



# On the oxidation of CaF<sub>2</sub> in transmission electron microscope

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## ABSTRACT

Electron stimulated oxidation of CaF<sub>2</sub> in transmission electron microscope has been thoroughly studied using various electron microscopy techniques, including imaging, electron diffraction and electron energy-loss spectroscopy. It found that the electron irradiation induced CaO locate on the edge of specimen. The oxidation process is associated with desorption of F by electron irradiation, and originates from O impurities in the specimen. Driven by electric field produced by electron irradiation, the O ions inside bulk diffuse to the edge region, occupying the interstitials of metallized Ca lattice. Therefore, the accumulation of O along the edge of specimen results in forming CaO.

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## 1. Introduction

(Scanning) transmission electron microscopy ((S)TEM) is a unique and powerful experimental tool, which has been widely used to probe structural, physical and chemical properties of materials at atomic resolution (Williams and Barry, 1996). It uses high energy (e.g., 80–400 keV) and high intense (e.g., 10–10<sup>6</sup> A/cm<sup>2</sup>) electron beam under ultrahigh vacuum condition (~10<sup>-7</sup>–10<sup>-9</sup> Torr). Although the specimen suitable for (S)TEM study is very thin (e.g., 10–100 nm) and some of incident electrons pass through the specimen unscattered, a large portion of incident electrons lose energy to excite atom electrons through inelastic scattering, resulting in excitations and ionizations of atoms (Egerton et al., 2006). Therefore, (S)TEM is also a destructive experimental tool. The specimen under investigation may suffer severe radiation damage. The usual damage phenomena vary from minor changes, such as introducing defects (Hobbs, 1979) and driving atom migration (Jiang and Spence, 2010), to drastic phase transitions (e.g., from crystal to amorphous (Hobbs and Pascucci, 1980)). Perhaps the most common damage phenomenon, which may be observed in all specimens, is the loss of single or multiple components at the same or different rates, into vacuum due to surface sputtering (Egerton et al., 2006) or lateral ejection by electric field (Jiang et al., 2002, 2003a). In addition, it has also been noticed that electron irradiation can stimulate oxidation process in TEM, although not intentionally (Smith and Patford-Long, 1987; Nouruzi-Khorasani et al., 1981; Petford-Long and Smith, 1986; Milne and Fan, 1987; Chen et al., 1996; Olivier, 1980; Olivier et al., 1980; Soonckindt et al., 1985). Usually, oxidation

only occurred for regions at the edge of specimen which had been exposed to an electron beam for some time (Smith and Patford-Long, 1987). In the early era, poor vacuum in the TEM column was blamed for the unwanted oxidation (Smith and Patford-Long, 1987; Nouruzi-Khorasani et al., 1981; Petford-Long and Smith, 1986). The contamination of O-related compounds (water) has also been suggested as the oxygen source, with which the Al<sub>2</sub>O<sub>3</sub> was formed due to the reaction of AlF<sub>3</sub> under electron irradiation (Chen et al., 1996). If oxygen is from extrinsic sources, such as poor vacuum and/or the specimen contamination, the oxidation under electron irradiation could be reduced or even eliminated with the advanced microscopy and sample preparation techniques. However, it has also been reported that in the ultrahigh vacuum STEM (UHV-VG501), Auger electron spectroscopy (AES) showed an increase of oxygen signal from the irradiated area in the InP (Milne and Fan, 1987). Electron stimulated oxidation of InP was even observed with partial oxygen pressure as low as 10<sup>-10</sup> Torr (Olivier, 1980; Olivier et al., 1980). The influence of sample preparation has also been excluded, since electron irradiation induced oxygen signals could be observed in all InP samples regardless their preparation methods (HF etched surface, cleaved in air, and AES UHV cleaved) (Soonckindt et al., 1985).

