Molecular beam epitaxy growth of the highly conductive oxide SrMoO$_3$

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(Dated: December 7, 2020)

SrMoO$_3$ is a promising material for its excellent electrical conductivity, but growing high-quality thin films remains a challenge. Here we synthesized epitaxial films of SrMoO$_3$ using molecular beam epitaxy (MBE) technique under low oxygen-flow rate. Introduction of SrTiO$_3$ buffer layers of 4–8 unit cells between the film and the (001)-oriented SrTiO$_3$ or KTaO$_3$ substrate was crucial to remove impurities and/or roughness of the film surface. The obtained film shows improved electrical conductivities as compared with films obtained by other techniques. The high quality of the SrMoO$_3$ film is also verified by angle resolved photoemission spectroscopy (ARPES) measurements showing a clear Fermi surfaces.

I. INTRODUCTION

Perovskite oxides with a general formula ABO$_3$ exhibit various intriguing properties such as ferroelectricity, piezoelectricity, ion conductivity, colossal magnetoresistance, and superconductivity.$^{1-3}$ SrMoO$_3$ is a Pauli paramagnetic metal with excellent electrical conductivity.$^{3,4}$ The room temperature (RT) resistivity $\rho$ of single-crystalline SrMoO$_3$ is as low as 5 $\mu\Omega$ cm, which is much lower than typical oxide materials$^4$ and is rather close to those of nearly free electron systems such as sodium and copper. The utmost feature of this oxide has stimulated intensive studies to grow epitaxial films$^{5-10}$ and transparent conductors.$^{11,12}$ Unfortunately, all the films, so far prepared by pulsed laser deposition (PLD)$^{7,13}$ or sputtering$^{14,15}$, show rather poor resistivity (27–150 $\mu\Omega$ cm) than that of the bulk single crystal, possibly due to the presence of defects or inclusion of impurity phases. It is notable that an insulating Mo$^{6+}$ phase is often found in the surface states.$^{10,12}$

Among available techniques of thin film preparation, molecular beam epitaxy (MBE) is known as a method that allows the growth of thin films with high quality.$^{12}$ This is because much smaller kinetic energy of constituent elements supplied in this process$^{13}$ provides an almost thermal equilibrium condition, avoiding an undesired oxide off-stoichiometry. For this reason, we have employed the MBE method, for the first time, to grow SrMoO$_3$ films, using elemental Sr and Mo as fluxes. By optimizing growth conditions such as O$_2$ flow rate, we have successfully obtained epitaxial thin film of SrMoO$_3$. In particular, the use of a SrTiO$_3$ buffer layer between the SrMoO$_3$ film and the substrate is found to be crucial to obtain high quality films with less impurities and/or roughness in the surface. The high-quality of the film is verified by X-ray diffraction (XRD) and angle resolved photoemission spectroscopy (ARPES) measurements. The film with the SrTiO$_3$ buffer layer exhibited an improved resistivity of 24 $\mu\Omega$ cm at RT as compared with the SrMoO$_3$ films by other techniques.$^{3,5,7,9,11,15,16}$

II. EXPERIMENTAL SECTION

Films of SrMoO$_3$ were grown on the (001)-oriented SrTiO$_3$ (STO) or KTaO$_3$ (KTO) substrates with a custom-made reactive MBE system (EGL-1420-E2, Biemtron). Elemental Sr and Mo fluxes were simultaneously provided from a conventional Knudsen cell and electron beam evaporation system. Typical flux rates were 0.04 A/s for Sr and 0.01 A/s for Mo, as determined by an INFICON quartz crystal microbalance system before growth. The growth temperature window was 450–600 $^\circ$C, which was monitored by an optical pyrometer. The optimal growth temperature was found to be 520 $^\circ$C. We flowed O$_2$ gas at a rate of 0.1 sccm, which gives a background pressure of about $4 \times 10^{-7}$ Torr. Lower quality SrMoO$_3$ films were obtained under a higher oxygen pressure, while under ozone flow, SrMoO$_3$ was not obtained. The surface structure of the film and substrate was monitored in-situ by reflection high-energy electron diffraction (RHEED) with an acceleration voltage of 20 keV.

X-ray diffraction (XRD) measurements after the growth were carried out at RT with a Rigaku SmartLab diffractometer equipped with a Cu K$_\alpha_1$ monochromator. The electrical resistivity $\rho$ was measured by using a standard four-probe method. Au/Ti metal electrodes were vacuum-evaporated on the films for electrical contacts, and gold wires ($\phi = 30 \mu$m) were attached with silver paste to these electrodes.

