In situ TEM studies of oxygen vacancy migration for electrically induced resistance change effect in cerium oxides

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1. Introduction

Recently, a large number of insulating oxides with resistance switching effect have attracted extensive interest, ranging from simple binary oxides of rutile, fluorite and related structures (e.g., TiO₂ (Yang et al., 2008), CeO₂ (Fors et al., 2005)), to the complex three-, four- and five-component perovskites and related structures (e.g., SrTiO₃ (Szot et al., 2006), Cr-doped SrTiO₃ (Beck et al., 2000) and Pr₁₋ₓCaₓMnO₃ (Liu et al., 2000)). Devices based on these oxides are very promising for next generation memory devices. However, the microscopic dynamic process of the resistance change is still elusive. Here, we use in situ transmission electron microscopy method to study the role of oxygen vacancies for the resistance switching effect in cerium oxides. The structure change during oxygen vacancy migration in CeO₂ induced by electric field was in situ imaged inside high-resolution transmission electron microscope, which gives a direct evidence for oxygen migration mechanism for the microscopic origin of resistance change effect in CeO₂. Our results have implications for understanding the nature of resistance change in metal oxides with mixed valence cations, such as fluorite, rutile and perovskite oxides.

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that the generation and the destruction of the conducting path are associated with the oxygen migration.

Here, we report on a direct evidence for oxygen migration mechanism for electrically induced resistance change effect in Au/CeO$_2$/Nb-STO heterostructures by using in situ TEM method. We have directly observed the dynamic process of resistance switching operation accompanying with oxygen migration in the cerium oxides at atomic level. Based on these observations, it is found that the formation of path of neighboring oxygen vacancies could be the origin of the resistance switching effect in cerium oxides. Our results may also be extended to other oxide systems that have mixed valence cations.

2. Experiments

Experimentally, epitaxial CeO$_2$ films are grown by pulsed-laser deposition (PLD) on Nb-STO (1 0 0) substrates (0.7% Nb doped SrTiO$_3$), with different thicknesses ranging from 20 to 200 nm. The growth direction of CeO$_2$ film is [1 0 0] (data not shown here). We first fabricated Au electrodes on top of the CeO$_2$ film to form the sandwiched structures using a standard photolithographic technique and magnetron sputtering. Typical $I$–$V$ characteristics of Au/CeO$_2$/Nb-STO device are shown in Fig. 1. The loops, $0 \to V_{\text{max}} \to 0 \to -V_{\text{max}} \to 0$, were demonstrated and they have high degree of repeatability. Positive voltages are corresponding to positive biases applied on the gold electrode, while the bottom electrode (metallic Nb-STO has good electric conductivity, as shown in inset of Fig. 1) was grounded. To show the resistance switching effect, the applied voltages were swept from a HRS (curve 1) until the decrease of the resistance after a positive bias threshold ($\sim +1.5$ V). This means the conducting path was generated between the electrodes. The device would stay at the LRS even bias decrease of the resistance after a positive bias threshold ($\sim +1.5$ V). The inset: TEM image of metal-tip/CeO$_2$/Nb-STO structure.

To explore the microscopic dynamic process for the resistance switching effect, we first made sample Au/CeO$_2$/Nb-STO junction for in situ TEM measurements. The electron transparent cross-section samples were prepared by conventional mechanical polishing and argon ion milling to a thickness of around 30–60 nm. Then a bias voltage was applied across the sandwiched junction inside a TEM (JOEL 2010F microscope with vacuum $2 \times 10^{-5}$ Pa at room temperature) as illustrated in Fig. 2a. A sharp gold tip driven by piezo-controller moved forward to contact the CeO$_2$ film of TEM-ready cross-section sample which loaded on a home-made specimen holder. For electrical measurements, the TEM electron beam was blanked out. The loop of in situ $I$–$V$ sweep also displayed the resistance switching effect, as shown in Fig. 2b.

3. Results and discussion

3.1. Structure

Fig. 3a and b show the high-resolution TEM image and the electron diffraction pattern detected along the (1 1 0) axis before applying electric field, and Fig. 3c displays the solid sphere model. By applying a bias of 1 V to the junction for a few seconds [the device is still at the HRS], both the TEM image and the diffraction pattern remained unchanged. Then we applied a bias of 5 V to make sure the device was at LRS (electric field $E \sim 7.5 \times 10^7$ V/m), as shown in Fig. 3d, the structural transition took place with the appearance of wavy structures in the high-resolution TEM image. The extra diffraction spots were also observed (Fig. 3e). These superlattice reflections indicate that oxygen anions had been removed from the ceria film and the introduced oxygen vacancies were ordered as CeO$_2$ by the applied electric field (Wang and Kang, 1998; Sharma et al., 2004; Crozier et al., 2008). The structure model for the process of forming ordered oxygen vacancies is represented in Fig. 3f, where the rectangle shows the unit cell of sesqui-oxide of the cerium oxide in the (1 1 0) orientation resulted by ordered oxygen vacancies.
3.2. EELS