Oxygen is readily incorporated into the bulk during material growth and it is very difficult to avoid this contamination or to remove contaminants after growth (Molchanov et al., 2005). Oxygen also penetrates into the crystal upon exposure to ambient air (Jacobs and Ong, 1980). Therefore, it is possible that the electron stimulated oxidation may also be due to O impurities in materials. In some cases, although a small amount of oxygen impurity may not affect the properties of materials, the accumulation of O at the edge of the specimen in (S)TEM could affect the accuracy of quantitative imaging and microanalysis, especially if the single atom sensitivity is concerned. This is because both high resolution atomic

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imaging and microanalysis require thin specimen. Therefore, understanding of the mechanism for electron stimulated oxidation process in ultrahigh vacuum (S)TEM is very important to electron microscopists.

Here we reinvestigate the oxidation phenomenon in the modern (S)TEM with ultrahigh vacuum, using  $\text{CaF}_2$  as a model specimen.  $\text{CaF}_2$  has a wide range of applications and fundamental interest (Druon et al., 2011). Oxygen is a major impurity in  $\text{CaF}_2$ , which leads to formation of color centers (Mysovsky et al., 2005). Nowadays, the oxygen contamination in  $\text{CaF}_2$  has still been considered as one of the major problems for producing high purity crystal for optical applications (Mouhovski, 2007). Radiation effect in  $\text{CaF}_2$  has also attracted much attention. Irradiation induced defects (color centers) and metallization have been intensively investigated (Bennewitz et al., 1999). The transition from  $\text{CaF}_2$  to CaO during electron irradiation has also been observed in TEM (Mankiewich et al., 1984; Scheinfein and Isaacson, 1986; Kogure et al., 1998). The oxidation was interpreted as due to the electron-induced radiolysis of  $\text{CaF}_2$  to  $\text{F}_2$  and Ca, the Ca is immediately oxidized by  $\text{O}_2$  and/or O-containing residual gases in vacuum chamber (Mankiewich et al., 1984). However, our recent studies on various metal fluorides, including  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  and  $\text{LaF}_3$ , indicated that the oxidation may be not caused by the residual gases but rather by the O impurities inside the samples. In this study, we carried out comprehensive study of electron stimulated oxidation in  $\text{CaF}_2$ , using techniques including imaging, electron diffraction and electron energy-loss spectroscopy (EELS). The mechanism for oxidation is also thoroughly discussed.

## 2. Experimental and simulations

The  $\text{CaF}_2$  crystals containing O impurity were used in this study (Alfa Aesar). The energy dispersive characteristic X-ray analysis indicated that there are no other measurable impurities but O in the crystal. The composition ratio of O to F was estimated from EELS analysis, which was in between 1/4 and 1/5. Therefore, the chemical formula is approximately  $\text{CaF}_{1.65}\text{O}_{0.35}$ . TEM specimens were prepared by grinding the samples into powders in acetone (purity 99.6%, Thermo Fisher Scientific Inc.), and picking them up using a Cu grid covered with a lacy carbon thin film. The specimens were then immediately transferred into a 200 kV JEOL-2010F (S)TEM equipped with Gatan Enfina electron spectrometer. The pressure in the specimen chamber was about  $2.0 \times 10^{-6}$  Torr. The energy resolution of EELS was 1.0 eV, and the dispersion of the spectrometer was 0.2 eV/channel. The EELS entrance aperture was 1.0 mm in diameter for low-energy loss spectra and 3.0 mm for O K and F K-edge spectra. Low energy-loss spectra were acquired using image mode without objective aperture for not saturating detector, while O K and F K-edge EELS were acquired using diffraction mode for higher count rates.

The accurate electron beam current should be measured with a Faraday cage at the side of the specimens. For convenience, we used the current density readout from the small view screen to approximate beam intensity. Here we ignored the loss of electrons in the path from specimen chamber to the view screen if the specimen was not illuminated by electron beam. The typical current density readout in this study was in range of 10–100 pA/cm<sup>2</sup>, and the magnification was  $10^5$ . Therefore, the estimated current density on specimen was 0.1–1.0 A/cm<sup>2</sup> (C/s cm<sup>2</sup>). It should be pointed out these current densities are almost  $10^6$  magnitudes weaker than the probe used in the aberration corrected STEM (Lupini et al., 2001).