Soft x-ray photoemission measurements were performed at $T = 20$ K with a synchrotron-radiation photoemission spectroscopy system at Photon Factory BL-2. The film used in these measurements was deposited after...
the growth of a STO buffer layer on the Nb-doped (001)-STO substrate to eliminate the charging effect. The thickness of the SrMoO$_3$ film used in experiments was 14.6 nm. The top of the film was capped with one unit cell of STO to protect the SrMoO$_3$-film surface from further oxidation. Thus no surface cleaning was conducted. ARPES was performed for the same sample. The position of Fermi energy $E_F$ was determined by measuring the spectra of gold which was electrically connected to the sample.

For the theoretical reference of ARPES results, electronic structures were calculated using the QUANTUM ESPRESSO package. We used projector-augmented wave pseudopotentials and the Perdew-Burke-Ernzerhof parameterization of the generalized gradient approximation. The cutoff energies in the wave function and charge densities were 80 and 500 Ry, respectively. A $10 \times 10 \times 10$ k-mesh in the first Brillouin zone was used. It is worth noting that the bulk SrMoO$_3$ exhibits structural transitions, upon heating, from an orthorhombic phase to a tetragonal phase at $T = 150$ K, and to a cubic phase at $250$ K. However, the distortion from the cubic symmetry is subtle and does not largely alter its band structure. Our band structure calculations also confirmed this result. We will show the result for the cubic SrMoO$_3$ unless otherwise specified.

**III. RESULTS AND DISCUSSION**

For the growth of high quality SrMoO$_3$ films, we used a buffer layer of STO with 4–8 unit cells, between the SrMoO$_3$ film and the STO (or KTO) substrate. Such buffer layer has been used for the growth of SrMoO$_3$ and EuMoO$_3$ by PLD. In this study, we firstly deposited SrTiO$_3$ using Sr and Ti under O$_2$ gas flow, and then we started the growth of SrMoO$_3$ films at the peak top of oscillation in RHEED for SrTiO$_3$ (Figs. 1(a) and (b)). The interval between each peak corresponds to one unit cell of SrMoO$_3$ (or SrTiO$_3$). For substrates of SrTiO$_3$ and Nb-doped SrTiO$_3$, the oscillation amplitude gradually reduced after the growth of 10–15 unit cells of SrMoO$_3$ (Fig. 1(a)), while it retained almost constant in the case of the KTaO$_3$ substrate (Fig. 1(b)). For comparison, we present RHEED intensity profiles during the growth of the SrMoO$_3$ film on the non-buffered KTO substrate (Fig. 1(c)). It is seen that the RHEED intensity oscillation soon disappears when no buffer is used (Fig. 1(c)). The growth of 25–40 unit cells of SrMoO$_3$ (10–16 nm) was checked by the RHEED intensity oscillations or estimating time with the average interval of oscillation peaks or with the growth rates. Figures 1(d)–(f) display RHEED patterns at the end of the growth for the same samples in Figs. 1(a)–(c), respectively. Streaky RHEED patterns ensure flat surface of the films (Figs. 1(d)–(e)), while the spot-like (or slightly modulated) features are observed along with original streaks for the film without the buffer layer (Fig. 1(f)), suggesting roughening of the film surface. We also used the so-called STEP substrate of SrTiO$_3$ with 100% TiO$_2$-terminated surface, but epitaxial growth was not possible in the current growth condition. The difference between the presence and absence of the buffer layer for the electrical conductance will be discussed in a later section.

