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Title	Electronic transport properties in SrTiO_3_-LaAlO_3_ solid-solution films
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Citation	Applied Physics Letters, Vol. 88, No. 23,
Pub. date	2006, 6
URL	http://scitation.aip.org/content/aip/journal/apl
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Electronic transport properties in $SrTiO_3$–$LaAlO_3$ solid-solution films

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(Received 3 February 2006; accepted 26 April 2006; published online 6 June 2006)

We report on the structural and electronic properties of solid-solution films consisting of perovskite band insulators, $SrTiO_3$ and $LaAlO_3$, with a chemical formula of $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$. Single crystalline films grown by pulsed-laser deposition are fairly insulating below 300 K when having $x \geqslant 0.6$, while $x < 0.6$ films exhibit electronic conduction accountable with a variable-range hopping. Room temperature conductivity has a maximum value of $20\ \Omega^{-1}\,cm^{-1}$ at $x \sim 0.2$. Hall measurements reveal that the density of the carriers varies as $x(1-x)$ per Ti site up to $x \sim 0.35$, apparently indicating that La^{3+} donates one electron to a remaining Ti site. The results are discussed in comparison with the electronic properties of $La_ySr_{1-y}TiO_3$ films in terms of different carrier localization mechanisms. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2210297]

Physical properties of doped $SrTiO_3$ have been studied in various aspects, including metal–Mott-insulator transition and ferroelectric phase transition. Substitution of a trivalent rare-earth ion to the Sr site induces free electrons resulting in metallic conduction. The $Sr_{1-x}La_xTiO_3$ system undergoes from metal to Mott-insulator transition above $x \sim 0.95$ due to electron correlation accompanied with antiferromagnetic ordering of $3d$ electron spin.[1] $SrTiO_3$ is known to be an incipient ferroelectric, which exhibits a ferroelectric phase transition by doping with a small amount of off-center ions such as Ca^{2+} (Ref. 2) and Ba^{2+} (Ref. 3). Phase transition to a polar glasslike state has also been studied in a solid solution with $KTaO_3$, in which different heterovalent ions occupy simultaneously Sr and Ti sites, providing random distribution of dipoles.[4] Another interest may arise in terms of oxide ion conductor composed of $SrTiO_3$ and related ABO_3 perovskites. A large number of oxygen vacancies can be introduced into the lattice by partial substitution of A or B cation with lower valence cations. Indeed, such compounds as $CaTi_{1-x}Al_xO_{3-\delta}$ and $La_{1-x}Sr_xGaO_{3-\delta}$ exhibit high ionic conductivity at high temperatures (ca. 800 °C).[5,6]

In this letter, we examine electronic transport properties of solid-solution films consisting of $SrTiO_3$ and $LaAlO_3$ and their composition dependences. The present system can be considered as a mixed configuration of $Sr_{1-x}La_xTiO_3$ and $SrTi_{1-x}Al_xO_{3-\delta}$, and thus expressed by a chemical formula of $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$. One may expect that a wide range of oxygen nonstoichiometry is introduced giving rise to electronic compensation with Ti $3d$ electrons. Early studies revealed that this system continuously formed solid solutions over the whole composition range either in single crystalline[7] or in polycrystalline forms.[8] These crystals were fully oxidized and fairly insulating. In the present study, however, it is found that the films having $x \geqslant 0.6$ are insulating, while $x < 0.6$ films exhibit a hopping conduction. We observe strong effect of carrier localization in low x region, which is ascribed to a large disorder induced by randomly distributed dipoles formed by the excess and deficient charges of the La^{3+} and Al^{3+} ions, respectively. The results are compared with the electronic properties of $La_xSr_{1-x}TiO_3$ films in the case of absent dipole.

