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Epitaxial growth of semiconducting $LaVO_3$ thin films

Woong Choi[a] and Timothy Sands
Department of Materials Science & Mineral Engineering, University of California, Berkeley, California 94720

Kwang-Young Kim
Display R&D Center, LG Electronics, 16 Woomyeon-Dong, Seocho-Gu, Seoul 137-724, Korea

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Epitaxial thin films of $LaVO_3$ were grown on (001) $LaAlO_3$ substrates by pulsed laser deposition from a $LaVO_4$ target in a vacuum ambient at substrate temperatures $\geqslant$500 °C. X-ray diffraction studies showed that epitaxial $LaVO_3$ films consist of mixed domains of [110] and [001] orientations. Thermoprobe and four-probe conductivity measurements demonstrated the *p*-type semiconducting behavior of the epitaxial $LaVO_3$ films. The temperature dependence of the conductivity is consistent with a thermally activated hopping mechanism with an activation barrier of 0.16 eV.

There has been increasing interest in growing epitaxial thin film heterostructures consisting of materials that have similar crystalline structures but possess remarkably different physical properties. Prime emphasis has been put on perovskite oxides exhibiting wide ranges of electrical, magnetic, and optical properties since the combination of such diverse materials offers attractive possibilities for novel device structures. Although conductive oxide thin films have been extensively investigated due to their potential applications in a number of different fields,[1–3] little attention has been given to semiconducting oxide thin films. As components of a ferroelectric nonvolatile memory device in the ferroelectric field-effect transistor (FET) configuration, epitaxial thin films of the semiconducting oxides can enhance the device performance by improving the interface quality between the ferroelectric and semiconducting layers.[4,5] Moreover, epitaxial thin films of the semiconducting oxides in an FET can be utilized to make optically transparent switches, with potential on-screen display applications.[6]

Among numerous semiconducting oxides, $LaVO_3$ shows many interesting properties. It has a $GdFeO_3$-type orthorhombic structure (space group *Pbnm*) with lattice constants of $a = 0.555548$ nm, $b = 0.555349$ nm, and $c = 0.784868$ nm.[7] The structure can be considered as a pseudocubic perovskite with a lattice constant of ~0.39 nm, revealing the structural compatibility of this phase with other perovskite-type materials. $LaVO_3$ undergoes an orthorhombic-to-monoclinic structure transition at about 140 K accompanied by a paramagnetic-to-antiferromagnetic transition as the temperature decreases.[7] $LaVO_3$ behaves as a *p*-type semiconductor with an optical band gap of ~1.1 eV.[8] The *p*-type doping of $LaVO_3$ arises from cation deficiency with an activation energy for conduction in the range 0.1–0.2 eV.[9–12] The resistivity of $LaVO_3$ can be controlled by using its strontium-doped analogue $La_{1-x}Sr_x VO_3$, whose electrical properties change from those of a semiconductor to a metal as the strontium content is increased.[12,13]

Although the electrical transport and magnetic properties of bulk $LaVO_3$ have been investigated, there has been no report on $LaVO_3$ thin films to the authors' knowledge. In this study, epitaxial $LaVO_3$ thin films were grown and characterized by structural and electrical transport measurements.

$LaVO_3$ thin films were deposited on $LaAlO_3$(001) pseudocubic ($a = 0.3792$ nm) single-crystal substrates by pulsed laser deposition (PLD). The PLD system consisted of a KrF excimer laser (Lambda Physik, Lextra 200) with a 34-ns pulsewidth and wavelength of 248 nm, external optics, and a vacuum chamber. The laser beam was focused down at the target to yield an approximate energy density of 2 J/cm^2 and a pulse repetition rate of 5 Hz. The $LaVO_4$ target was purchased from Praxair Specialty Ceramics. The substrates were mounted with

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[a] Address all correspondence to this author.
e-mail: woongch@uclink4.berkeley.edu

silver paste on a heater block 5 cm from the target. After a chamber base pressure below 2 × 10^{-6} torr was reached, the substrates were heated at 30 °C/min to 400–700 °C. Films were deposited either under vacuum (<2 × 10^{-6} torr) or with flowing oxygen at pressures ranging from 1 to 200 mtorr. After deposition, the substrates were cooled to room temperature at 5 °C/min.

Films were deposited with thickness in the range 100–500 nm as measured by stylus profilometry. The deposition rate was estimated to be 0.06 ± 0.01 nm/pulse. The crystal structure and orientation of the thin films were determined by x-ray diffraction (XRD) using a Siemens D5000 four-circle diffractometer. The conduction type was determined by the thermoprobe method. Conductivity measurements were performed by the four-probe van der Pauw technique using indium contacts.

