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# Structural and electrical properties of transparent conductor SrVO<sub>3</sub> thin films grown using radio frequency sputtering deposition

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# Structural and electrical properties of transparent conductor SrVO<sub>3</sub> thin films grown using radio frequency sputtering deposition

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Transparent conductor SrVO<sub>3</sub> thin films were grown on (LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.7</sub> (LSAT), SiO<sub>2</sub>/Si, LaAlO<sub>3</sub>, and sapphire substrates using RF magnetron sputtering deposition with commercial SrVO<sub>3</sub> targets at temperatures as low as 400 °C. Considering the complex phases of SrVO<sub>3</sub> material systems, the growth temperature and sputtering gases were optimized and precisely controlled to yield a transparent and conductive SrVO<sub>3</sub> phase. The authors used a mixed gas atmosphere of Ar and H<sub>2</sub> during growth for reduction. Structural and morphological properties of all SrVO<sub>3</sub> films were investigated using x-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and scanning electron microscopy. XRD and HRTEM showed a highly crystalline cubic phase of SrVO<sub>3</sub> films. In addition, HRTEM showed that a superstructure along the [100] direction could be formed due to Jahn-Teller distortion in the cubic phase of SrVO<sub>3</sub> films. The authors obtained a resistivity of  $0.2 \times 10^{-3} \Omega \text{ cm}$ , mobility of  $1.82 \text{ cm}^2/(\text{V s})$ , and carrier concentration of  $1.57 \times 10^{22} \text{ cm}^{-3}$  for SrVO<sub>3</sub>/LSAT films. Optical transmittance was measured as 88% at a photon wavelength of 633 nm for 39-nm-thick SrVO<sub>3</sub> films. Using x-ray photoemission spectroscopy (XPS) and its depth profile analysis, the authors investigated chemical compositions and binding energies of Sr, V, and O atoms in SrVO<sub>3</sub> films, and their depth profiles. The authors found a correlation between the resistivities and XPS binding energy spectra for SrVO<sub>3</sub> films as functions of film thickness and substrates. *Published by the AVS.* <https://doi.org/10.1116/1.5054666>

## I. INTRODUCTION

Highly conductive and yet highly transparent materials can be used for applications such as electric devices, displays, and energy devices. However, the two characteristics of transparency and conductivity are mutually exclusive and it is difficult to find transparent conductors that use electrons and holes as charge carriers.<sup>1</sup> In general, the resistivity of thin films is higher than that of bulk materials due to the surface scattering of electron carriers. Transparent electrodes are used for optoelectronics devices. Presently, ITO films are the most widely used transparent electrodes. Furthermore, SnO<sub>2</sub>:X (X: F, Sb) and ZnO:X (X: Al, Ga) are also used for transparent conducting oxide (TCO) materials.<sup>2</sup> These TCO materials have a band gap energy larger than 3 eV and are transparent in the visible spectral range, and their resistivities are less than  $10^{-3} \Omega \text{ cm}$ .

To increase the performance of the TCO, it is necessary to increase the carrier concentrations, while maintaining a high mobility. ITO films have high transparency and high conductivity. However, the element indium (In) is becoming scarcer and its resistivity is high in ultrathin films due to increased surface scattering. Therefore, we need new TCO materials. SnO<sub>2</sub> films are cheap and chemically stable whereas their resistivities are high and processing temperature is relatively high. ZnO films have excellent electrical and optical properties, comparable to those of ITOs, whereas they are chemically unstable and are vulnerable to acid and alkalinity. Recently, transition metal oxides (TMO) were proposed as promising

TCO materials.<sup>3,4</sup> Zhang *et al.* proposed TMO as transparent conductors such as SrVO<sub>3</sub> and CaVO<sub>3</sub> films.<sup>4</sup> These perovskite oxide materials have strongly correlated electrons. Their carrier electron masses increase due to renormalization, and SrVO<sub>3</sub> and CaVO<sub>3</sub> films become transparent in the visible spectral range with low screened plasma energy (<1.33 eV).

Metallic SrVO<sub>3</sub> crystals have a cubic perovskite structure, and the lattice parameter is  $a = 3.842 \text{ \AA}$ . Valance bands of SrVO<sub>3</sub> crystals originate from oxygen 2p orbitals. Vanadium 3d orbitals are split into e<sub>g</sub> group (duplet state) and t<sub>2g</sub> group (triplet state) due to the crystal field effect.<sup>4</sup> Here, the t<sub>2g</sub> group forms the conduction band. The interband transition is weak in the visible spectral range. SrVO<sub>3</sub> forms a simple Fermi liquid system. The electrons are strongly correlated and spectral weight transfer occurs. The imaginary dielectric function of SrVO<sub>3</sub> films is still as large as 1 in the 1.2–2.7 eV spectral range, and ultrathin films less than 30 nm are required for greater than 90% transmittance in the visible range. Since the mean free path of electron carriers in the SrVO<sub>3</sub> films is 5.6 nm,<sup>4</sup> low resistivity persists in ultrathin ( $\approx 10 \text{ nm}$ ) SrVO<sub>3</sub> film.

Growth of cubic phase SrVO<sub>3</sub> films was carried out using various growing methods, including hydride MBE,<sup>4,5</sup> pulsed laser deposition (PLD),<sup>6,7</sup> electron-beam evaporation,<sup>8,9</sup> and chemical vapor deposition.<sup>10</sup> There are few reports on sputtering deposition of cubic phase SrVO<sub>3</sub> films.<sup>11</sup> We note that Sharma *et al.* grew orthorhombic SrVO<sub>3</sub> films, which were both transparent and highly resistive, using sputtering deposition.<sup>12</sup>

Several substrates have been used to grow SrVO<sub>3</sub> films: (LaAlO<sub>3</sub>)<sub>0.3</sub>(Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.7</sub> (LSAT),<sup>4–6</sup> LaAlO<sub>3</sub> (LAO),<sup>13</sup> SrTiO<sub>3</sub>,<sup>7,14,15</sup> Si,<sup>16</sup> and yttria-stabilized zirconia (YSZ)/Si.<sup>13</sup>

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LSAT substrates have similar lattice constants to SrVO<sub>3</sub> films, and SrVO<sub>3</sub> films grown on LSAT substrates showed the best electrical and optical properties compared to other substrates.<sup>4,5</sup> Commercial SrVO<sub>3</sub> targets are composed of a Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phase, and a high growth temperature under vacuum deposition or H<sub>2</sub> gas is needed for a reducing environment to grow cubic phase SrVO<sub>3</sub> films.<sup>5,10</sup> Hybrid MBE methods require high temperature growth, as high as 900 °C, as well as appropriate stoichiometry of the SrVO<sub>3</sub> film for high conductivity.<sup>17</sup> However, Jung *et al.*<sup>11</sup> reported that Sr deficiency (Sr<sub>0.9</sub>VO<sub>3</sub>) was required and low temperature growth as low as 10 °C can be used for the growth of high conductivity SrVO<sub>3</sub> films.