Composition-spread films of $LaAlO_3$–$SrTiO_3$ and $LaTiO_3$–$SrTiO_3$ were grown on (100) $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$ (LSAT) substrates at 830 °C in 1×10^{-6} Torr of oxygen by pulsed-laser deposition using a KrF excimer laser. $SrTiO_3$ and $LaAlO_3$ single crystals ($SrTiO_3$ single crystal and a $La_2Ti_2O_7$ ceramic) were used to prepare the former (the latter). A sliding mask was employed to make a composition gradient.[9] Using the intensity oscillation of reflection high-energy electron diffraction, film thickness was regulated to be approximately 200 nm. A concurrent x-ray diffraction apparatus was used to perform structural characterization.[10] Temperature dependences of resistivity and Hall coefficient were measured for micropatterned small Hall-bar ($220 \times 60\ \mu m^2$) arrays with evaporated Al contacts.[11]

All of the films were of high quality and single phase as verified by narrow width of x-ray diffraction peak and clear Laue oscillations. Figure 1 shows composition dependences of the in-plane and out-of-plane lattice constants and cell volume per formula (V). Coherent- epitaxial relationship is established in $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films over the whole composition range and $Sr_{1-y}La_yTiO_3$ films with $y < 0.3$ (hereafter La concentration in the latter system is represented by y to distinguish from x of the former). V increases as going from $LaAlO_3$ to $LaTiO_3$, agreeing with variation in powder samples indicated by broken lines.[8,12]

The composition dependence of electronic properties of $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ and $Sr_{1-y}La_yTiO_3$ films at 300 K is summarized in Fig. 2. The conductivity (σ_{xx}) in $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ has a maximum value of $20\ \Omega^{-1}\,cm^{-1}$ at $x \sim 0.2$. The data obtained for $Sr_{1-y}La_yTiO_3$ films including their temperature dependences (not shown) quantitatively

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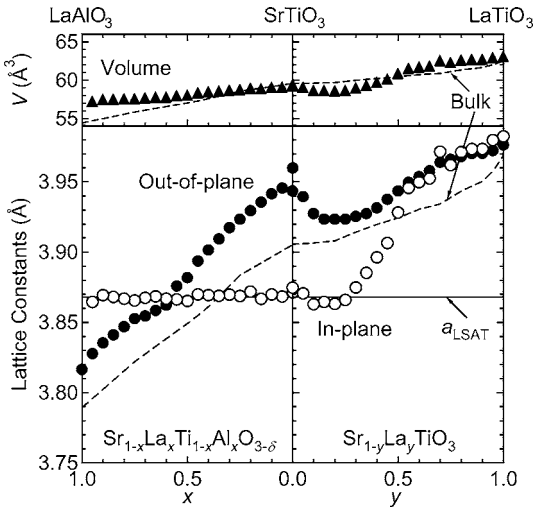

FIG. 1. Composition (x,y) dependence of the in-plane (open circles) and out-of-plane (closed circles) lattice constants and volume (V) per formula for $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ and $Sr_{1-y}La_yTiO_3$ films grown on the (100) LSAT substrates. The parameters reported for powder samples are shown by the dashed lines (Refs. 8 and 12).

agreed with those of bulk single crystals,[1] indicating that the present films were stoichiometric. A film nominally assigned as $SrTiO_3$ in this study was not insulating with a carrier density of $\sim 5\times 10^{19}$ cm^{-2} due to oxygen vacancies, indicating some limitation of growth optimization to control oxygen nonstoichiometry as well as to keep high crystallinity in the entire region of the samples. It should be mentioned that we found surface depletion layers, especially thicker in the films having low carrier density. Thickness of depletion layer is estimated to be at most 16 nm from thickness dependence of carrier density measured for several films.[13] All quantities discussed here are thus corrected using thickness of conducting layers, i.e., physical thickness subtracted by thickness of depletion layer.

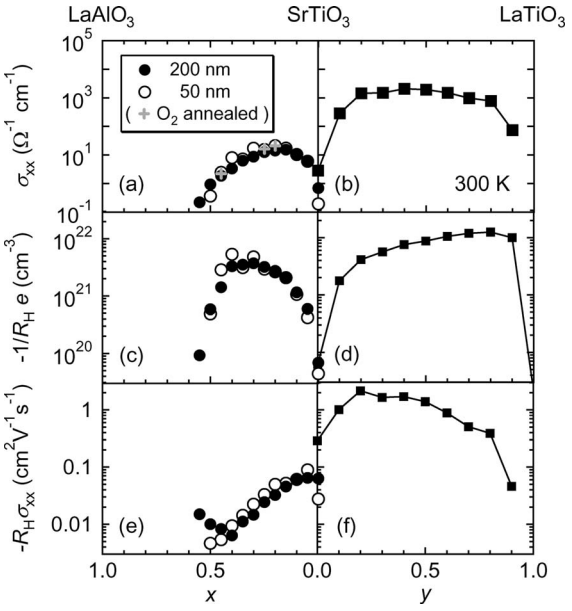

FIG. 2. [(a), (c), and (e)] Composition dependence of conductivity (σ_{xx}), carrier density $(-1/R_He)$, and Hall mobility $(-R_H\sigma_{xx})$ at 300 K for $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films, respectively. The data taken from 50- and 200 -nm-thick films and the oxygen-annealed 50-nm-thick films are shown by the open circles, closed circles, and gray crossing bars, respectively. [(b), (d), and (f)] The same plots, but for $Sr_{1-y}La_yTiO_3$ films.

