxation by removing the substrate, a single-domain structure of the film will transform into multidomain structures and produce a number of domain walls which have a strong influence on the properties of the thin film.

IV. CONCLUSION

In conclusion, we have observed the effect of lattice stress relaxation on the microstructures of thin films by domain structure studies of epitaxial $SrRuO_3$ thin films epitaxially grown on vicinal (001) $SrTiO_3$ substrates. The lattice stress relaxation occurs on the TEM specimens and the lift-off films as the substrate material is eliminated by ion milling or etching, resulting in the formation of elastic domains with different crystallographic orientations. These studies have directly revealed that lattice stress relaxation in the epitaxial $SrRuO_3$ thin films has a crucial influence on the microstructures. Furthermore, the microstructure of thick and strained thin films observed by TEM, especially in plan-view specimens, may not reflect the real structure of the as-grown stressed film.

ACKNOWLEDGMENTS

This work was supported by the college of Engineering, the University of Michigan, Ann Arbor, Michigan and NSF CAREER Award (X.Q.P.) NSF Grant No. DMR 9875405. The work at Duke was supported by ONR Grant No. N00014-95-1-0513, NSF Grant No. DMR 9421947, a NSF Young Investigator Award (C.B.E.) and a David and Lucile Packard Fellowship (C.B.E.).

[1] S. Jin, T. H. Tiefel, M. McCormack, R. A. Pastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
[2] C. B. Eom, R. J. Cava, R. M. Fleming, J. M. Philips, R. B. van Dover, J. H. Marshall, J. W. P. Hsu, J. J. Krajewski, and W. F. Peck, Science **258**, 258 (1992).
[3] C. B. Eom, R. B. Van Dover, J. M. Philips, D. J. Werder, J. H. Marshall, C. H. Chen, R. J. Cava, R. M. Fleming, and D. K. Fork, Appl. Phys. Lett. **63**, 2570 (1993).
[4] L. Klein, J. S. Dodge, C. H. Ahn, G. J. Snyder, T. J. Geballe, M. R. Beasley, and A. Kapitulnik, Phys. Rev. Lett. **77**, 2774 (1996); L. Klein, J. S. Dodge, T. H. Geballe, A. Kapitulnik, A. F. Marshall, L. Antognazza, and K. Char, Appl. Phys. Lett. **66**, 2427 (1995).
[5] D. B. Kacedon, R. A. Rao, and C. B. Eom, Appl. Phys. Lett. **71**, 1724 (1997).
[6] S. C. Gausepohl, M. Lee, K. Char, R. A. Rao, and C. B. Eom, Phys. Rev. B **52**, 3459 (1995).
[7] S. C. Gausepohl, M. Lee, R. A. Rao, and C. B. Eom, Phys. Rev. B **54**, 8996 (1996).
[8] R. A. Rao, Q. Gan, and C. B. Eom, Appl. Phys. Lett. **71**, 1171 (1997).
[9] J. C. Jiang, X. Pan, and C. L. Chen, Appl. Phys. Lett. **72**, 909 (1998).
[10] J. C. Jiang, X. Pan, W. Tian, Q. Gan, and C. B. Eom, Appl. Phys. Lett. **72**, 2963 (1998).
[11] Q. Gan, R. A. Rao, and C. B. Eom, Appl. Phys. Lett. **70**, 1962 (1997).
[12] S. Geller, J. Chem. Phys. **24**, 1236 (1956).
[13] C. W. Jones, P. D. Battle, P. Lightfoot, and W. T. A. Harrison, Acta Crystallogr; Sect. C: Cryst. Struct. Comm. **C45**, 365 (1989).
[14] Q. Gan, R. A. Rao, C. B. Eom, J. L. Garrett, and M. Lee, Appl. Phys. Lett. **72**, 978 (1998).