Sputtering growth of SrVO<sub>3</sub> films has not been reported so far in the literature. Furthermore, using commercial SrVO<sub>3</sub> targets (actually Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> targets) is very desirable for the sputtering growth of SrVO<sub>3</sub> films because of low cost and simple growth methods, which is essential for industrial applications.

In this work, we used a RF magnetron sputtering deposition method to grow transparent conductor SrVO<sub>3</sub> films on various substrates in a mixture of Ar and H<sub>2</sub> gas using a commercial Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> target. We investigated the structural, optical, and electrical properties of SrVO<sub>3</sub> films. We found a correlation among resistivity, V<sup>4+</sup>/V<sup>5+</sup> ratio, and the composition gradients in Sr, V, and O atoms as a function of SrVO<sub>3</sub> film thicknesses. We found that almost lattice-matched LSAT substrates provided the lowest resistivity values and high optical transmittance for SrVO<sub>3</sub> films at a growth temperature as low as 400 °C. We found a superstructure along the [100] direction, which could be formed due to Jahn-Teller distortion in the cubic phase of SrVO<sub>3</sub> films.

## II. EXPERIMENT

SrVO<sub>3</sub> thin films with thicknesses between 39 and 90 nm were grown on a-plane, c-plane, r-plane, and m-plane sapphire, Si, SiO<sub>2</sub>/Si, LAO, and LSAT substrates under identical conditions by sputtering deposition using commercial SrVO<sub>3</sub> targets (99.5 wt. %). Nominal SrVO<sub>3</sub> targets from RNDKOREA (Republic of Korea) and LTS Research Laboratories, Inc. (USA) were used. The targets were actually composed of a Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phase. Considering the complex phases of the SrVO<sub>3</sub> material system, the growth temperature and sputtering gas atmosphere were optimized and precisely controlled to yield conductive SrVO<sub>3</sub> films of cubic phase. Sputtering pressure was set at 6 mTorr with 25% H<sub>2</sub>/(Ar + H<sub>2</sub>) gas. The flow rate was 10–20 sccm. SrVO<sub>3</sub> films were grown at 350–500 °C. After sputtering, SrVO<sub>3</sub> films were annealed. We note that only Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phase was grown using Ar or a mixture of Ar and O<sub>2</sub> gas.

The structural and morphological properties of all SrVO<sub>3</sub> films were studied using  $\Theta$ -2 $\Theta$  x-ray diffraction (XRD) spectroscopy, grazing incidence of angle x-ray diffraction (GIXRD), high-resolution field-effect scanning electron microscopy (FE-SEM), and high-resolution transmission electron microscopy (HRTEM).  $\Theta$ -2 $\Theta$  XRD was performed for SrVO<sub>3</sub> films using standard XRD equipment. GIXRD was measured to enhance XRD signals from SrVO<sub>3</sub> films with Cu K $\alpha$  x-ray line

(wavelength 1.5406 Å) using an x-ray diffractometer (Model: SmartLab, Rigaku). Resistivities were measured using a Keithley 4200-SCS system. Hall mobilities ( $\mu_{\text{Hall}}$ ) and carrier concentrations ( $N_{\text{Hall}}$ ) were determined via Hall effect measurements (Model: H-50, MMR) in the Van der Pauw configuration. The electronic structure, atomic compositions, and depth profiles of SrVO<sub>3</sub> films were investigated using x-ray photoemission spectroscopy (XPS) (Model: K-Alpha, Thermo Electron). The incident x-ray photon source was Al K $\alpha$  line (1486.6 eV). Surface morphologies of the SrVO<sub>3</sub> thin films were investigated via FE-SEM (Model: Merlin, Carl Zeiss). Cross-sectional HRTEM data were also measured (Model: JEM-2100F, JEOL). Raman scattering spectra were measured by using a McPherson 207 spectrometer equipped with a nitrogen-cooled charge-coupled-device array detector. SrVO<sub>3</sub> films were excited by a 488 nm diode laser with a power less than 0.5 mW to minimize heating effects.

## III. RESULTS AND DISCUSSION

Figure 1 shows the FE-SEM images of SrVO<sub>3</sub> films grown on (a) (100) LSAT, (b) (100) LaAlO<sub>3</sub>, and (c) SiO<sub>2</sub>/Si substrates. In Fig. 1(a), SrVO<sub>3</sub> films grown on LSAT substrates showed grains with sizes of 88 × 88 nm. In Figs. 1(b) and 1(c), SrVO<sub>3</sub> films grown on LaAlO<sub>3</sub> and SiO<sub>2</sub>/Si substrates showed grains with size of 74 × 74 nm and 85 × 85 nm, respectively.

Figures 2(a)–2(f) show the GIXRD pattern of SrVO<sub>3</sub> films grown on LSAT substrates with the film thickness: (a) 39 nm, (b) 51 nm, (c) 64 nm, (d) 77 nm, (e) 90 nm, and (f) SiO<sub>2</sub>/Si substrates, and Figs. 2(g) and 2(h) show the (210) lattice parameter and the size of nanocrystallites, respectively.