Figures 2(a)–(b) show the out-of-plane $\theta$–2$\theta$ XRD patterns for the same samples in Figs. 1(a)–(c). Sharp peaks
The lattice parameters of the SrMoO$_3$ film on the STO-buffered STO (S-STO) and non-buffered KTO substrates, respectively. These values agree with the thickness estimated from the interval of RHEED oscillation peak and time as well as the growth rate. The rocking curve of the XRD peak around the 001 peak for the film on the STO substrate (2$\theta$ $\simeq$ 22$^\circ$) is $\Delta \omega$ = 0.097$^\circ$ (inset of Fig. 2(a)). This value is slightly broader than that of SrMoO$_3$ films on the GdScO$_3$ substrate with PLD, which is probably because our film is thinner. An alternate possibility is a lattice mismatch between the bulk SrMoO$_3$ ($a = 3.975$ Å) and SrTiO$_3$ ($a = 3.905$ Å), leading to a strain effect. In fact, a pseudocubic lattice constant of GdScO$_3$ ($a = 3.973$ Å) is closer to that of bulk cubic SrMoO$_3$. The rocking curve of the (00) peaks of the SrMoO$_3$ films on the KTO substrates was not measured due to the fact that the sample peaks are overlapped with the substrate peaks. Figure 2(c) and (d) show the reciprocal space mappings around the 103 peak of SrMoO$_3$ for the film on the S-STO and S-KTO substrates. The 103 peaks of the films are located near the same $q_z$ value of the 103 peaks of the substrates, indicating a coherent growth of the target film, with an in-plane lattice parameter almost identical to that of the substrate. The lattice parameters of the SrMoO$_3$ film on the S-STO substrate are $a = 3.90$ Å, and $c = 4.02$ Å, meaning that the cell volume is reduced by about 3% relative to the bulk sample. The reduced/expanded $a/c$ axis is reasonable given the compressive strain from the SrTiO$_3$ substrate. The lattice parameters of the SrMoO$_3$ film on the S-KTO substrate are $a = 3.99$ Å (in-plane) and $c = 3.99$ Å (out of plane). The overall lattice expansion of the film about 1% in volume with respect to bulk SrMoO$_3$ may result

FIG. 2. Out-of-plane $\theta$–2$\theta$ XRD patterns of the films on (a) the STO substrate and (b) the KTO substrate. Data of the same samples of Figs. (a)–(c) are presented in (a)–(b). Substrate peaks are marked with an asterisk. The insets of (a) and (b) shows the rocking curve of the 001 peak around 22$^\circ$, and the elongation of the 26scan around 45$^\circ$, respectively. (c)–(d) X-ray reciprocal space mapping around the 103 reflection.

with distinct fringes are observed around 2$\theta$ = 22$^\circ$ and 45$^\circ$ for the SrMoO$_3$ film on the STO-buffered STO (S-STO) substrate (Fig. 2(a)), indicating excellent orientation and atomic scale smoothness of the interface between the substrate and the film. A similar tendency of the XRD profile and fringes is observed in the films on the STO-buffered KTO (S-KTO) and non-buffered substrates (Fig. 2(b)), where the XRD peaks of the films are overlapped with those of the KTO substrates. It is seen that fringes of the XRD spectrum of the SrMoO$_3$ film on the non-buffered KTO substrate are weakened (the inset of Fig. 2(b)), implying poorer quality of the film interface with the substrate. This result is consistent with the RHEED observation (Fig. 1(f)), suggesting island growth and its coalescence accompanied by the generation of grain boundaries and/or impurities. The film thickness estimated from the spacing of fringes is 11.3 nm, 15.6 nm, and 16 nm for the films on the S-STO, S-KTO, and non-buffered KTO substrates, respectively. These values agree with the thickness estimated from the interval of RHEED oscillation peak and time as well as the growth rate. The rocking curve of the XRD peak around the 001 peak for the film on the STO substrate (2$\theta$ $\simeq$ 22$^\circ$) is $\Delta \omega$ = 0.097$^\circ$ (inset of Fig. 2(a)). This value is slightly broader than that of SrMoO$_3$ films on the GdScO$_3$ substrate with PLD, which is probably because our film is thinner. An alternate possibility is a lattice mismatch between the bulk SrMoO$_3$ ($a = 3.975$ Å) and SrTiO$_3$ ($a = 3.905$ Å), leading to a strain effect. In fact, a pseudocubic lattice constant of GdScO$_3$ ($a = 3.973$ Å) is closer to that of bulk cubic SrMoO$_3$. The rocking curve of the (00) peaks of the SrMoO$_3$ films on the KTO substrates was not measured due to the fact that the sample peaks are overlapped with the substrate peaks. Figure 2(c) and (d) show the reciprocal space mappings around the 103 peak of SrMoO$_3$ for the film on the S-STO and S-KTO substrates. The 103 peaks of the films are located near the same $q_z$ value of the 103 peaks of the substrates, indicating a coherent growth of the target film, with an in-plane lattice parameter almost identical to that of the substrate. The lattice parameters of the SrMoO$_3$ film on the S-STO substrate are $a = 3.90$ Å, and $c = 4.02$ Å, meaning that the cell volume is reduced by about 3% relative to the bulk sample. The reduced/expanded $a/c$ axis is reasonable given the compressive strain from the SrTiO$_3$ substrate. The lattice parameters of the SrMoO$_3$ film on the S-KTO substrate are $a = 3.99$ Å (in-plane) and $c = 3.99$ Å (out of plane). The overall lattice expansion of the film about 1% in volume with respect to bulk SrMoO$_3$ may result
from the tensile substrate strain which could also induce oxygen vacancies.