One of the critical parameters for the optimization of the growth process is the oxygen pressure. Unlike other ABO_3 perovskite-type oxides, $LaVO_3$ is not stable at high oxygen partial pressures.[14] In Fig. 1, θ–2θ XRD scans of the films deposited at 500 °C under two different oxygen pressures are shown. Only the $\bar{2}01$ reflection of monoclinic $LaVO_4$ is observed in the film deposited with 10 mtorr oxygen. Films deposited with an oxygen pressure ⩾10 mtorr showed the same XRD patterns indicating that the films are monoclinic $LaVO_4$ with ($\bar{2}01$) preferred orientation. The film deposited in vacuum shows only the 110/002 reflections of $LaVO_3$ along with substrate reflections. The full width at half-maximum (FWHM) of the rocking curve for the 220/004 peak of $LaVO_3$ is ~0.8°. The $LaVO_3$ thin films deposited in vacuum showed the same 110/002 preferential orientation as long as the substrate temperature was ⩾500 °C.

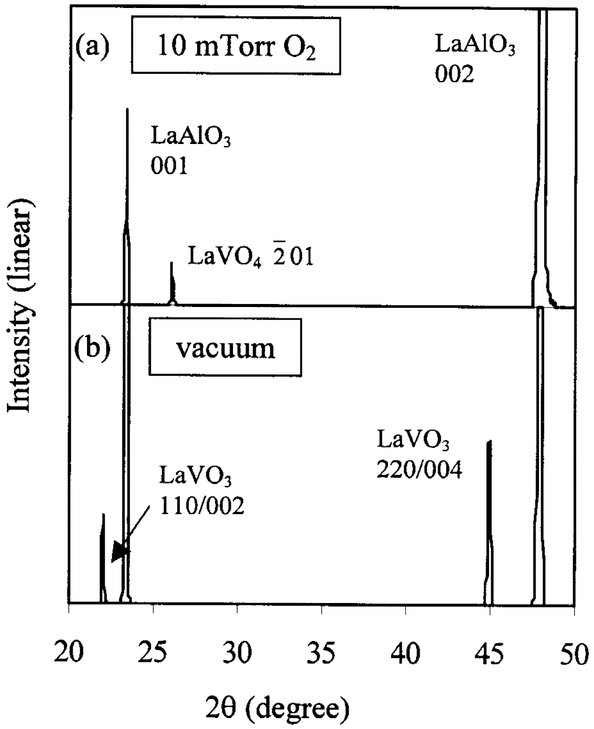

FIG. 1. X-ray diffraction θ–2θ scans of thin films deposited at 500 °C on $LaAlO_3$(001) substrates (a) with oxygen pressure of 10 m torr and (b) in vacuum.

Once $LaVO_3$ films with preferential orientation were grown, the orientation relationship was investigated. Simple inspection of the lattice parameters of $LaVO_3$ and $LaAlO_3$ suggests the following orientation relationship, which is schematically depicted in Fig. 2:

(a) $(110)_{LaVO_3} \| (001)_{LaAlO_3}$ and $[001]_{LaVO_3} \| [010]_{LaAlO_3}$,

(b) $(001)_{LaVO_3} \| (001)_{LaAlO_3}$ and $[100]_{LaVO_3} \| [110]_{LaAlO_3}$.

The systematic absence of the 00*l* peaks (l = odd integer) as well as the degeneracy of d_{110} and d_{002} spacings in orthorhombic $LaVO_3$ make it impossible to distinguish from the normal θ–2θ scans alone whether the film is 110 or 002 oriented. This ambiguity can be resolved by XRD ϕ-scans (angle around the normal to the film) on the $LaVO_3$(111) reflection as shown in Fig. 3. The χ angle (tilt angle of the substrate) at which the (111) reflections are observed should be either (a) 26.6° for the orientation relationship or (b) 63.5° for the orientation relationship. The (111) reflections were observed at χ of both 26.6° and 63.5° indicating that the film is composed of domains with [110] and [001] orientations. The fourfold symmetry in Fig. 3(a) suggests that there are two [110] variants of $LaVO_3$ with the *c* axis in the plane of the substrate parallel to either the [100] or [010] $LaAlO_3$ directions.