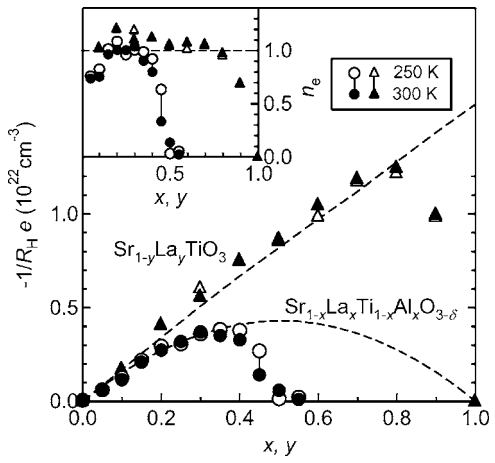

FIG. 3. Linear-scale plots of Figs. 2(c) and 2(d). Open and closed symbols indicate the values measured at 250 and 300 K, respectively. Dashed lines are the calculated ones (see text). Inset depicts composition dependence of number of electrons (n_e) per Ti site divided by La concentration (x,y).

The most striking difference between two systems is seen in their composition dependences of Hall mobility $(-R_H\sigma_{xx})$ estimated from Hall coefficient (R_H) and σ_{xx} [Figs. 2(e) and 2(f)]. $Sr_{1-y}La_yTiO_3$ films show almost constant mobility after initial increase with y. In $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films, on the other hand, small amount of doping induces dramatic decrease in mobility (data apparently located at $x=0$) and it continuously decreases with further increasing x. We attribute this behavior to significant carrier scattering due to large disorder induced by randomly distributed dipoles, which is the most probable arrangements of La^{3+} and Al^{3+} ions due to electrostatic attraction between positive and negative charges on them.

σ_{xx} of $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films hardly changed after annealing at 400 °C in air for 1 h, as shown by gray crossing bars in Fig. 2(a). This annealing condition sufficiently expeled conductivity in $SrTiO_{3-\delta}$. When annealing temperature is raised up to 600 °C, slight decrease in σ_{xx} was observed. Unusual stability of oxygen vacancies in $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ was also observed for a bulk single crystal, to which extremely high temperature annealing (ca. 1500 °C) was necessary to obtain an insulating crystal.[7] We also measured transport properties of films grown on $LaAlO_3$ and SrO-terminated $SrTiO_3$ substrate and found any systematic difference from those grown on LSAT substrate. Finally we note that any contribution of ionic conduction in $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films should be negligibly small below room temperature even if any.[5,6]

The carrier density $(-1/R_He)$ is plotted as a function of composition in Figs. 2(c), 2(d), and 3. In $Sr_{1-y}La_yTiO_3$ films, carrier density varies proportionally to y up to the vicinity of phase boundary to Mott insulator $(y\sim 0.9)$, indicating that La^{3+} dopes one electron per Ti site. This simple picture also appears in $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films $(x\leqslant 0.35)$, where $-1/R_He$ is proportional to $x(1-x)$, implying that La^{3+} donates one electron to a *remaining* Ti site $(1-x)$. These common observations can be much clearly seen in the inset of Fig. 3, where the observed carrier density is normalized by y for $Sr_{1-y}La_yTiO_{3-\delta}$ as $n_e/V=-1/(R_Hey)$ and by $x(1-x)$ for $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ as $n_e/V=-1/[R_Hex(1-x)]$. When x increases beyond 0.35, n_e gradually deviates from unity presumably due to a percolationlike clustering of $LaAlO_3$. Car-