Because oxygen vacancy migration is accompanied with the valence change in oxides, to gain further evidence of the oxygen vacancy diffusion process, we have performed electron energy loss spectroscopy (EELS) experiments on the samples to show the change of chemical valence of the Ce ions. When applying a bias of 5 V, a reversal in the intensity of Ce M45-white lines was observed [Fig. 4a and b], suggesting that Ce has undergone a transition from 4+ to 3+ oxide state (Garvie and Buseck, 1999). The disappearance of the shoulder (indicated by arrowhead in Fig. 4a) suggests that the strong covalence hybridization between Ce 4f and O 2p states was vanished under the applied electric field. In fact, the influence of TEM electron beam irradiation can be ruled out in this study. We found that significant change in the white-line ratio occur by dose more than 1.8 × 10^6 electron/A^2 from a sample with about 35 nm thickness at the edge region, and in our in situ TEM experiments, we kept the electron dose lower than 3 × 10^5 electron/A^2, which should ensure that our measured changes in Ce oxidation state under the electric field are not caused by electron irradiation.

![Figure 4](image1.png)

**Fig. 4.** (a) EEL spectra of Ce-M edge at zero bias. (b) A reversal in the intensity of Ce M45 white lines was observed; and the shoulder indicated by arrow in (a) disappeared after applying the electric field.

3.3. Mechanism

The cerium oxide is facile to create anion deficiency because the oxygen anions of fluorite structure are very active, and can move though the lattice relatively easily (Trovarelli, 1996). In the presence of electric field (positive bias on the Au electrode), the oxygen anions (O^{2-}) will move toward the anode where they have taken electron and evolve oxygen gas. Concurrently, the oxygen vacancies will diffuse into the crystal interior, and then assembled near the cathode to reduce CeO_2 to Ce_2O_3. For stoichiometric CeO_2, which is an insulator with band gap 6 eV (Koelling et al., 1983), the oxygen p band has two extra electrons provided by Ce atom and there is a narrow empty Ce f band in the gap between the valence and conducting bands, as shown in Fig. 5. When an oxygen atom is leaving its lattice position, the two electrons may occupy the lowest possible empty state that is the f band of nearest Ce atoms, tuning Ce4+ to Ce3+ with electron hopping (Skorodumova et al., 2002). It means that the oxygen migration process simultaneously accompanies with the ionic and electron conductivity. The presence of Ce3+ ions (or oxygen vacancies) enhances the local...
electron conductivity of the cerium oxide (band gap of CeO₂ is about 2.4 eV (Prokofiev et al., 1996)). In the electric field, if the domain of Ce³⁺ ions bridged the two electrodes, conductive paths will be formed and the device will be switched from HRS to LRS.

In the case of a sufficient negative voltage on the Au electrode, the oxygen anions are driven to move toward the interface of CeO₂/Nb-STO (anode). As we know, the CeO₂ layer is blanket film and epitaxial growth on the STO, so the oxygen anions will be blocked by interface, and cannot be released as easily as at the surface (at the metal electrode). The cerium oxide film near the interface would likely form the stoichiometric dioxide (CeO₂) and turn off the conducting path, and hence the high resistance state (HRS). At the same time, the vacancies migrate to the surface (at metal electrode). Oxygen gas will diffuse into the metal/oxide interface layer due to that the density of the vacancies near the surface region is higher than the equilibrium concentration. Fig. 6 shows the vacancies could be recovered and the wave sweeping disappeared when ~ 7 V bias applied to the gold tip. It is worthy to point out that the residual oxygen in the chamber of the TEM is enough to recover the vacancies even under the vacuum of approximately 10⁻⁵ Pa (Bevan and Kordis, 1964).

Moreover, the communication between oxygen anions and gas oxygen is also found in a number of other oxides (Waser and Aono, 2007). For instance, Szot et al. (2006) discovered that gas bubbles had developed under the anode when the electric field was applied to single crystalline SrTiO₃. When an oxygen atom moves away from their lattice positions, the two electrons will localize on cerium atoms (transition from Ce⁴⁺ to Ce³⁺). Thus, the electron conductivity is enhanced.

**Fig. 5.** Left: the energy band of perfect CeO₂, whose band gap is 6 eV (Koelling et al., 1983). There is a narrow empty Ce 4f band in the gap. Right: the energy band of CeO₂₋. When an oxygen atom moves away from their lattice positions, the two electrons will localize on cerium atoms (transition from Ce⁴⁺ to Ce³⁺). Thus, the electron conductivity is enhanced.

**Fig. 6.** The TEM image after a voltage of ~ 7 V was applied between the gold tip and Nb-STO. The white line (left) indicates the interface of the CeO₂/Nb-STO.

**4. Conclusion**

In summary, we have studied the role of oxygen vacancy migration for the electrically induced resistance effect in Au/CeO₂/Nb-STO junctions by using in situ TEM method. For the first time, the dynamic process of resistance switching accompanying with the oxygen migration has been directly imaged at atomic level. Our in situ TEM studies unambiguously demonstrate that the migration of the oxygen vacancies is responsible for the resistance switching effect in cerium oxides. This mechanism might provide new insight on the physical and chemical nature of resistance switching effect for the oxide systems which have the properties of creating anion deficiency, such as fluorite oxides, rutile and perovskite oxides.

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**References**


