Synthesis and electronic structure of epitaxially stabilized $\text{Sr}_2-x\text{La}_x\text{VO}_4$ ($0 \leq x \leq 1$) thin films

J. Matsuno,$^a$ b) Y. Okimoto, M. Kawasaki,$^b$ and Y. Tokura$^c$

Correlated Electron Research Center (CERC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8562, Japan

(Received 12 September 2002; accepted 15 November 2002)

We have synthesized $a$-axis-oriented epitaxial thin films of layered vanadate $\text{Sr}_2-x\text{La}_x\text{VO}_4$ on $\text{LaSrAlO}_4$ (100) substrates using a pulsed-laser deposition technique. Epitaxial interface energy stabilizes compounds from $\text{V}^{4+}$ ($x=0$) to $\text{V}^{3+}$ ($x=1$), for which none of bulk single crystal has been synthesized. The transport property including its anisotropy has been studied to reveal metallic conduction for $x=0.15$ and 0.2. The two-dimensional nature of the crystals gives insulating behavior along the $c$ axis for all the compositions. Optical measurements indicate that the doped electrons are responsible for the insulator-to-metal transition as well as for the systematic variation of electronic structure from $\text{V}^{4+}$ to $\text{V}^{3+}$-based Mott insulators. © 2003 American Institute of Physics. [DOI: 10.1063/1.1536030]

Layered perovskites are well known to exhibit various intriguing physical phenomena such as high-$T_c$ superconductivity in cuprates and spin/charge stripe in nickelates. In general, however, it is far more difficult to synthesize layered perovskites in single-crystalline form than cubic perovskites. Therefore, only a few systems have been unveiled so far and interesting physical properties may remain unexplored. Epitaxial thin-film growth is a promising technique to make single-crystalline thin films of layered vanadate $\text{Sr}_2\text{VO}_4$ with $\text{K}_2\text{NiF}_4$-type structure. There have been several studies dealing with this compound, motivated by the similarity in the electronic configuration between $\text{V}^{4+}$ in $\text{Sr}_2\text{VO}_4$ (one 3$d$ electron) and Cu$^{2+}$ in cuprates (one 3$d$ hole). It has been reported that $\text{Sr}_2\text{VO}_4$ is an antiferromagnetic insulator with its Néel temperature of 45 K. Deslandes et al. has reported the synthesis of Ln-doped ($\text{Ln}=$ La, Ce, Pr, Nd, and Eu) ceramics samples. In the case of La, a range of solid solution is $0.4 \leq x \leq 1.0$ and all the compounds are semiconducting in spite of the electron doping. Thus, fabrication of single-crystalline thin films is of great interest for a more precise examination of this system since carrier doping is generally expected to cause a transition from a Mott insulator to a metal. The present study demonstrates synthesis of high-quality $a$-axis-oriented epitaxial thin films of $\text{Sr}_2-x\text{La}_x\text{VO}_4$ (SLVO) and reveals their transport and optical properties.

The $a$-axis-oriented epitaxial thin films of SLVO ($0 \leq x \leq 1.0$) have been grown by pulsed-laser deposition using a KrF excimer laser ($\lambda=248$ nm) to deposit 1000–1500 Å films. Target pellets were prepared by solid-state reaction of $\text{La}_2\text{O}_3$, $\text{SrCO}_3$, and $\text{V}_2\text{O}_5$ at 800 °C, which did not produce $\text{K}_2\text{NiF}_4$-phase compounds: Targets were mixtures of oxides including $\text{V}^{5+}$ ions at that point. The films were epitaxially grown on $\text{LaSrAlO}_4$ (100) ([LSAO] $a=b=3.756$, $c=12.63$ Å) with a $\text{K}_2\text{NiF}_4$ structure. Typical growth temperature was around 820 °C–860 °C and oxygen pressure was $6 \times 10^{-7}$ Torr. In order to avoid the peroxidation of as-deposited films, they were in situ cooled down to room temperature without flowing oxygen gas. The resistivity was measured employing a standard four-probe method. For the anisotropic measurements, we cut the films into thin pieces and evaporated silver electrodes so that the current direction was limited to the respective in-plane axes. Optical measurements were performed using a Fourier transform interferometer and a grating monochromator equipped with a microscope to cover a region of 0.2–4.5 eV where the LSAO substrate is transparent. Optical conductivity spectra $\sigma(\omega)$ were obtained from reflectance $R(\omega)$ and transmittance spectra $T(\omega)$.