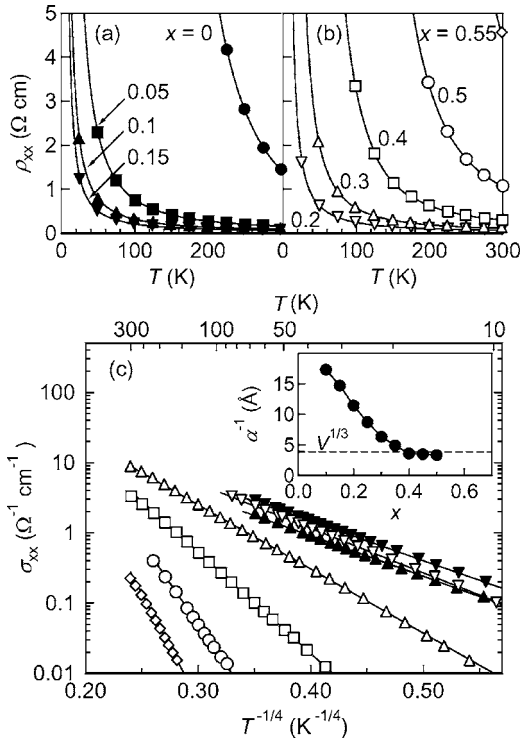

FIG. 4. [(a) and (b)] Temperature dependence of resistivity for $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films. (c) log σ_{xx} vs $T^{1/4}$ indicates variable-range hopping conduction. Symbols in (c) correspond to those shown in (a) and (b) with different x values. Inset depicts composition dependence of localization length (α^{-1}) estimated from Eq. (1).

rier densities in both systems were found to be nearly independent of temperature. Here we note that the condition of mutual charge compensation requires that oxygen deficiency δ in $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films be equal to a half of electron density [$\sim x(1-x)/2$]. This situation leads to another viewpoint that oxygen vacancy induces free electrons in a $LaAlO_3-SrTiO_3$ solid solution as it happens in a pure $SrTiO_3$.

Now we discuss the electronic conduction mechanism in $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films. Figures 4(a) and 4(b) show temperature dependence of resistivity (ρ_{xx}). In contrast to the $Sr_{1-y}La_yTiO_3$ films, where metallic conduction took place in a composition range of $0<x\leqslant 0.9$, all the $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films show nonmetallic behavior. $\sigma_{xx}(T)$ curves for $x\leqslant 0.1$ samples can be reasonably fitted by $\sigma_{xx}\propto\exp(-1/T)$. For $x>0.1$ samples, however, a satisfactory result is rather obtained by fitting with a variable-range hopping mechanism [see Fig. 4(c)], given by the following equation:[14]

$$\sigma_{xx}(T)=\sigma_0\exp[-(T_0/T)^{1/4}], \tag{1}$$

where σ_0 is the preexponential term, $T_0=16\alpha^3/k_B\rho_0$, α^{-1} is the localization length, which describes spatial extent of the wave function localized at a single site, k_B is Boltzmann's constant, and ρ_0 is the density of states at the Fermi level. Assuming that ρ_0 equals to the density of mobile electrons ($-1/R_He$), we deduced α^{-1} from the gradient of the fitted curves. Notably, α^{-1} approaches to a value close to the distance between the nearest-neighbor B sites (shown by horizontal broken line) with increasing x, as shown in the inset of Fig. 4(c). This result implies that hopping conduction vanishes in the vicinity of percolation threshold of simple cubic ($x\sim 0.69$), if octahedral sublattice is considered in the degree of $3d$ state connectivity between neighboring Ti atoms.

In conclusion we have studied the electronic properties of $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ films integrated on a substrate with composition-spread method. Single crystalline films exhibit variable-range hopping conduction in a composition range of $0<x<0.6$, and particularly films with $0<x<0.35$ has carrier density proportional to $x(1-x)$. Carrier localization mechanism can be ascribed to large disorder induced by randomly distributed dipoles, which evidently differs from the one in $Sr_{1-x}La_xTiO_3$ system. Further study on the system having different La/Al ratio may be of interest especially to address how these two different features appeared in $Sr_{1-x}La_xTiO_3$ and $Sr_{1-x}La_xTi_{1-x}Al_xO_{3-\delta}$ crossover in a complete phase diagram.

This research was partially supported by the MEXT Grant of Creative Scientific Research Grant No. 14GS0204. One of the authors (J.N.) is supported by the MEXT through a 21st Century COE Program.

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