It was reported by Lu *et al.* that epitaxial films of $SrRuO_3$ on $LaAlO_3$ were also observed to be a mixture of both [110] and [001] domains.[15] Their reasoning can be applied to explain the above results since $SrRuO_3$ has the same crystal structure as $LaVO_3$ and its lattice constants are quite close to those of $LaVO_3$. Considering

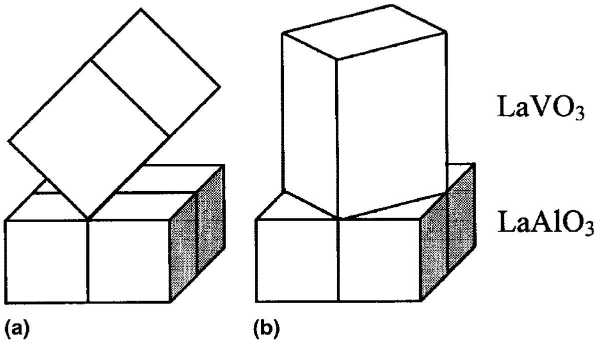

FIG. 2. Schematic illustration of the orientation relationships (a) and (b) for the growth of $LaVO_3$ on (001) $LaAlO_3$.

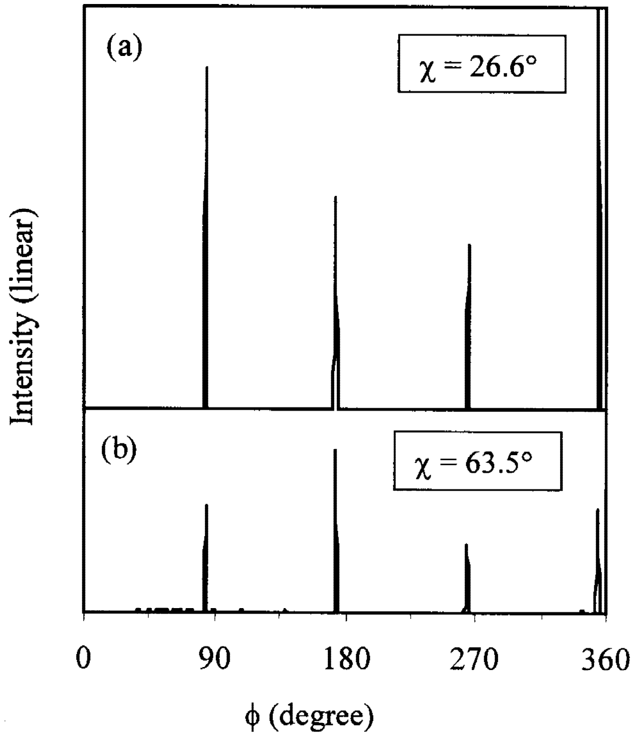

FIG. 3. X-ray diffraction ϕ-scans on $LaVO_3$ 111 reflection (a) at $\chi = 26.6°$ and (b) at $\chi = 63.5°$.

the orthorhombic $LaVO_3$ structure to be pseudocubic, lattice constants of $LaVO_3$ are given as $a_{pc} = b_{pc} = 0.3928$ nm $\cong c_{pc} = 0.3924$ nm. These almost identical lattice constants give a negligible difference in misfit for the two different orientation relationships.

The thermoprobe indicated *p*-type conduction as expected from the properties of bulk $LaVO_3$. The temperature dependence of the conductivity in the temperature range 295–358 K is shown in Fig. 4. The result is consistent with semiconducting behavior resulting from the thermally activated hopping mechanism that has been invoked to describe the extrinsic conductivity of bulk $LaVO_3$ for $T < 400$ K.[10,11] The estimated activation energy of 0.16 ± 0.06 eV as well as the conductivity at room temperature of $\sim 7.7 \times 10^{-2}$ $(\Omega\ \mathrm{cm})^{-1}$ is in good agreement with that of bulk $LaVO_3$.[10–12]

In conclusion, epitaxial $LaVO_3$ thin films can be grown on $LaAlO_3$ substrates by pulsed laser deposition under vacuum at temperatures $\geqslant 500$ °C. The epitaxial films are composed of two domains of [110] and one domain of [001] orientation. The $LaVO_3$ films show *p*-type semiconducting behavior by the hopping mechanism with an activation energy of 0.16 eV.

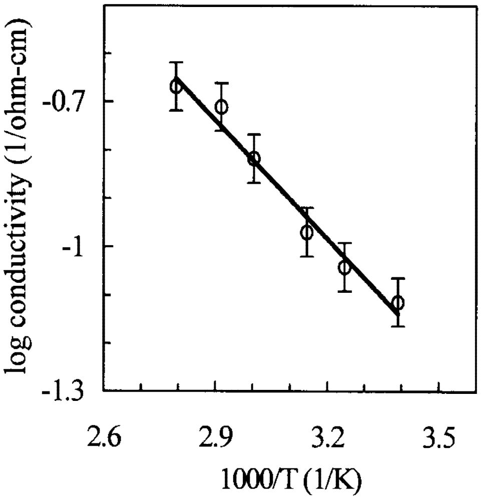

FIG. 4. Temperature dependence of conductivity for epitaxial $LaVO_3$ thin film grown at 600 °C.

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