We found a (210) GIXRD peak at  $2\theta$  ( $d_{(210)}$ ) = 52.44° (1.744 Å), 52.52° (1.742 Å), 53.07° (1.724 Å), 53.67° (1.706 Å), and 53.50° (1.713 Å) for the film thickness of 39, 64, 51, 77, and 90 nm, respectively, as shown in Fig. 2(g).<sup>18</sup> The average error bar was ±0.002 Å. The same peak was measured at 53.17° (1.722 Å) for SrVO<sub>3</sub>/SiO<sub>2</sub>/Si. SrVO<sub>3</sub>/LSAT films showed a single phase for all the films except the 51 nm-thick films in Fig. 2(b). The SrVO<sub>3</sub> film of 51 nm thickness in Fig. 2(b) showed 28.88° and 55.01° peaks in addition to the (210) 52.52° peak. The 28.88° peak arose from either a tetragonal Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> (204) phase or orthorhombic SrVO<sub>3</sub> (020) phase. The 55.01° peak arose from the orthorhombic SrVO<sub>3</sub> (311) peak. The decrease of (210) lattice parameters with increasing film thickness may be due to the decrease of oxygen deficiency or other defects. Or it could be due to strain relaxation with increasing film thickness. Using XRD, Rey *et al.* measured the (210) lattice parameters as 1.723 and 1.717 Å for SrVO<sub>2.88</sub> and SrVO<sub>3</sub>, respectively.<sup>19</sup> Brahlek *et al.* also reported that the lattice constants were minimized when defect densities were lowest and SrVO<sub>3</sub> was stoichiometric.<sup>17</sup> In this sense, the 77-nm-thick SrVO<sub>3</sub> film has the fewest defect densities, i.e., the highest stoichiometry [Fig. 2(g)]. The lattice parameters for bulk SrVO<sub>3</sub> crystals are a = 3.842 Å for cubic phase,<sup>4</sup> and a = 6.156 Å, b = 7.701 Å, c = 5.367 Å for orthorhombic phase.<sup>12</sup>

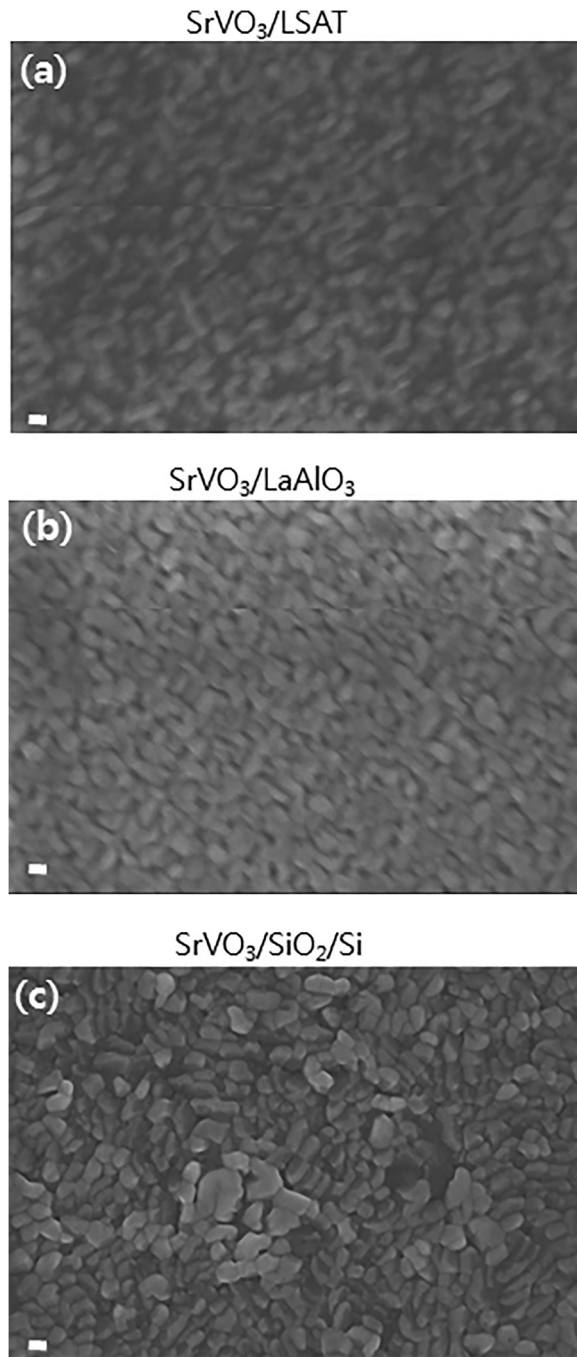


FIG. 1. FE-SEM images of SrVO<sub>3</sub> films (thickness: 77 nm) grown on (a) LSAT, (b) LaAlO<sub>3</sub>, and (c) SiO<sub>2</sub>/Si substrates. The marker size denotes 100 nm.

Figure 2(h) shows the size of the nanocrystallites estimated from the FWHM of the (210) XRD peak. The Scherrer equation was employed as follows:

$$d = \frac{K\lambda}{\beta \cos\theta}, \quad (1)$$

where  $K$  is the shape factor ( $= 0.9$ ),  $\lambda$  is the x-ray wavelength of the Cu  $K\alpha$  line,  $\beta$  is the FWHM in radians,  $\theta$  is the Bragg angle, and  $d$  is the mean nanocrystallite size. The nanocrystallite size was about 8 nm up to 51 nm film thickness, and then decreased abruptly to approximately 4.5 nm as the film

thickness increased further, as shown in Fig. 2(h). The average error bar was  $\pm 0.3$  nm. Since the grain sizes shown in Fig. 1 were an order of magnitude larger than the nanocrystallite size measured with XRD, the grains must be composed of smaller nanocrystallites.

We found a mixture of cubic and orthorhombic phases from SrVO<sub>3</sub> films grown on SiO<sub>2</sub>/Si, namely, 28.97° (020), 43.59° (212), 49.27° (123) for orthorhombic SrVO<sub>3</sub> phases; 53.17° (210) for cubic SrVO<sub>3</sub> phases; and 55.29° (330) for the orthorhombic Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> peak.<sup>20,21</sup> Some of the orthorhombic Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> peaks may be identified as a tetragonal phase of Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> such as 28.97° (204), 43.59° (2 0 10), and 49.27° (1 1 13). Since orthorhombic phases of SrVO<sub>3</sub> films are insulating, we expect that SrVO<sub>3</sub> films grown on SiO<sub>2</sub>/Si will have higher resistance than SrVO<sub>3</sub> films grown on LSAT. XRD showed that LSAT substrates had a dominant (400) phase with minor phases of (222), (442), and (420) (not shown here).

