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A novel structural expansion in SrTiO$_3$ tuned by electric field and visible-light

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SrTiO$_3$ is a model perovskite oxide of abundant physical properties, which are closely associated with internal oxygen vacancy (V$_O$) defects. Through in situ X-ray diffraction measurements, we observed a remarkable structural expansion in the near-surface region of (001)-SrTiO$_3$ induced by an external electric field. By repeated scanning and consistently monitoring the 002 reflections, forming process of the unique structural distortion was obtained and considered to be the results of electromigration and redistribution of V$_O$s. Peculiarly, it was found that a much greater lattice distortion would occur rapidly in SrTiO$_3$ under the illumination of visible light, and be effectively tuned depending on wavelength. We propose that the light effect stems from photo-excitation, which generates extra carriers and remarkably speeds up the diffusion of V$_O$s. This work provides a feasible way towards tuning the kinetics of V$_O$s and structure of SrTiO$_3$ by combined stimuli of electric field and light illumination, yielding novel properties in above films as well as hetero-interface at SrTiO$_3$-based oxide system. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

SrTiO$_3$ (STO) is a model perovskite transition-metal oxide (ABO$_3$) which is extensively studied for its versatile physical properties including high dielectric constant $k$, good catalytic activity, excellent thermostability and so on. It has been widely applied for sensors, microwave devices, resistance switching random access memories and so on. In addition to these, STO is one of the most commonly used substrates for the epitaxial growth of ABO$_3$ thin films due to its compatible lattice parameters and chemical stability. In recent years, ABO$_3$ thin films and junctions have been the focus of research due to their novel electro-magnetic properties. Considering the significant effect of substrate on epitaxial films, an intensive study on the properties of STO is of great importance and necessity.

Oxygen vacancy (V$_O$) is the most common defect inside STO, which acts as most mobile ionic specie and introduces charge carriers of electrons with high mobility (up to 6000 cm$^2$/Vs). STO could exhibit a special capability in accommodating V$_O$s, especially when it is oxygen-deficient. It is worth noting that V$_O$ plays an important role in the properties of STO. Typically, STO is known as a wide-band gap semiconductor with high dielectric constant, which can become a high-mobility metal or even a superconductor when introducing V$_O$s. Until now, plenty of researches on V$_O$s have been done. Studies have found that, V$_O$s exist in different forms in STO (isolated V$_O$ or V$_O$ pairs and so on), and prefer to diffuse towards surface, yielding a concentration gradient from surface to...
to interior in bulk STO. However, data regarding some questions haven’t reached a consensus yet, for example, an mobility of VO at room temperature (RT) was reported to be on the order of $10^{-19} \sim 10^{-20}$ m$^2$/V·s by McIntyre, in disagreement with the value of $10^{-17}$ m$^2$/V·s in other works. Activation energy for VO$_x$ diffusion is also quit different reported by Paladino and Waser (0.67 and 1.1 eV). Obviously, further researches dealing with VO$_x$ diffusion in STO are needed in future.

In our previous work, a dramatic lattice structural distortion in STO crystal induced by applied gate voltage ($V_G$) at RT has been observed. Some other works also reported on the observation of this peculiar effect. However, since STO is ordinarily quantum-paraelectric at ambient temperature, the cause for the electric field-induced distortion wasn’t clear yet. Hanzig et al. suggested that the structural distortion is ascribed to field-driven redistribution of VO$_x$s, accompanied by formation of a polar phase in STO. Meyer et al. proposed that the formation of SrO (SrTiO$_3$)$_n$ Ruddlesden-Popper phases has introduced stress which expands the lattice. Hence the kinetics of the field-induced lattice distortions needs to be analyzed clearly.

Moreover, in our work, it was firstly found that the above field-induced distortion effect was enhanced greatly by simultaneously applied visible light illumination and $V_G$. The unique combined effect of electric field and light raises new questions as to the influence of different light wavelengths on the deformations and the underlying mechanism for the new effect. Here, the detailed evolution process of the lattice distortion in STO under different light wavelengths from 532 nm to 980 nm has been researched. It was found that the lattice distorted phase formed much more rapidly and significantly under short wavelength light (i.e. 532 nm) than in the other cases. By modeling the kinetic diffusion of VO$_x$, it is confirmed that the field-induced distortion is ascribed to the synchronous electromigration of VO$_x$s, and photo-excitation has facilitated the distortion by speeding up the diffusion of VO$_x$. The present work provides a novel way to tune the kinetics of VO$_x$s in STO, to further modulate the properties of above films and STO-based hetero-interface effectively.

