

## Stoichiometry of Nanocrystalline VO<sub>x</sub> Thin Films Determined by Electron Energy Loss Spectroscopy

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Rocksalt-structured vanadium oxide VO<sub>x</sub> ( $x = 0.8 - 1.3$ ) nanocrystal thin films are used in infrared imaging devices due to its high temperature coefficient of resistance (TCR). The stoichiometry of VO<sub>x</sub> is closely related with the defects in the crystalline lattice, which influence the TCR. However, it is very difficult to quantify the stoichiometry of VO<sub>x</sub> by energy-dispersive x-ray spectroscopy because of energy overlap and strong absorption of the low-energy V-L and O-K peaks. In general, electron energy loss spectroscopy (EELS) is useful for determining the stoichiometry and valence of transition metal oxides by using 1) the k-factor method, 2) the ratio of the L<sub>3</sub>/L<sub>2</sub> white line intensities or 3) the normalized white line intensity in reference to the continuum. But for VO<sub>x</sub>, the energy of the O-K edge is very close to that of the V-L edge. Consequently, EELS quantification techniques are still problematic due to difficulty of separating the O-K signal from the V-L signal. The energy loss near edge structure (ELNES) of the oxygen K-edge of vanadium oxides reflects the local density of states (DOS) at the oxygen site and can be taken as “finger print” of the oxidation states [1,2]. Also, there is a relative chemical shift between oxygen K-edge and vanadium L<sub>3</sub> edge caused by systematic change of the V valence [2,3].

Four single-phase vanadium oxides VO, V<sub>2</sub>O<sub>3</sub>, VO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> have been used as standards for EELS. The relative chemical shift was verified (Figs. 1a, 1b). The four standards have similar local symmetry in their crystal structures - VO<sub>6</sub> type octahedron structures around V atom [1], therefore have similar energy levels right above the Fermi level - two t<sub>2g</sub>+e<sub>g</sub> branches in DOS due to the V 3d - O 2p hybridization [1,2]. The change in the ELNES of oxygen K-edge when going from VO to V<sub>2</sub>O<sub>5</sub> (Fig. 1a) is due to the increased contribution from t<sub>2g</sub> peak to oxygen K-edge.

Close comparison of EEL spectra of VO and V<sub>2</sub>O<sub>3</sub> standards (Fig. 1c) reveals also an increased energy “span” ( $\Delta E_2$  in Fig. 1c) of the O pre-edge peak when changing from VO to V<sub>2</sub>O<sub>3</sub>. This is because with decreasing vanadium valence (going from V<sub>2</sub>O<sub>3</sub> to VO), the DOS above the Fermi level also decreases; thus it appears that the DOS of the t<sub>2g</sub> energy level is “truncated” by the Fermi level [1]. As the result, the energy “span” of t<sub>2g</sub>+e<sub>g</sub> branches decreases and energy width of O pre-edge peak decreases.

Fig. 2a shows a comparison of EEL spectra from an ion-beam sputtered VO<sub>x</sub> nanocrystalline thin film with that of VO and V<sub>2</sub>O<sub>3</sub> standards and indicates that VO<sub>x</sub> thin films have both a  $\Delta E_1$  and a  $\Delta E_2$  very similar to those of the VO standard. This reveals that the VO<sub>x</sub> nanocrystal thin film has stoichiometry very close to VO (V<sup>2+</sup>). Additional EELS data reveals that the same VO<sub>x</sub> thin film has spatial inhomogeneity in the stoichiometry. Fig. 2b shows a comparison of EEL spectra from different areas in the VO<sub>x</sub> thin film. The two spectra show differences both in chemical shift ( $\Delta E_1$ ) and in the energy width of O pre-edge peak ( $\Delta E_2$ ), corresponding to VO (area 1) and V<sub>2</sub>O<sub>3</sub> (area 2), respectively. Also, the V-L<sub>3</sub>, L<sub>2</sub> peaks exhibit broadening in the spectra from “area 2” suggesting

that the electron beam had passed through an area with overlapping of VO and V<sub>2</sub>O<sub>3</sub> type stoichiometries in the sample. Structural models correlated with local high V vacancy concentration to explain observed stoichiometry inhomogeneity will be discussed.

