Interface chemistry and electrical properties of $SrVO_3/LaAlO_3$ heterostructures

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$SrVO_3$ films were grown by laser molecular beam epitaxy on $LaAlO_3$ substrates. For a 10-nm-thick film, its resistivity could be reduced by a factor of 4 by inserting a single La–O atomic layer on an oxygen-annealed $LaAlO_3$ substrate. X-ray diffraction and x-ray photoelectron spectroscopy measurements revealed that oxygen defect concentrations could be varied significantly by controlling the substrate terminations, i.e., interface chemistry. It was suggested that the interface chemistry could influence formation of extended defects and result in changes in electrical properties. © *2000 American Institute of Physics.* [S0021-8979(01)04501-7]

I. INTRODUCTION

Transition metal oxides exhibit a variety of interesting physical properties and have attracted much attention due to their intrinsic scientific interest and possible applications. Thin films often show quite different properties from those of bulk materials. Strain effects and oxygen concentrations are thought to play important roles in giving rise to such intriguing phenomena.[1–8] Strain effects have commonly been investigated by growing films on substrates with various lattice constants which can induce different strain states of the films.[4,5] The effects induced by oxygen stoichiometry have been investigated by varying oxygenation conditions and observing the physical properties of the oxide thin films.[6–8]

Recently, we found that variation of substrate termination could alter the strain relief process of an oxide thin film.[9] This result clearly suggests that interface chemistry, i.e., structure and stoichiometry of an interfacial layer, should be taken into account in controlling physical properties of oxide heterostructures. To gain a better insight into the role of interface chemistry in oxide heterostructures, we grew SVO_3 (SVO) thin films on $LaAlO_3$ (LAO) substrates. SVO is a metallic oxide and has a cubic perovskite structure with a lattice constant of 3.842 Å.[10–12] In this article, we will show that electrical properties of the epitaxial SVO/LAO thin films can be varied significantly depending on the substrate termination.

II. EXPERIMENTS AND RESULTS

LAO(001) substrates with two kinds of terminations were prepared: AlO_2-terminated LAO substrates [AlO_2-LAO] could be obtained by oxygen annealing treatment and LaO-terminated LAO substrates [LaO-LAO] by growth of a single La–O atomic layer.[9,13] Figure 1 shows the intensity variations of reflection high energy electron diffraction (RHEED) patterns during the growth of the SVO films by our laser molecular beam epitaxy system.[12,14] As shown in the inset of Fig. 1(a), the initial oscillation of the first-order diffraction spot intensity was absent in the SVO/AlO_2-LAO film; however, such an oscillation could be clearly seen in the SVO/LaO-LAO film. This suggests that the SVO film on the AlO_2-LAO might be grown with a larger number of defects near the interface than on the LaO-LAO.

As shown in Fig. 1(b), a dip of the specular beam intensity can be seen just after the growth of the SVO layers on the LaO-LAO, and this transient behavior is not yet clearly understood. It is likely that this might be related to the complicated surface diffusion processes of adatoms and/or evolution of surface morphology.[14] For both of the SVO/AlO_2-LAO and the SVO/LaO-LAO films, the RHEED oscillation amplitude started to become dampened after the growth of about 10 ML. This indicated that surfaces of the grown SVO films should be rougher than those of the original substrates. By atomic force microscope measurements, root-mean-square (rms) roughnesses of the 10-nm-thick films were estimated: 2.3 Å for the SVO/AlO_2-LAO and 4.6 Å for the SVO/LaO-LAO. These values were larger than those of the original substrate, i.e., 0.87 Å.

Figure 2 shows the temperature dependent resistivity (ρ) curves of 10-nm-thick SVO films grown on the AlO_2-LAO and the LaO-LAO. For comparison, the ρ-T curve of a SVO film grown on an annealed $SrTiO_3$ (STO) substrate, which is

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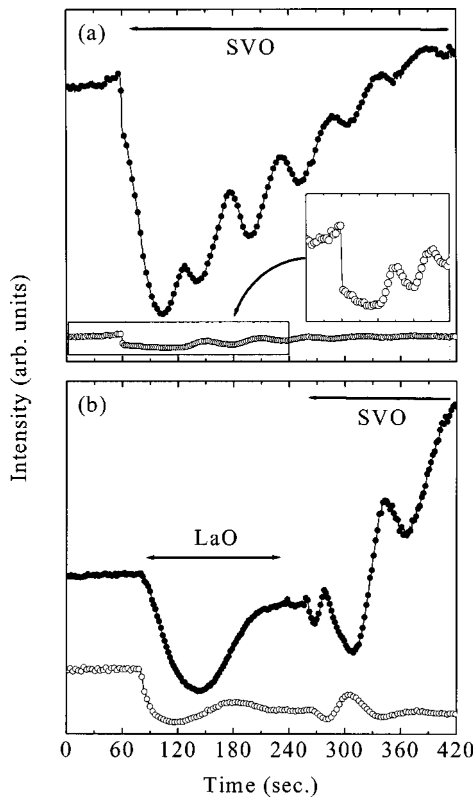