Figure 1 shows typical examples of the reciprocal-space mapping of x-ray diffraction (XRD) around the (303) [Fig. 1(a)] and (310) [Fig. 1(b)] reflections for an SLVO ($x=0.4$) film on LSAO. The definition of each axis is displayed in the inset schematic of Fig. 1(c). The mapping data indicate that all the films are single phase, (100) oriented, and in-plane aligned with the (001) direction being parallel with the (001) direction of the substrates. In Fig. 1(c), we plot the lattice constants $a$, $c$, and $b$ deduced from the reciprocal-space mapping as a function of $x$. A systematic change of the lattice constants ensures that there is no phase separation and the solid solution is realized in the whole composition range studied here. The lattice constants of $x=0$ film are coincident with those of the bulk crystals. The filling dependence of the lattice constants can be classified into two regions, (i) $0 \leq x \leq 0.15$: the $a$- and $b$ axes decrease.

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$^a$Electronic mail: j-matsuno@aist.go.jp
$^b$Also at: Institute for Materials Research, Tohoku University Sendai 980-8577, Japan.
$^c$Also at: Department of Applied Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan.
and c axis increases with x and (ii) 0.2 ≤ x ≤ 1.0: the c axis of the film is kept identical to that of the substrate while the a and b axes increase. In the former region (i), the lattice mismatch for both b and c axes is too large to maintain coherent epitaxial growth. As a result, lattice constants show their intrinsic variation as a function of x. In the latter region (ii), the film is compressively strained along the c axis to satisfy in-plane matching to the substrate. It is to be noted here that symmetry of the films is almost tetragonal for x = 0, while it becomes orthorhombic for x > 0.1 although the orthorhombicity defined as (a-b)/a is as small as 0.4—0.7%. Probably due to the good lattice matching, the crystallinity of the latter films are fairly good; typical full width at half maximum of the rocking curve for (200) XRD peak is ~ 0.05°, while it is ~ 0.1° for the former films. Thus, the concept of graphoepitaxy between K2NiF4-structure compounds provides us with SLVO single-crystalline films not only for compounds (x = 0 and 0.4 ≤ x ≤ 1.0), where only ceramics samples are available, but also for those (0 < x < 0.4) where the compounds themselves have not been synthesized. As described later, the latter specimens show an insulator-to-metal transition as a generic feature for doped Mott insulators.

Figure 2 shows the temperature dependence of in-plane resistivity, ρb, along the b axis and ρc, along the c axis. The undoped Sr2VO4 shows insulating behavior as observed in bulk crystals and the anisotropy in the resistivity (ρc/ρb) is ~ 30 at room temperature. The data below 250 K fit well with the thermally activated transport with an activation energy of ~ 70 meV for both ρb and ρc. This value is consistent with the result by Nozaki et al. and Sr2VO4 is considered to be a Mott insulator with a rather small energy gap.