Figure 3 shows the HRTEM image of SrVO<sub>3</sub> films grown on LSAT with 90 nm film thickness: (a) cross-sectional HRTEM data and fast Fourier transform (FFT) transform from (b) Region 1 and (c) Region 2 in (a). Figure 3 shows highly crystalline SrVO<sub>3</sub> films grown on LSAT with (b) FFT pattern of cubic phase of ABO<sub>3</sub> cubic structure and (c) FFT pattern of super-structured cubic phases. We note that the satellite peaks in Fig. 3(c) arose from the formation of a super structure along the [200] direction of SrVO<sub>3</sub> phase. Using GATAN analysis software, we determined the direction of FFT spots, as in Fig. 3(b). We found lattice parameters of 2.771 Å (Region 1) and 2.755 Å (Region 2) for a (110) cubic SrVO<sub>3</sub> phase. We observed lattice parameters (100) 3.969 Å and (110) 2.773 Å from LSAT substrates using HRTEM (not shown here).<sup>22</sup> According to FFT images of both SrVO<sub>3</sub> films and LSAT substrates, the SrVO<sub>3</sub> film orientation was [100] direction, considering the orientation of the LSAT substrate. We note that the lattice parameter 3.969 Å (100) of the LSAT substrate is larger than the reference value of 3.870 Å.<sup>23</sup> However, the XRD data of the LSAT substrate in this work provided the lattice parameter of (100) LSAT substrate as 3.858 Å, which is similar to the reference value. HRTEM is a local probe whereas XRD is a nonlocal probe. The large lattice parameter of 3.969 Å (100) of the LSAT substrate which was measured using HRTEM should be a local phenomenon and could be due to either local interface strain or local expansion of lattice constant due to oxygen vacancy.

Figure 4 shows (a) the binding energy spectra of vanadium ions for SrVO<sub>3</sub> films with various thicknesses measured using XPS, and the depth profiles of SrVO<sub>3</sub> films (thickness: 77 nm) grown on (b) LSAT, (c) SiO<sub>2</sub>/Si, and (d) LAO. We found that the V<sup>5+</sup> valence state transformed to V<sup>4+</sup> as the SrVO<sub>3</sub> film thicknesses increased. The valence state of the V atom in stoichiometric SrVO<sub>3</sub> films should be V<sup>4+</sup>. The V<sup>5+</sup> valence state is attributed to the Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phase. It appears that the surface layers of SrVO<sub>3</sub> films were oxidized to the Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phase. The binding energy of V decreased from 516.83 eV (39 nm, V<sup>5+</sup>) to 516.30 eV (77 nm, V<sup>4+</sup>) as the film thickness increased.<sup>24,25</sup> The XPS depth profiles in Fig. 4(b) show that SrVO<sub>3</sub> films grown on LSAT substrates



