Redox Controllable Switch of Crystalline Phase and Physical Property in SrVO$_x$ Epitaxial Films

Xue-jiao Gu$^a$, Zhen-lin Luo$^{a,*}$, Yong-qi Dong$^a$, Jing-tian Zhou$^a$, Han Xu$^a$, Bin Hong$^b$, Chen Gao$^{a,b,*}$

*a. National Synchrotron Radiation Laboratory & CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei 230026, China
b. Hefei Innovation Research Institute, School of Microelectronics, Beihang University, Hefei 230013, China
c. Beijing Advanced Sciences and Innovation Center of Chinese Academy of Sciences, Beijing 101407, China

(Dated: Received on March 1, 2019; Accepted on April 26, 2019)

Transition-metal oxides have attracted much attention due to its abundant crystalline phases and intriguing physical properties. However, some of these compounds are difficult to be fabricated directly in film form due to the ease of valence variation of transition-metal elements.

In this work, we reveal the reversible structural transition between SrVO$_3$ and Sr$_2$V$_2$O$_7$ films via thermal treatment in oxygen atmosphere or in vacuum. Based on this, Sr$_2$V$_2$O$_7$ epitaxial films are successfully synthesized and studied. Property characterizations show that the semitransparent and metallic SrVO$_3$ could reversibly switch into transparent and insulating Sr$_2$V$_2$O$_7$, implying potential applications in controllable electronic and optical devices.

Key words: Transition-metal oxides, Reversible transition, Controllable electronic and optical devices

I. INTRODUCTION

For transition-metal oxides (TMOs), a small change in the oxygen proportion often results in the variation of valence state of the transition metal elements especially for V [1–5], Fe [6, 7], Co [8–15], Cr [16], and Mn [17, 19], which in-turn dramatically modifies the physical properties of materials such as electrical conductivity, magnetic state, and optical transparency. This characteristic of transition element leads to narrow process windows for some specific crystalline phases and makes the fabrication difficult. On the other hand, the oxidation stoichiometry of these TMOs can be manipulated by treatment in an oxidizing or reducing atmosphere, thereby achieving conversion between different phases [14, 16]. Based on the above reasons, a reasonable pathway for synthesis of some complex or difficult TMO phases can be carried out via preparing an adjacent phase first and then changing the redox states. Taking SrCoO$_4$ as an example, high-quality films of brownmillerite phase SrCoO$_{2.5}$ could be fabricated directly while it is difficult to synthesize perovskite phase SrVO$_3$. Jeen et al. [13] demonstrated that perovskite SrVO$_3$ films could be achieved by oxidation heat-treatment of brownmillerite SrCoO$_{2.5}$, or reversely via a heat-treatment in reducing atmosphere.

For the materials of SrVO$_x$ series, much attention has been paid recently to the SrVO$_3$ phase due to its excellent conductivity [20, 21], while less attention was attracted by the transparent Sr$_2$V$_2$O$_7$ phase due to the difficulty in preparation. In this work, SrVO$_3$ and Sr$_2$V$_2$O$_7$ films were successfully synthesized, and their electrical and optical properties were studied. It was found that high quality SrVO$_3$ film was much easier to be fabricated than the Sr$_2$V$_2$O$_7$, and a phase-transition method as mentioned above was used to get the Sr$_2$V$_2$O$_7$ epitaxial films.

II. EXPERIMENTS

In this study, the SrVO$_3$ films were deposited on single crystal substrates of SrTiO$_3$ (STO) with (001) orientation using pulsed laser deposition (PLD). The Sr$_2$V$_2$O$_7$ target was prepared by solid-state reaction method using SrCO$_3$ and NH$_4$VO$_3$ powders as starting materials. During the deposition, a KrF excimer laser ($\lambda=248$ nm) with a 1 Hz repetition rate and 350 mJ/pulse energy was used. Samples were grown at the substrate temperature of 700 °C under an oxygen pressure of $2\times10^{-3}$ Pa.