The ρb decreases with x up to x = 0.2 and the film with x = 0.2 shows a metallic behavior in the VO2 plane that has never been reported before, to our knowledge. For x = 0.15, the ρb also indicates a metallic behavior over a wide temperature region (> 100 K), whereas an upturn at lower temperatures may imply an insulating ground state. This metallic conduction can be assigned to the collapse of the Mott gap by electron doping. At these compositions, the ρc is still insulating, reflecting the two-dimensional nature of this system. Actually, the ρc is insulating for all of the compositions although only a part of the data are plotted for clarity. We note that the ρc for the metallic x = 0.2 film points a finite value at T = 0 K, while its origin has been unidentified. Beyond x > 0.2, however, all of the ρb show semiconducting behavior again as displayed in Fig. 2(b). For x = 0.8 and 1.0, the ρb increases with x and ρc for x = 1.0 is higher than that for x = 0. This can be understood as the strong electron correlation inherent to V3+ (S = 1), which manifests itself in cases of cubic perovskites; LaVO3 (V3+) is a well-known Mott insulator whereas SrVO3 (V3+) is metallic.

One may see a hump structure at ~ 50 K for x = 0.15 and 0.2 films followed by a decrease of the resistivity below that temperature. Similar structures have been observed for the other compositions as well at similar temperatures. Previously, the Néel temperature of ~ 50 K is reported to be independent of x in Sr2−xEu3+VO4.11 Therefore, the observed hump may be assigned to some kind of magnetic ordering, the latter reducing carrier scattering, although no proof has been obtained because the antiferromagnetic transition in a thin film is practically difficult to determine by the magnetic susceptibility measurement.

In order to see the filling-dependent change of the electronic structure, we display, in Fig. 3(a), the spectra of the optical conductivity σ(ω) in SLVO (0 ≤ x ≤ 1.0) with polarization E∥b. The spectral feature can be decomposed to the two parts below and above hω = 2.5 eV. A higher-lying structure is assigned to the charge-transfer (CT) transitions from O2p bands to V 3d bands above ~ 2.5 eV. The CT band structure of the spectra shifts to the higher-energy side with electron doping as shown in Fig. 3(a). Here, vertical bars indicate the onset of the CT band or the CT gap ∆ as estimated as a maximum curvature by the second derivative of the spectra. The ∆ shows a monotonous increase with x as clearly shown in Fig. 3(b). This is partly due to the shift of the ρb
In order to estimate the spectral weight of the lower-lying component quantitatively, we have plotted, in Fig. 3(c), the effective number of electrons $N_{\text{eff}}$ measured at $\hbar \omega = 2.5$ eV. Here, $N_{\text{eff}}$ is defined as

$$N_{\text{eff}}(\omega) = \frac{2m}{\pi e^2 N} \int_0^\omega \sigma(\omega')d\omega'$$

where $N$ represents the number of V atoms per unit volume, and $m$ and $e$ are the mass and charge of free electrons. With doping electrons, $N_{\text{eff}}$ increases rapidly from $x = 0$ to 0.1. Then, $N_{\text{eff}}$ reaches a broad maximum around $x \approx 0.3$ followed by a decrease toward the $V^{3+}$-based Mott insulator of $x = 1.0$. The variation of $N_{\text{eff}}$ is much steeper around $x = 0$ than around $x = 1.0$, indicating that the Mott gap for the $V^{4+}$-based state is easily collapsed upon doping, giving rise to the metallic state ($x = 0.15\ldots0.2$) near the $x = 0$ end.

In summary, we have synthesized epitaxial thin films of $\alpha$-axis-oriented $\text{Sr}_2-x\text{La}_x\text{VO}_4$ on LSAO (100) substrates. We have found that the resistivity in the VO$_2$ plane can be metallic for $x = 0.15$ and 0.2 films, while that across the VO$_2$ plane is insulating for all of the compositions. From the optical conductivity spectra, the systematic variation of the electronic structure is revealed and the metallic conduction is assigned as a collapse of the Mott–Hubbard gap with doped electrons.

The authors thank A. Sawa, Hiroyuki Yamada, and C. U. Jung for valuable discussions.

7. It is not clear, at present, whether the observed orthorhombicity is due to the intrinsic crystal structure or to the slight compressive strain to make the in-plane $b$ axis closer to that of the substrate. Such "partially relaxed" lattice distortion has been frequently seen in perovskite heteroepitaxy for lattice mismatched combinations.