FIG. 1. RHEED intensity oscillations obtained during growth of (a) SVO/AlO_2-LAO and (b) SVO/LaO-LAO films. The solid and open circles denote intensities of the specular beam and the first-order diffraction spot, respectively.

predominantly terminated by TiO_2 layers,[13] is also shown. All the films show metallic behavior and their resistivity values are comparable to the single crystalline value.[10] Note that ρ of the SVO/AlO_2-LAO film was nearly four times larger than that of the SVO/STO film. However, ρ of the SVO/LaO-LAO film is close to that of the SVO/STO film. It is

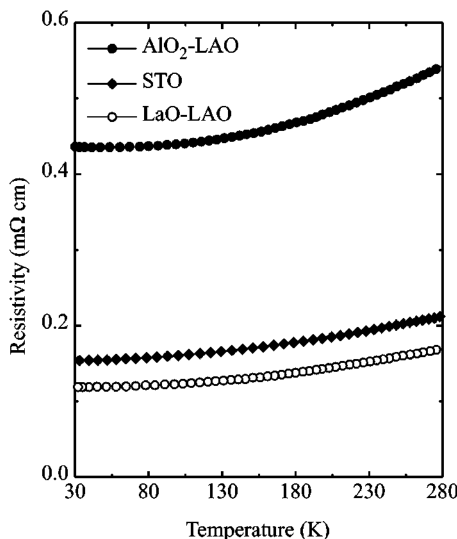

FIG. 2. Temperature dependent resistivity curves of 10-nm-thick SVO films grown on AlO_2-LAO (solid circles), LaO-LAO (open circles), and annealed STO (solid diamonds) substrates.

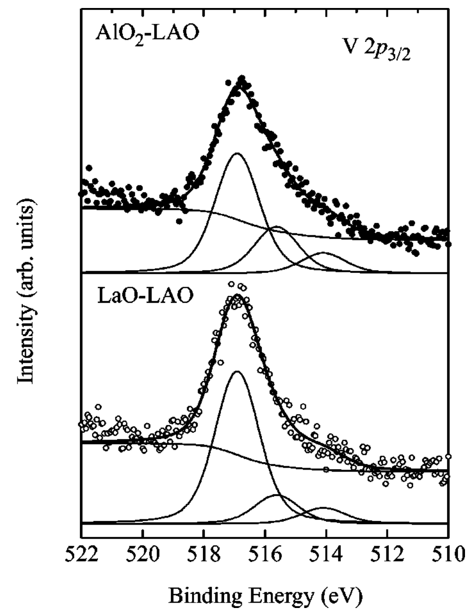

FIG. 3. V $2p_{3/2}$ core-level XPS spectra of the 10-nm-thick SVO films grown on the AlO_2-LAO (solid circles) and the LaO-LAO (open circles) substrates. The spectra were analyzed by fitting with three Lorentzians convoluted by Gaussians and the solid lines represent fitting results. These three peaks might originate from V^{4+}, V^{3+}, and V^{2+} states.

quite surprising to find that *we can vary the resistivities of SVO films by a factor of 4 merely by inserting one extra La–O atomic layer*.

In order to clarify the role of the one extra LaO layer, x-ray photoelectron spectroscopy (XPS) measurements were performed. Figure 3 shows XPS spectra of V $2p_{3/2}$ core levels for the SVO films. The binding energies were referenced by the contaminated C $1s$ core level (284.5 eV) and the spectra were normalized by their areas. The solid and the open circles represent the spectra of the SVO/AlO_2-LAO and the SVO/LaO-LAO films, respectively. The V $2p_{3/2}$ core levels peak at about 517 eV, which is similar to the binding energy of VO_2.[15] There are strong tails toward lower binding energies, which implies that the SVO films have some lower-oxidation-state V ions due to oxygen vacancies. This behavior was analyzed quantitatively by fitting the spectra with three Lorentzians convoluted by Gaussians, whose peak positions and widths were fixed to remove some arbitrariness in the procedure. Comparison with established data suggests that the three peaks might originate from V^{4+}, V^{3+}, and V^{2+} states.[15] The fitting results show that the oxygen vacancies in the SVO/LaO-LAO film are reduced by about 50% compared to those in the SVO/AlO_2-LAO film.