II. EXPERIMENTS

Commercial (001)-orientated STO single crystal was sandwiched between two 30-nm-thick Ti electrode layers deposited through magnetron sputtering. The schematic experimental setup is shown in Fig. 1(a). A gate voltage ($V_G$) up to ±400 V was applied to STO. Visible light (wavelength

![FIG. 1. (a) A sketch of the experimental set-up for the structural measurements by XRD. (b) XRD of the 002 reflection of STO under $V_G$ was fitted by Gaussian function. RSMs of the 103 reflections measured under (c) $V_G = 0$ V, (d) $V_G = 400$ V, (e) $V_G = 400$ V with light illumination of P=30 mW (λ=532 nm).](image)
of 532 nm \sim 980 \text{ nm}, \text{ power of } \sim 30 \text{ mW}) \text{ was focused on the top-layer of STO, and } \textit{in situ} \text{ x-ray diffraction (XRD) was conducted simultaneously to characterize the top-layer structure, including symmetrical 002 reflection and reciprocal space mapping (RSM) of the asymmetric 103 reflection. All of the experiments were conducted at RT.}

\section{RESULTS AND DISCUSSIONS}

\subsection{Electric field-induced structural expansion}

The structure of (001)-STO under $V_G$ was firstly studied. The typical XRD spectra of 002 Bragg reflection of STO under $V_G = 400 \text{ V}$ over 30 min was presented in Fig. 1(b). The 002 main peak deviated to little angle forming an abnormal shoulder, implying an appearance of distortion with a larger lattice parameter than that of STO (3.905 Å) in the direction of out-of-plane $c$-[001] axis. Two distinctly characteristic peaks were obtained from the spectra through Gaussian fitting, where peak$_1$ and peak$_2$ correspond to the normal bulk STO and deformed volumes, respectively. Surprisingly, no visible change was observed on the XRD spectra when bias was switched ($V_G < 0$), indicating that the lattice distortions occur only in the near-surface region underneath anode.

Similar behaviors of the asymmetric 103 reflections were also detected. Figs. 1(c)–(e) are the RSMs of asymmetric 103 reflections of STO, which provide information on in-plane lattice structure. Compared with Fig. 1(c), downward tail of the 103 reflection was shown in Fig. 1(d) under $V_G = 400 \text{ V}$, indicating an elongated $c$-[001] axis but unchanged $a$- or $b$-axis in-plane ([100] or [010] direction). Thus there is no transversal contraction but an out-of-plane lattice spacing expansion, causing a novel change of unit cell volume in cubic STO. It’s very interesting and needs to be further studied. The above results suggest that the application of $V_G$ will yield a sizable lattice expansion in STO along the direction parallel to the electric field.

The experiment was further extended by monitoring the time evolution of the shoulder of STO 002 reflections under $V_G$. As shown in Fig. 2(a), the lattice distortion phases go through a developing process with time, starts from the initial state (black line), grows gradually upon applying $V_G$, and eventually reaches steady state. From the 2θ angle of peak$_2$ marked in Fig. 1(b) which represents the deformed volumes, the elongated lattice parameter $c$ of the deformed layer can be derived. Fig. 2(b) shows that the lattice parameter $c$ grows continually and linearly with time, and saturates to a constant after 40 min. To our knowledge, neither ferroelectricity, piezoelectricity, nor flexoelectricity are allowed in STO at RT. The electric field-induced structural expansion cannot be ascribed to electrostrictive effect, since no distortion occurs at the side underneath cathode. During the experiment, the electric current flowing through STO was lower than 10 nA, excluding the Joule heating effect as well.

As mentioned, the positively charged $\text{VO}_5$ are the most mobile ionic specie in STO. Under the external electric field, $V_{05}$ will drift from anode to cathode forming a current density $j_E$, following the equation: \cite{16,23}

$$j_E = \mu n_{\text{vo}} E,$$  \hspace{1cm} (1)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_2.png}
\caption{(a) The time evolution of the abnormal shoulder of 002 reflections measured immediately after applying a bias of $V_G \sim 400 \text{ V}$, and (b) the corresponding distorted lattice parameter deduced.}
\end{figure}
where $n_{vo}$ is the $V_{OS}$ concentration, $\mu$ is the mobility of $V_{OS}$, $E$ is electric field. Adopting $n_{vo} \sim 10^{18}$ cm$^{-3}$, $\mu \sim 1 \times 10^{-13}$ cm$^2$/V$s$, $E \sim 8 \times 10^3$ V/cm, $j_E$ is calculated to be $\sim 1.28 \times 10^{-10}$ A/cm$^2$.

The electromigration of $V_{OS}$ establishes a vacancy depletion region near the anode with thickness, which is estimated to be equal to the maximum drift distance $d$ as:

$$d = t \mu E,$$

where $t$ is the mean depletion time for $V_{OS}$ to drift within a distance $d$.