X-ray diffraction (XRD) structural analysis was performed on Smartlab diffractometer (Rigaku, Japan). Film morphology was characterized using atomic force microscopy (AFM, Park Systems XE7). X-ray absorption spectroscopy (XAS) measurements were performed on the beamline BL12B in the National Syn-
chrotron Radiation Laboratory (NSRL). Optical transparency in the UV-near infrared range was measured using a SOLID3700 spectrophotometer operating in the transmission mode. Electrical transport properties were measured by physical property measurement system (Quantum Design).

To investigate the reversible phase transformation between SrVO$_3$ and Sr$_2$V$_2$O$_7$ phases, temperature-dependent XRD measurements were performed for the SrVO$_3$ films. For in situ monitoring the oxidation process (that is, SrVO$_3$ to Sr$_2$V$_2$O$_7$ transformation), the temperature was increased up to 800 °C with several internal hold-steps of 30 min for XRD measurements. After this heating process, the sample was cooled down to room temperature in the same atmosphere at a rate of 10 °C/min. For the reduction process (that is, Sr$_2$V$_2$O$_7$ to SrVO$_3$ transformation), since in situ vacuum condition is not available to the diffractometer that we used, the Sr$_2$V$_2$O$_7$ film was firstly heat-treated at 800 °C in a tube furnace for a specific period of time under vacuum condition, and subsequently was characterized at room temperature.

III. RESULTS AND DISCUSSION

In FIG. 1(a), the in-situ temperature-dependent X-ray diffraction patterns show the oxidation process of SrVO$_3$. With the increasing temperature, it can be noticed that the 002 peak of SrVO$_3$ disappears above 300 °C, and then completely transforms to Sr$_2$V$_2$O$_7$ above 575 °C. This pure Sr$_2$V$_2$O$_7$ phase persists even when the temperature is decreased to room temperature. Actually, the SrVO$_3$ film is verified to be epitaxial. The absence of film peaks from 400 °C to 575 °C might be ascribed to an intermediate amorphous state. By the way, all the peaks shift during the heat-treatment due to thermal expansion. The XRD patterns for the reduction process are plotted in FIG. 1(b). From bottom to top, an increasing time period is used for the heat-treatment of Sr$_2$V$_2$O$_7$ at 800 °C in vacuum. It is obvious that the Sr$_2$V$_2$O$_7$ transforms to SrVO$_3$ completely after annealing of 3 h. In addition, during this reducing process, the appearance of Sr$_6$V$_6$O$_{19}$ phase is observed. Actually, this Sr$_6$V$_6$O$_{19}$ phase can also be detected sometimes in the oxidation process, but not in the in-situ XRD patterns plotted in FIG. 1(a). A possible reason is the temperature step that we used is too large with respect to the narrow temperature window for Sr$_6$V$_6$O$_{19}$.

FIG. 2 presents the surface morphology information of the finally-obtained SrVO$_3$ and Sr$_2$V$_2$O$_7$ films measured by AFM. In FIG. 2(a), the 15 nm-thick SrVO$_3$ film deposited on STO(001) shows a flat surface with roughness of 181.6 pm (root mean square). In FIG. 2(b), after high-temperature annealing in oxidation atmosphere, the obtained Sr$_2$V$_2$O$_7$ film possesses a roughness of 185.8 pm, indicating the high quality was preserved.

In order to confirm the valence state of vanadium in the two samples, XAS measurements were performed at the V L-edge, and the results are plotted in FIG. 2(c). As can be seen, the V L-edge spectra consist of two main peaks belonging to the low-energy $L_3$ and the high-energy $L_2$. Obviously, the $L_2$-edge of Sr$_2$V$_2$O$_7$ shifts to 521.8 eV, about 0.4 eV higher than that of SrVO$_3$. This energy shift indicates that the stoichiometry of the final compound after oxidation is Sr$_2$V$_2$O$_{7-δ}$ ($δ=0.3$), according to the linear relationship between valence state and $L_2$-edge energy for vanadium, i.e., 0.6 eV per oxidation state found by Chen [22]. This XAS results, although still qualitative, help us to recognize the redox nature for the observed phase transition.