The SVO/LAO films (−1.3% lattice mismatch) and the SVO/STO films (+1.6% lattice mismatch) might suffer from compressive and tensile stresses, respectively. Moreover, all of the films in this study were grown under the same growth conditions, including oxygen pressures. Therefore, it seems difficult to explain the change in the resistivities of the two SVO/LAO films by strain effects and/or differences in oxygenation conditions. Between the SVO/AlO_2-LAO and the SVO/LaO-LAO films, a significant difference can be found in their atomic configurations at the interfaces: [SrO]/[AlO_2]

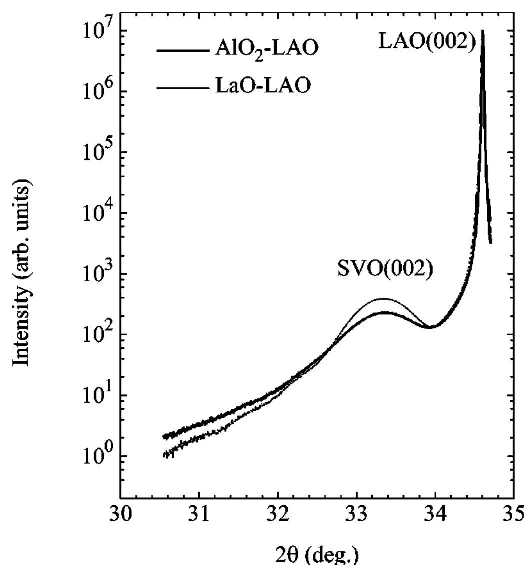

FIG. 4. XRD θ-2θ patterns of 10-nm- thick SVO films on the AlO_2-LAO (thick line) and the LaO-LAO (thin line) substrates.

for the former and $[VO_2]$/[LaO] for the latter. Even though the detailed mechanism producing variation of the electrical properties of the films is not clearly understood at the present stage, we can say that the interface chemistry affects the electrical properties of the SVO films.

We can conceive of two possible mechanisms to explain how the interface chemistry can cause variation in the electrical properties: A-site termination and charge compensation in the interface. In the case of $YBa_2Cu_3O_7$ films, Kubo *et al.*, carried out molecular dynamics simulations and reported that suitable atomic buffer layers can reduce stress imposed by substrates.[16] There are also previous experimental results asserting that A-site termination of substrates is helpful for improving film qualities.[13,17] In heterostructures, uncompensated electrical charges at interfaces will make the structures unstable and charge redistribution will occur to minimize interface energies.[19] In semiconductors, such a problem is a long-standing one and has been called the ''polarity matching.''[20] In the interface of the SVO/LaO-LAO film, variable oxidation states of V ions might compensate for extra holes of $[LaO]^+$ layers without forming defects such as vacancies and interstitials.[18] However, in the case of SVO/AlO_2-LAO film, oxygen vacancies of the SrO layers seem to be indispensable to compensate for the extra electrons of $[AlO_2]^-$ layers. As a result, oxygen vacancies of the SVO/LaO-LAO film could be much smaller than those of the SVO/AlO_2-LAO film. A more complicated scenario can also be proposed in which intermixing of ions in the interface might assist in achieving charge neutrality.[21]

Since differences in the microstructures could be expected from the above considerations, the amount of extended defects was investigated using x-ray diffraction (XRD) measurements. Figure 4 shows the θ-2θ scan results for 10-nm-thick SVO films on the AlO_2-LAO and the LaO-LAO, which were taken at the Pohang Light Source with a wavelength of 1.127 Å. The peak positions were nearly the same for the two films and out-of-plane lattice constants were estimated to be about 3.93 Å. In-plane-lattice constants were also estimated from the film (101) reflections and they were determined to be about 3.8 Å for both films, suggesting that there was no noticeable difference in the strain states between the SVO/AlO_2-LAO and the SVO/LaO-LAO films. On the other hand, the peak of the SVO/AlO_2-LAO film is broader and much weaker than that of the SVO/LaO-LAO film. Since peak widths are known to result from defects of the films, such as dislocations and mosaic spread,[21] the differences in the XRD patterns indicate that there should be a significant difference in the defect concentrations between the two films. Further studies, including transmission electron microscope observations which can provide more information on the extended defect states, are highly desirable.

Another interesting fact is that the interface chemistry can influence electrical resistivities of *thick* SVO films. Some 100-nm-thick SVO films were also grown on the LAO substrates with two kinds of terminations. XRD measurements were performed for (002) and (101) reflections. This showed that nearly cubic structures were obtained and that the lattice constants of the two films were nearly the same as the bulk value. The peaks of the SVO/AlO_2-LAO film were weaker and broader than those of the SVO/LaO-LAO film. The electrical resistivity of the former film was still nearly two times larger than that of the latter film. All these observations suggest that the initial formation of the extended defect states, influenced by the interface chemistry, should play an important role even for 100-nm-thick films.

III. SUMMARY

In summary, we grew $SrVO_3$ films on $LaAlO_3$ substrates with two kinds of terminations, i.e., AlO_2 and LaO layers. The resistivity of the former was larger than that of the latter. X-ray photoelectron spectra and x-ray diffraction patterns showed that oxygen vacancies of the former were much larger than those of the latter. The interface chemistry determined by the substrate terminations seems to affect initial formation of extended defects and leads to a significant variation of electrical properties of the $SrVO_3$/$LaAlO_3$ heterostructures.

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