## References

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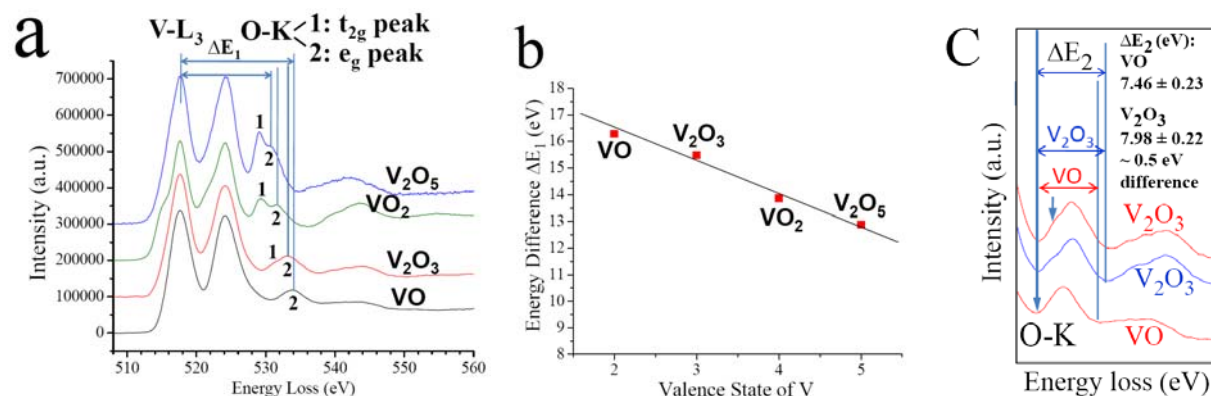


Fig. 1. (a) EEL spectra of vanadium oxides standards showing relative chemical shift (decreased  $\Delta E_1$  when going from VO to V<sub>2</sub>O<sub>5</sub>) between V-L<sub>3</sub> edge and O-K edge (e<sub>g</sub> peak as reference). (b) A plot for  $\Delta E_1$  for 4 standards in Fig. 1a. (c) EEL spectra of O-K edge of VO and V<sub>2</sub>O<sub>3</sub> standards, aligned to the minima before the O t<sub>2g</sub> peak, showing increased energy “span” ( $\Delta E_2$ ) of the O pre-edge peak for V<sub>2</sub>O<sub>3</sub> standard. The small vertical blue arrow indicates a small shoulder for V<sub>2</sub>O<sub>3</sub> from the contribution of the t<sub>2g</sub> peak.

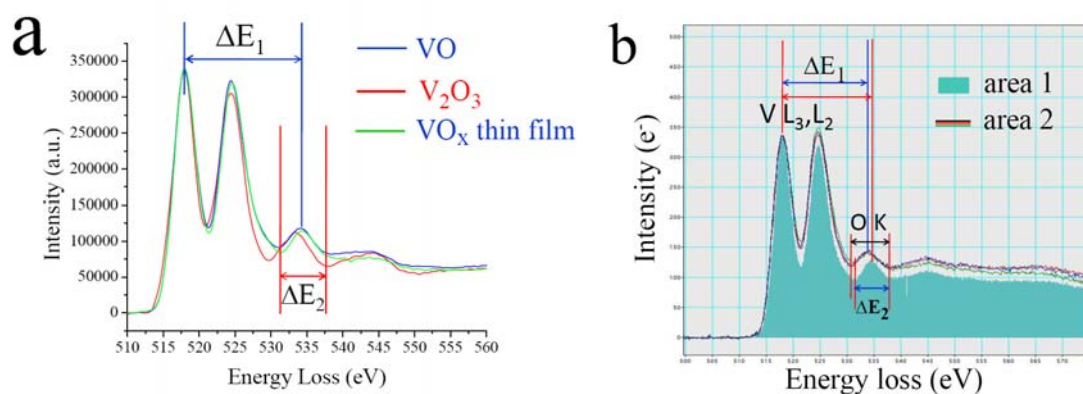


Fig. 2. (a) Comparison of EEL spectra of a VO<sub>x</sub> nanocrystal thin film with that of VO and V<sub>2</sub>O<sub>3</sub> standards, indicating that the VO<sub>x</sub> thin film has stoichiometry very close to VO. (b) Comparison of two types of typical EEL spectra from different areas in VO<sub>x</sub> thin film. The two spectra show differences both in chemical shift ( $\Delta E_1$ ) and energy width of O pre-edge peak ( $\Delta E_2$ ). Also, the V-L<sub>3</sub>, L<sub>2</sub> peaks exhibit broadening for the spectra from “area 2”.