The depth of the distorted lattice region beneath the surface is estimated to be $10 \text{ nm} \sim 20 \text{ nm}$ by Meyer.$^{16}$ Supposing that $d$ is comparable to the depth of the distortion regions to be $\sim 20$ nm, which is verified to be reasonable, froms Eq. (2), the characteristic time $t$ for $V_{OS}$ to deplete a layer of $d = 20$ nm thickness by the field-driven current is obtained as $t = d / \mu E \approx 2500$ s (40 min).

According to Fig. 2(b), the time for appearance of the steady distorted state is about 40 min, which is in good agreement with the depletion time for $V_{OS}$ electromigration estimated above. In addition, results of the leakage current of circuit carried by $V_{OS}$ (not shown here)$^{22}$ also verify the corresponding and synchronization between the distortion process and evolution of leakage current. Therefore, it is concluded that the distortion of STO is mostly induced by electromigration of $V_{OS}$ driven by electric field.$^{17,24}$

**B. Electric field and visible-light induced structural expansion**

Compared with the distortion induced by $V_G$ in Fig. 1(d), a much more severe structural expansion along [001] axis was observed on the RSM of 103 reflection (Fig. 1(e)) when imposing additional light illumination on STO, indicating that the field-induced distortion effect is enhanced greatly by light illumination. To further investigate the novel light effect, the development of STO 002 reflections was measured with time under different light wavelengths (0 nm, 980 nm, 780 nm, 650 nm, 532 nm) and constant $V_G$. According to Fig. 3, the lattice distorted shoulder grows much more rapidly under short light wavelength (Fig. 3(d)) than in other cases (Figs. 3(a)–(c)) through comparing the peak broadening at the same time. In Fig. 3(e), the evolution of $c$ over time under different light wavelengths was summarized. The light effect is evident: without illumination, $c/t$ curves increases slowly even up to 40–60 min. While in the presence of light, $c/t$ curves rises rapidly with time, almost steeply at $\lambda \sim 532$ nm and saturates within 30 min. Not only the slope of $c/t$ curve but also the maximum elongation $c_{max}$ is greatly dependent on light wavelength, such as for $\lambda = 532$ nm or 980 nm, $c_{max}$ increases from 3.905 Å in initial state (0 V) to 3.920 Å or 3.915 Å, obtaining the distortion degree of $\Delta c/c = 0.38\%$ or 0.26\% respectively. These results strongly demonstrate that illumination of visible light markedly accelerates the electric field-induced distortion and enhances the distortion degree by different wavelengths.

A further issue to be addressed is the underlying mechanism for the light effect on the lattice deformation, especially the pronounced effect of short-wavelength light (i. e. 532 nm). The light

![FIG. 3. Development of the shoulder beside STO 002 reflection with time under different light wavelengths (P=30 mW) (a) 0 nm, (b) 780 nm, (c) 650 nm, (d) 532 nm and constant $V_G$. (e) The time development of distorted lattice parameter deduced.](image-url)
structural deformation in STO was induced by the electromigration of V far beyond the phonon energy (effect could not be a thermal activation effect, as the photon energy of different light wavelengths of photons should fascinate the distortion process through mobilizing V. Declared that singly ionized state with one deeply trapped electron could be favorable for V in the conduction band about . 0.6 eV. It is generally believed that V are doubly ionized and exist in the form of isolated V:s at high temperature. At low temperature, however, Moos et al.26 declared that singly ionized state with one deeply trapped electron could be favorable for V (i.e., V:s) when vacancy content is high. Further studies found that singly ionized V prefers to form V-O-complexes of Ti3+-V or V-O-Ti-V chain by sharing the electrons with two adjacent Ti ions, and forms in-gap states underneath conduction band ~1 eV. On the basis of the above analyses, we present the scenario for the light illumination effect. Photon excites the shared electrons of V-O-complexes and breaks down the V-O-complexes into isolated V:s, producing extra mobile V:s defects, which is much more susceptible to external field, and speeding up the diffusion of V:s. In this manner, light has promoted formation of lattice structural deformation macroscopically, and the light wavelength dependence is understandable.

IV. CONCLUSIONS

In summary, a dramatic lattice deformation in STO induced by electric field at RT was observed. Most notably, it was found that the above distortion is enhanced greatly by simultaneously applying visible light illumination and V, which is effectively tuned by different light wavelengths. By monitoring the detailed evolution process of the deformed structure and modeling the kinetic diffusion of V:s in STO, it was confirmed that the field-induced distortion is ascribed to the synchronous electromigration of V:s, and photo-excitation has facilitated this distortion by exciting in-gap V-O-complexes states to generate extra carriers and remarkably speeding up the diffusion of V:s.

Considering that STO is quantum paraelectrics, our works are valuable finding a unique method to tune its lattice structure at RT through modulating the kinetics of V:s. These results allow us to further design and tune the properties of above films as well as STO-based hetero-interface in RT range, towards exploring the emergent phenomenon at oxide system.14

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