Simulations of F K and O K-edge EELS were performed using the computer code FEFF8, which is based on real-space full multiple scattering theory within the self-consistent muffin-tin potential approximation (Ankudinov et al., 2002). The core-hole effect was

included in the simulations using the final state approximation, in which one core electron was placed in the valence band. The clusters, including 190 atoms, were generated from the crystal structure of  $\text{CaF}_2$ .

## 3. Results

Fig. 1 shows typical changes in electron diffraction during electron irradiation damage of  $\text{CaF}_2$  in TEM. Fig. 1a–c was selected from a time series acquired with a very weak beam of which the current density was about 0.046 C/s cm<sup>2</sup>. Initially, the  $\text{CaF}_2$  crystal was orientated to (0 1 1) direction, as shown in Fig. 1a. The beam illuminated area within the select area (SA) aperture can be considered as a single crystal. After about 1 min of irradiation, several extra diffraction strips occurred, as indicated by white arrows in Fig. 1b. These strips gradually form ring-type patterns and can be indexed by CaO structure. After about 15 min of further irradiation (Fig. 1c), the intensities of these CaO diffraction rings become strong. Other than these rings of CaO, the diffraction patterns in Fig. 1c are exactly the same with that in Fig. 1a.

After Fig. 1c, we acquired a low-loss EELS spectrum from the same area, which is marked as “A” in Fig. 1e. For comparison, an EELS spectrum acquired from a fresh area of the same  $\text{CaF}_2$  sample indicated as “reference” is also plotted in Fig. 1e. In the reference spectrum, the estimated band gap of  $\text{CaF}_2$  is about 11.0 eV, which is consistent with the previous reports (Rubloff, 1972). A sharp peak at 17.5 eV corresponds to the plasmon excitation of valence electrons (Frandon et al., 1972; Saiki et al., 1987). On the lower energy side of the plasmon peak, there are a small bump and other faint features, which correspond to the interband transitions from the fluorine 2p valence band to the unoccupied band (Heaton and Lin, 1980). The strong peak at about 38 eV and several small peaks below are mainly due to the transition from Ca 3p semi-core to unoccupied states, and thus can be approximately assigned to Ca  $M_{23}$ -edge. A small bump around 45 eV corresponds to the transition from F 2s state to unoccupied states.

The main difference between spectrum A and reference is that spectrum A has strong intensities in the band gap region. The band gap energy for the CaO is only about 7.1 eV (Whited et al., 1973). Therefore, the strong intensities below 10 eV observed in spectrum A may be from the CaO. In addition, other defects induced by electron irradiation may also attribute to the intensities in the band gap region (Si et al., 2007). Surprisingly, the bulk plasmon peak of metal Ca was not observed.

According to the previous study, no difference could be observed in the diffractions between Ca and  $\text{CaF}_2$  due to the small difference in their lattice parameters (Kogure et al., 1998). However, this is different from our experiment. After recoding spectrum A (Fig. 1e), the beam density was increased to 0.67 A/cm<sup>2</sup> to irradiate the same area for about 1 min, and then was returned to the previously used 0.046 A/cm<sup>2</sup>. Immediately, the diffraction pattern (Fig. 1d) and EELS spectrum (spectrum B in Fig. 1e) were recorded from the same area. The diffraction rings of CaO did not change significantly, but the reciprocal space distances of diffractions decreases slightly, as shown in Fig. 1f. As we knew, both  $\text{CaF}_2$  and Ca have the same structure, but the unit cell of Ca is slightly larger than that of  $\text{CaF}_2$ , i.e.,  $\Delta a = 0.113 \text{ \AA}$  (Wyckoff, 1963). The difference can well interpret experimental value as shown in Fig. 1f. The metal Ca remains the same crystallographic property as the original  $\text{CaF}_2$ . Correspondingly, the strong bulk plasmon peak (9.0 eV) of metal Ca appears in Fig. 1e. A small peak at 14.5 eV is due to the bulk plasmon excitation of CaO (Yamasaki and Fujiwara, 2002).

It is also noticed that the distribution of CaO is not uniform, but always scatters along the edge of the specimen. As shown in Fig. 2a, the enclosed area is a CaO rich region. Two spots indicated as “on

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