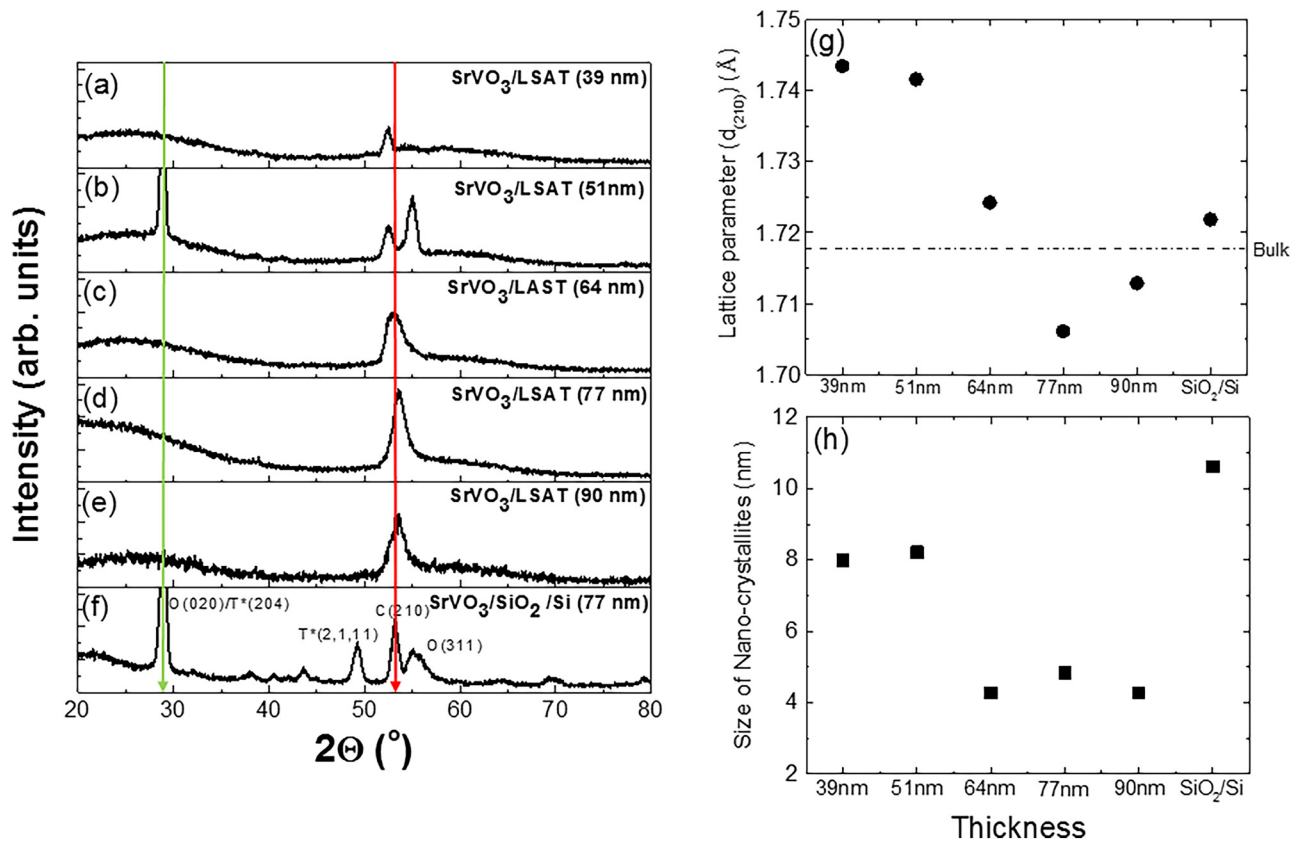


FIG. 2. GIXRD pattern of SrVO<sub>3</sub> films grown on LSAT films of thickness: (a) 39 nm, (b) 51 nm, (c) 64 nm, (d) 77 nm, (e) 90 nm, and (f) SiO<sub>2</sub>/Si substrates. (g) and (h) show the (210) lattice parameter and nanocrystallite size, respectively, as a function of SrVO<sub>3</sub> films thickness. The error bars were  $\pm 0.002$  Å and  $\pm 0.3$  nm, respectively. In (f), C and O denote cubic and orthorhombic phases, respectively, of the SrVO<sub>3</sub> film, and T\* denotes tetragonal phase of the Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> film. In (g), dashed line denotes bulk value.

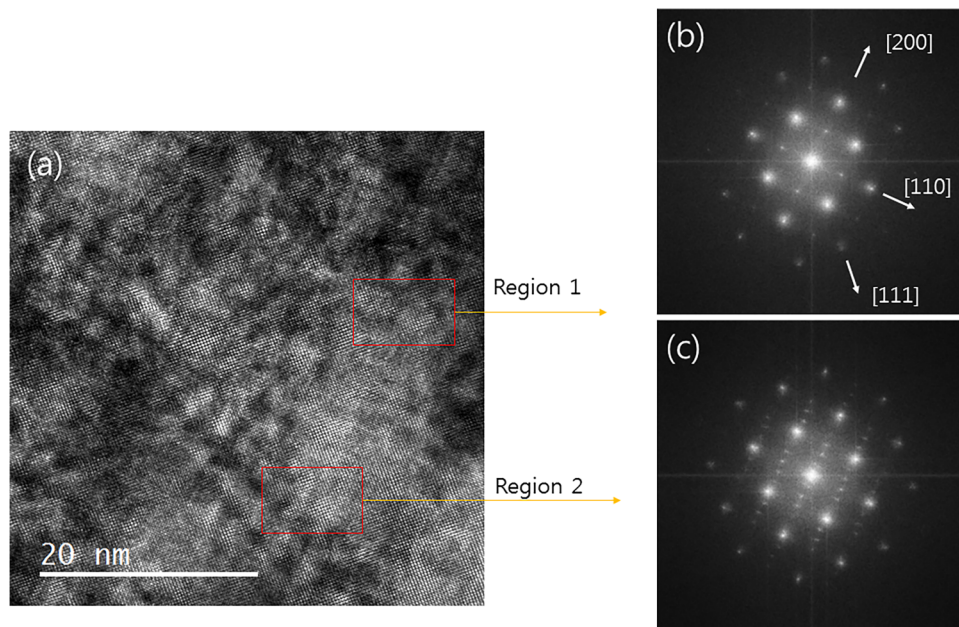


FIG. 3. HRTEM images of SrVO<sub>3</sub> films grown on LSAT with 90 nm thickness: (a) cross-sectional HRTEM data and FFT transform from (b) Region 1 and (c) Region 2 in (a).