Core-level photoemission spectrum of the SrMoO$_3$ film provided evidence for the Mo$^{4+}$ state associated with two sharp peaks at the binding energy of 229.3 eV and 232.6 eV for the photon energy of 1486.8 eV (Fig. 3(a)). A broad satellite was also observed next to the sharp peaks, which is likely Mo$^{4+}$ 3$d$ emission of unscreened final states. We also collected a spectrum at a lower photon energy (600 eV), which is more sensitive for the film near the surface, and observed additional features at 233.1 eV and 236.4 eV. These peaks are attributed to Mo$^{6+}$ 3$d$ emissions as observed in MoO$_3$, suggesting the oxidation of Mo around the interface with the topmost capping layer of STO ($\sim 0.4$ nm). Note that the broad feature at about 235 eV cannot readily be explained by a simple component of Mo states; it may be due to plasmon satellite as discussed by Wadati et al.

In order to investigate the electronic structure of the SrMoO$_3$ film, we performed ARPES measurements in the two-dimensional $k$ space. Here one can ignore the contribution of Mo$^{6+}$ in the surface to the obtained data near $E_F$, owning to its insulating $d^0$ state. The Fermi surface (FS) mapping on the $k_x$-$k_y$ plane and the $k_x$-$k_z$ plane (Figs. 4(c) and (d)), recorded with varying $h\nu$ from 500 to 700 eV, exhibits strong intensity with parallel-cross and ellipse patterns. These results can be reproduced computationally (see FS in Figs. 4(a) and (b)), and assure the high quality of the film (apart from Mo$^{6+}$ in the surface). It is remarkable that in Fig. 4(e), a parabolic-like dispersion is clearly seen from ARPES spectra near $E_F$ along the $X$–$\Gamma$–$X$ path (the cut in Fig. 4(c) for the $k_x$ direction with $k_y = 0$). In the present experimental geometry, where $p$-polarized incident light and the analyzer slit are in the $xz$ mirror plane of the sample, the $d_{xz}$ band having even parity with respect to the $xz$ mirror plane is observable, while the $d_{xy}$ and $d_{yz}$ bands having odd parity are not. These considerations led us to conclude that the observed dispersion originates from the $d_{xz}$-derived band, which is again supported by the band structures (Fig. 4(f)).

Figure 5 displays the temperature dependence of electrical resistivity $\rho$ of SrMoO$_3$ films of thickness of about...
of SrMoO$_3$ films, in conjunction with the clarification of the role of the presence and absence of the buffer layer for the amount of impurities with the Mo$^{6+}$ state.

IV. CONCLUSION

We have succeeded in growing SrMoO$_3$ films using MBE growth technique. Introduction of SrTiO$_3$ buffer layer of 4–8 unit cells between the SrMoO$_3$ film and the (001)-oriented SrTiO$_3$ or KTaO$_3$ substrate improves the quality of the film, showing the five-times smaller resistivity than that of the film without the buffer layer. Clear observation of FS in ARPES measurements also ensures the high quality of the SrMoO$_3$ film grown by MBE.

ACKNOWLEDGEMENTS

This work was supported by CREST (JPMJCR1421) and JSPS KAKENHI Grants (No. 16H06439 and No. 17H04849).

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16. (,) it has been reported that the value of the RT resistivity $\rho_{RT}$ decreases from 34 $\mu$Ω cm to 27 $\mu$Ω cm with increasing the film thickness from 15 nm to 60 nm. This result implies the influence of the oxidized surface of SrMoO$_3$ films. Compared with samples with the same thickness, $\rho_{RT}$ of our films in this study is 30% smaller than that of previous reports.
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(), using the QUASES-IMFP-TPP2M software, the inelastic mean free path (IMFP) of photoelectron from O 1s is about 2 nm in SrMoO$_3$ for $h\nu = 1486.8$ eV. With these IMFP and $h\nu$ values, we roughly estimated 20% (80%) contributions from SrTiO$_3$ (SrMoO$_3$) to the O 1s spectrum. We also obtained 15–18% contributions from SrTiO$_3$ to the Sr 3d spectrum, using the estimated IMFP of 2.3–2.5 nm and $h\nu = 1486.8$ eV.

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