To investigate the annealing-induced change of physical properties, optical and electrical measurements were performed on the SrVO$_3$ films. FIG. 3(a) shows the optical transmittance spectra of SrVO$_3$ in the wavelength range of 340–2000 nm. The SrVO$_3$ thin film exhibits an optical transmittance of ~60% in the range of visible wavelengths, approximately 25% lower than that.
FIG. 2 AFM features of (a) SrVO$_3$ and (b) Sr$_2$V$_2$O$_7$ films. (c) XAS spectra of SVO$_x$ measured at the V L-edge.

FIG. 3 (a) Optical transmission spectra of SrVO$_3$ and Sr$_2$V$_2$O$_7$ films, and the inset displays the optical photograph of the SrVO$_3$ films covering corresponding printed text. (b) Temperature dependence of resistance of the obtained SrVO$_3$ and Sr$_2$V$_2$O$_7$ films.

FIG. 4 DFT calculated band structure and density of state of (a) SrVO$_3$ and (b) Sr$_2$V$_2$O$_7$.

of Sr$_2$V$_2$O$_7$ film. This result indicates that the semi-transparent SrVO$_3$ becomes transparent after thermal treatment in oxygen atmosphere, which is also verified by the optical photo presented in the inset where the printed text ‘Sr$_2$V$_2$O$_7$’ is much more clear than ‘SrVO$_3$’ on the white paper covered by corresponding SrVO$_x$ films. FIG. 3(b) plots the temperature-dependent electrical transport curves of the SrVO$_x$ films. The initial SrVO$_3$ film shows a typical metallic performance, which is consistent with previous report [20]. After oxidation treatment, at least 5 orders increase of amplitude was found in the resistance, indicating an obvious insulating characteristic of the obtained Sr$_2$V$_2$O$_7$ film. The above results show obvious switching effects of transparency and electricity, which could be used for novel devices in the future.

To further understand the property change of the SrVO$_x$ films, density functional theory (DFT) calculations were performed using the Cambridge serial total energy package software (CASTEP), based on the structural information that we obtained. FIG. 4(a) shows the calculation results of SrVO$_3$. The d and p electrons occupy the Fermi level, indicating SrVO$_3$ has good electrical conductivity. In contrast, as presented in FIG. 4(b), the Sr$_2$V$_2$O$_7$ phase possess a band gap $E_g$ of $\sim$3.403 eV [23], which implies obvious insulating. This calculation also confirms the above results of conductivity and transmittance.
IV. CONCLUSION

To summarize, we have fabricated high-quality SrVO₃ epitaxial thin films on STO(001) by PLD. More interestingly, we reveal the redox-induced reversible structural phase transition between SrVO₃ and Sr₂V₂O₇ via thermal treatment in oxygen or in vacuum. Based on this discovery, we successfully prepared Sr₂V₂O₇ epitaxial films with high quality, which is regarded to be difficult to be fabricated previously. Property investigation shows that the obtained Sr₂V₂O₇ is transparent and insulating, totally different from its parent SrVO₃ thin film which is semitransparent and metallic. These controllable switches of properties imply potential applications in electronic and optical devices. This study verifies that thermal treatment is an effective way to fabricate high-quality films of vanadium oxides with varied valence, and this approach could also be applied for plenty of transition-metal oxides.

V. ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (No.2016YFA0300102), the National Natural Science Foundation of China (No.11675179, No.11434009, and No.11374010), and the Fundamental Research Funds for the Central Universities (No.WK2340000065). This work was partially carried out at the University of Science and Technology (USTC) center for Micro and Nanoscale Research and Fabrication. We thank the support from the magnetic circular dichroism endstation at Hefei Light Source.