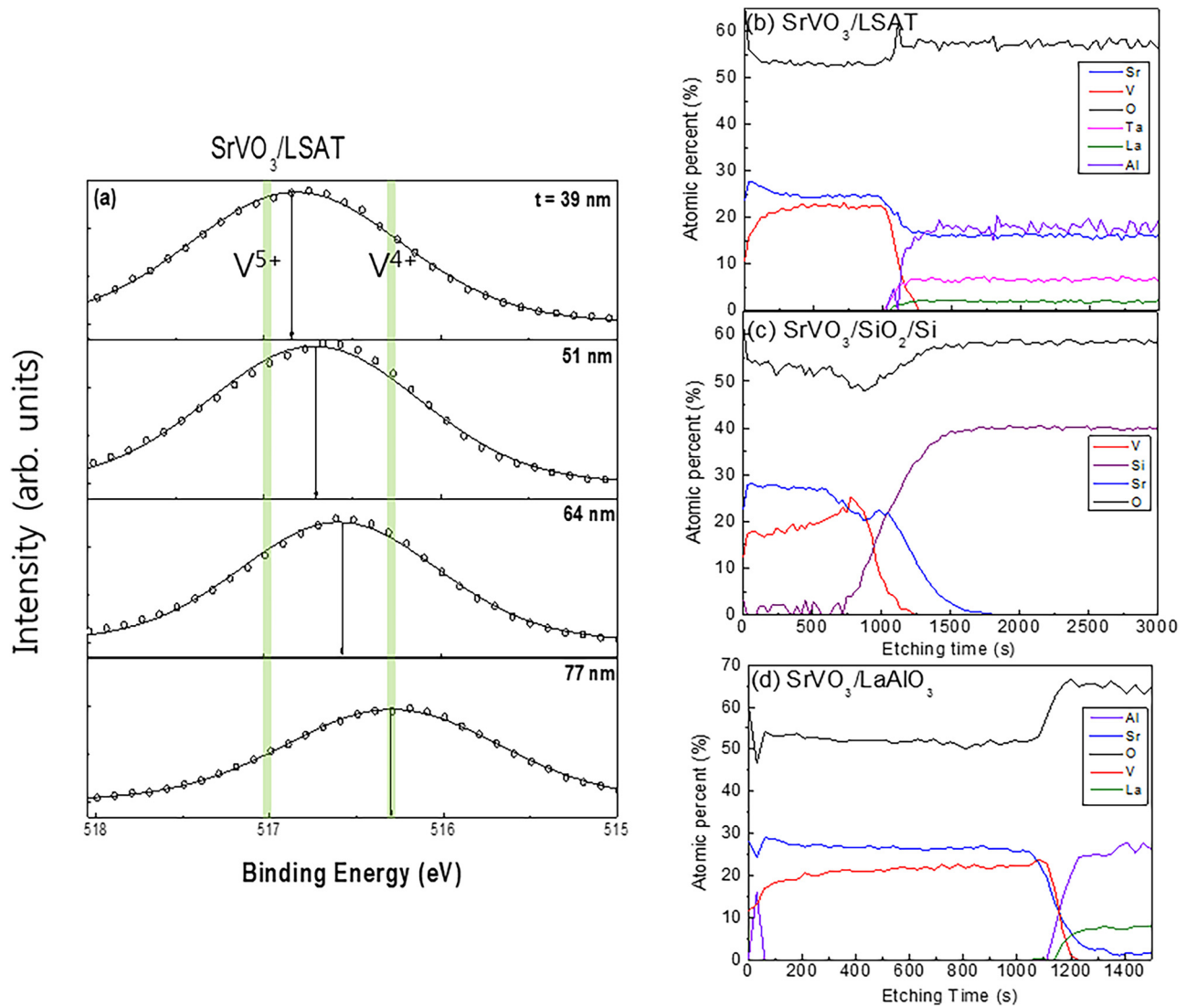


FIG. 4. (a) Binding energy spectra of vanadium ions for SrVO<sub>3</sub>/LSAT films with various thicknesses measured using XPS, and the depth profiles of SrVO<sub>3</sub> films (thickness: 77 nm) grown on (b) LSAT, (c) SiO<sub>2</sub>/Si, and (d) LaAlO<sub>3</sub> substrates.

showed homogeneous distribution of SrVO<sub>3</sub> compositions and sharp interfaces between SrVO<sub>3</sub> films and LSAT substrates. However, we found an oxidized surface layer of about 10 nm. Furthermore, the surface composition of SrVO<sub>3</sub> films was V deficient with excess Sr. In Fig. 4(c), SrVO<sub>3</sub> films grown on SiO<sub>2</sub>/Si substrates showed excess Sr and V deficiencies compared to SrVO<sub>3</sub> films grown on LSAT, as in Fig. 4(b), and showed a Sr<sub>x</sub>Si<sub>y</sub>O phase near interfaces. The Sr<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> phase near the interface is consistent with the literature.<sup>11,15,26</sup> Ishiwaru and Jyokyu<sup>26</sup> reported that SrVO<sub>3</sub> films directly grown on Si form an insulating interface phase of SiSrO<sub>3</sub> because of Si diffusion and depletion of V atoms. Ritums *et al.*<sup>13</sup> used a YSZ buffer layer on an Si substrate to prevent the formation of an insulating Sr<sub>x</sub>Si<sub>y</sub>O<sub>z</sub> interface phase. In Figs. 4(c) and 4(d), SrVO<sub>3</sub> films grown on SiO<sub>2</sub>/Si (LAO) substrates showed large (small) composition gradients for Sr, V, and O atoms in the layer. Sr content had the most significant composition gradient in SrVO<sub>3</sub> films grown on SiO<sub>2</sub>/Si substrates, as in Fig. 4(c). Note that SrVO<sub>3</sub> films grown on

LAO substrates showed sharp interfaces between SrVO<sub>3</sub> films and the LAO substrates, similar to SrVO<sub>3</sub> films grown on LSAT substrates.

Figure 5 shows (a) the substrate dependence of resistivities for SrVO<sub>3</sub> films, (b) the thickness, and (c) the growth temperature dependence of resistivities for SrVO<sub>3</sub> films grown on LSAT substrates. For evaluating substrate and growth temperature dependence, the SrVO<sub>3</sub> film thickness was fixed at 77 nm. In Fig. 5(b), the resistivity was lowest for SrVO<sub>3</sub> films with a thickness of 64 nm grown on LSAT substrates at 400 °C. A growth temperature of 500 °C did not show a noticeable improvement of resistivity values. As shown in Fig. 5(a), various substrates were used to grow low resistivity SrVO<sub>3</sub> films; LSAT, SiO<sub>2</sub>/Si, c- (a-, m-, r-plane) sapphire, TiO<sub>2</sub> (anatase phase)/Si, and LAO substrates. The smallest resistivity was  $0.20 \times 10^{-3} \Omega \text{ cm}$  for LSAT. In comparison, the resistivities were  $3.29 \times 10^{-3} \Omega \text{ cm}$  for SiO<sub>2</sub>/Si and  $4.03 \times 10^{-3} \Omega \text{ cm}$  for LAO substrates. For SrVO<sub>3</sub> films with a 77 nm thickness, we measured resistivity as

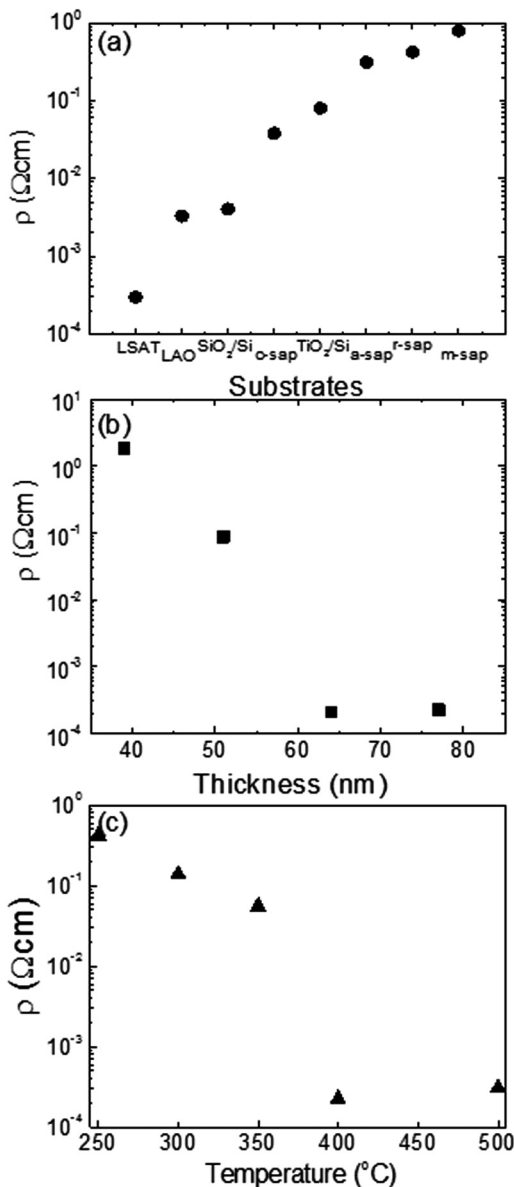


Fig. 5. (a) Substrate dependence of resistivities for SrVO<sub>3</sub> films, (b) thickness, and (c) growth temperature dependence of resistivities for SrVO<sub>3</sub> films grown on LSAT substrates.

$\rho = 0.22 \times 10^{-3} \Omega \text{ cm}$ , mobility as  $\mu = 1.82 \text{ cm}^2/(\text{V s})$ , and carrier concentration as  $N = 1.57 \times 10^{22} \text{ cm}^{-3}$  using Hall effect measurements. In Table I, we summarized the electrical properties of SrVO<sub>3</sub> films and bulk materials grown using various methods in the literature.<sup>4,5,7,14,15</sup> The lowest resistivity values were obtained using hydride MBE, PLD, or laser MBE with LSAT or SrTiO<sub>3</sub> substrates.

Figure 6 shows the transmittance of SrVO<sub>3</sub> films grown on LSAT substrates with various film thicknesses in the visible spectral range. Transmittance in Fig. 6 reached approximately 88%, 78%, 68%, and 57% at the photon wavelength of 633 nm for SrVO<sub>3</sub> films with thicknesses of 39, 51, 64, and 77 nm, respectively. The transmittance of SrVO<sub>3</sub>/LSAT films was normalized with respect to that of the LSAT substrate. Transmittance was suppressed for energies below 400 nm (i.e., above 3.1 eV), marking the onset of

strong interband optical transitions. We note that the transmittance of LSAT substrates is 80%.<sup>4</sup>

We need SrVO<sub>3</sub> films with thickness less than 39 nm to achieve a transmittance greater than 90% at 633 nm, because of the rather large extinction coefficient  $k$  ( $k \approx 0.23$  at  $\lambda = 500 \text{ nm}$ ) value in the visible range for SrVO<sub>3</sub> films.<sup>4</sup> Because of the small mean free path of electron carriers in SrVO<sub>3</sub> films, small resistivity values persist even below 10 nm. We note that transmittance is reduced by decreasing the film thickness in several p-type TCOs such as SnO, TaIrGe, and boron phosphide, because they have weak absorption in the visible range.<sup>32</sup>

Raman spectra showed no peaks from SrVO<sub>3</sub> films and showed only peaks from LSAT substrates (not shown here). This phenomenon is consistent with Raman selection rules which require no Raman-active peaks in SrVO<sub>3</sub> films.<sup>33</sup>

The satellite peaks for SrVO<sub>3</sub> films, shown in Fig. 3(c), may arise from Jahn-Teller distortion in SrVO<sub>3</sub> films. Oxygen defects may cause change of valences of vanadium atoms which can induce crystal fields and generate Jahn-Teller distortion.<sup>34</sup> The Jahn-Teller distortion may have induced distortion of cubic unit cells in SrVO<sub>3</sub> and produced spontaneous formation of superstructures which have periodicities of four to five unit cells. In general, Jahn-Teller distortions occur in  $e_g$  systems such as perovskite manganites (e.g., La<sub>1/3</sub>Ca<sub>2/3</sub>MnO<sub>3</sub>).<sup>35,36</sup> However, weak Jahn-Teller distortions are found in perovskite vanadates such as YVO<sub>3</sub>, LaVO<sub>3</sub>, and SrVO<sub>3</sub> even though they are  $t_{2g}$  systems.<sup>37–39</sup> According to HRTEM data [Fig. 3(c)], cubic SrVO<sub>3</sub> may have been transformed into an orthorhombic system possibly due to Jahn-Teller distortion or ordering of oxygen vacancies. More detailed HRTEM study are currently in progress to understand more accurately the origin of satellite structures. Jahn-Teller distortion is accompanied with distortion of MO<sub>6</sub> bonds along bond direction (i.e., along M–O direction) in  $e_g$  systems. In  $t_{2g}$  system, Jahn-Teller distortion is associated with the distortion in planar MO<sub>4</sub> squares, where the distortion occurs off the M–O bond direction.<sup>39</sup> Jahn-Teller distortion in ultrathin SrVO<sub>3</sub> films were proposed using density functional theory by Gupta *et al.*<sup>34</sup>

XPS analysis of vanadium ion valence states for SrVO<sub>3</sub> films in Fig. 5(a) shows that the increase of the valence state ratio of  $V^{4+}/V^{5+}$  is correlated with the decrease of resistivities with increasing SrVO<sub>3</sub> film thickness, as in Fig. 5(b). This phenomenon may be attributed to the amorphous Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> phase (or orthorhombic SrVO<sub>3</sub> phase) that is dominant at the surface of thin “SrVO<sub>3</sub>” films, the proportion of crystalline SrVO<sub>3</sub> phase increases with increasing thickness, and the SrVO<sub>3</sub> phase is dominant for 77-nm-thick SrVO<sub>3</sub> films. This explains why the thicker SrVO<sub>3</sub> films show a lower resistivity than thinner films (Fig. 6).

The XPS depth profile analysis in Figs. 5(b) and 5(c) shows that the depth profile of SrVO<sub>3</sub> compositions is constant for LSAT substrates whereas those of LAO and SiO<sub>2</sub>/Si substrates are depth-dependent. The composition gradients of Sr, V, and O atoms were negligible for SrVO<sub>3</sub>/LSAT, were largest for SrVO<sub>3</sub>/SiO<sub>2</sub>/Si, and were moderate for SrVO<sub>3</sub>/LAO. A large composition gradient means inhomogeneity of



TABLE I. Electrical properties of the bulk and thin film SrVO<sub>3</sub> at 300 K in the literature.

$\rho$ ( $\times 10^{-3} \Omega \text{ cm}$ )	$N$ ( $\times 10^{22} \text{ cm}^{-3}$ )	$\mu$ [ $\text{cm}^2/(\text{V s})$ ]	Substrate	Growth method	Reference
0.22	1.57	1.82	LSAT	Sputtering deposition	This work (thickness 77 nm)
0.03	2.26	9.0	LSAT	Hydride MBE	4
0.12	2.18	3.05	LSAT	PLD	6
0.045	3.25	0.81	SrTiO <sub>3</sub>	PLD	15
0.117	3.0	1.9	LSAT	Pulsed electron-beam deposition	9
0.11			LaAlO <sub>3</sub>	PLD	13
0.28			SrTiO <sub>3</sub>	PLD	27
0.34			Si	E-beam evaporation	8
0.05			SrTiO <sub>3</sub>	Laser MBE	14
2.5				Solid reaction (bulk)	28
0.222				Solid reaction (bulk)	29
41.8				Solid reaction (bulk)	30
0.75				Solid reaction (bulk)	31

SrVO<sub>3</sub> films and excess or deficiency of Sr, V, and O atoms compared to the stoichiometric SrVO<sub>3</sub> films.<sup>18</sup> In the case of LSAT substrates, SrVO<sub>3</sub> films and LSAT substrates were almost lattice-matched and high-quality SrVO<sub>3</sub> films grew without severe misfit strain. Therefore, SrVO<sub>3</sub>/LSAT showed the smallest resistivity among SrVO<sub>3</sub>/LAO and SrVO<sub>3</sub>/SiO<sub>2</sub>/Si [Fig. 5(a)]. Note that SrVO<sub>3</sub>/SiO<sub>2</sub>/Si produced an insulating Sr<sub>x</sub>V<sub>y</sub>O phase rather than a SrVO<sub>3</sub> phase in the interface; thus, the resistivity increased with the increase of Sr<sub>x</sub>V<sub>y</sub>O phase content.

In Fig. 4(a), the binding energy of V decreased from 516.83 eV (39 nm, V<sup>5+</sup>) to 516.30 eV (77 nm, V<sup>4+</sup>) as the film thickness increased. XPS is a surface-sensitive probe because it measures the kinetic energy of emitted electrons by incident x-ray. About 10 nm from the surface can be probed using XPS. It seems that surface oxide (Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub>) layer thickness decreased with increasing SrVO<sub>3</sub> film thickness. Then, the volume ratio of the surface oxide layer to the main layer will decrease with increasing film thickness.

We measured resistivity as  $\rho = 0.22 \times 10^{-3} \Omega \text{ cm}$ , mobility as  $\mu = 1.82 \text{ cm}^2/(\text{V s})$ , and carrier concentration as

$N = 1.57 \times 10^{22} \text{ cm}^{-3}$  using Hall effect measurements for SrVO<sub>3</sub> films with 77 nm thickness grown using RF sputtering deposition methods. The resistivity value is comparable to those of PLD-grown SrVO<sub>3</sub> films of Boileau *et al.*,<sup>6</sup> whereas the resistivity value is an order of magnitude larger than the resistivity of  $0.03 \times 10^{-3} \Omega \text{ cm}$  obtained for SrVO<sub>3</sub> films grown using hybrid MBE.<sup>4,5</sup> Boileau *et al.*<sup>6</sup> maintained that high-quality SrVO<sub>3</sub> films can be grown with temperatures as low as 400 °C using PLD, and that a front-end-of-line application such as TCO may be possible. Sputtering deposition method is a general-purpose deposition method and is widely used in industries because of its simplicity. This work shows that sputtering deposition of SrVO<sub>3</sub> films grown at 400 °C can be comparable to more sophisticated PLD-grown films, which expands the potential applications of SrVO<sub>3</sub> films as TCO materials.

#### IV. CONCLUSION

We grew transparent conductor SrVO<sub>3</sub> films on various substrates with commercial Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> targets using RF magnetron sputtering deposition. We used a 25% H<sub>2</sub> and Ar mixed gas atmosphere during growth to obtain SrVO<sub>3</sub> films from Sr<sub>2</sub>V<sub>2</sub>O<sub>7</sub> targets via reduction. The lowest resistivity value of  $0.20 \times 10^{-3} \Omega \text{ cm}$  was obtained using almost lattice-matched LSAT substrates at a growth temperature of 400 °C with SrVO<sub>3</sub> film thickness of 64 nm. Resistivity values of  $3.29 \times 10^{-3}$  and  $4.03 \times 10^{-3} \Omega \text{ cm}$  were obtained for SiO<sub>2</sub>/Si and LaAlO<sub>3</sub> substrates, respectively. Superstructures comprised of four or five unit cells were found using HRTEM and were attributed to Jahn-Teller distortion. Using x-ray photoemission spectroscopy and its depth profile analysis, we found correlation among the resistivities, V<sup>4+</sup>/V<sup>5+</sup> valence state ratio, and composition gradients of Sr, V, and O atoms. This work demonstrates that high-quality SrVO<sub>3</sub> films can be grown on LSAT substrates at temperatures as low as 400 °C as TCO films for use in high throughput and low cost indiumfree transparent electrodes.

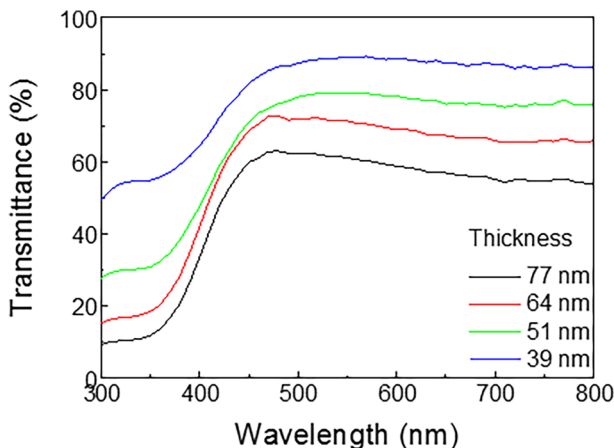


FIG. 6. Transmittance spectra of SrVO<sub>3</sub> films grown on LSAT substrates with various film thicknesses in the visible spectral range.

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