doi:10.1017/S1431927610060708
Microsc. Microanal. 16 (Suppl 2), 2010

Micro-Twinned VO_x Nanocrystalline Film and Hopping Conduction

J. Li,[a] B. D. Gauntt,[b] N. J. Podraza[c], T.N. Jackson[c] and E.C. Dickey[a,b]

[a] Materials Research Institute, Pennsylvania State University, University Park, PA 16802
[b] Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802
[c] Department of Electrical Engineering, Pennsylvania State University, University Park, PA 16802

Rocksalt-structured vanadium oxide VO_x nanocrystalline thin films are used in infrared imaging devices due to their high temperature coefficient of resistance (TCR). The electrical properties of VO_x thin films are closely related to their microstructure and defect structure. It has been found in a series of ion beam sputtered VO_x thin films that the conductivity increases with increasing film thickness (Fig. 1a). Cross-sectional transmission electron microscopy (TEM) was performed to understand the variation of resistivity with film thickness. The results indicate that there are two distinct regions in the films: f.c.c. rocksalt-structured grains containing micro-twins with sub-nanometer twin spacing and regions composed of a mixture of amorphous and f.c.c. rocksalt-structured nanocrystalline VO_x without the micro-twin structure. It has been found that the micro-twinned nanocrystallites nucleated at a film thickness of ~20 nm from the more disordered amorphous+nanocrystalline matrix, then evolved with increasing thickness of the film, resulting in cone shaped micro-twinned nanocrystals (Fig. 1b). Thus, the volume fraction of the micro-twinned nanocrystals grows preferentially over the surrounding material and thus increases with film thickness. Fig. 1c is SAED pattern of the micro-twinned nanocrystals, showing typical features of SAED of microtwins [1].

The stoichiometry of the VO_x micro-twins has been analyzed by energy electron loss spectroscopy (EELS) and compared to VO and V_2O_3 standards, see Fig. 2a. Variations of two characteristic features were analyzed: 1) the chemical shift of oxygen K-edge (e_g peak) relative to vanadium L_3 edge (ΔE_1) and 2) the width of the oxygen pre-edge peak (ΔE_2), which is sensitive to the density of state (DOS) directly above the Fermi level [2]. The comparisons reveal that the oxygen K-edge of the VO_x microtwins has an energy shift (ΔE_1) towards the energy of that of the V_2O_3 compared to VO_x nanocrystals without micro-twin features. The width of the oxygen pre-edge peak (ΔE_2) is also broad like that from V_2O_3. These changes indicate that the VO_x micro-twinned regions are able to accommodate a much larger degree of nonstoichiometry (ascribed to vanadium vacancies [3]) relative to the untwined regions.

The increase in the effective volume fraction of the nanocrystals with increasing film thickness is believed to be responsible for the decrease in resistivity with increasing film thickness. F.c.c. VO_x has been shown to exhibit conduction via the variable range hopping mechanism [4]; the charge carriers are either electrons or holes that hop from V^{2+} and V^{3+} sites. A structural model based on nonstoichiometric VO_x micro-twinned nanocrystals has been proposed (Fig. 2b) to explain how the micro-twinned structure impacts hopping conduction. As is found in other material systems, twin boundaries can accommodate nonstoichiometry [5]. In the Fig. 2b, it is assumed that V^{3+} is present at the twin boundary while the cations in the regions between the twin boundaries are predominately V^{2+}.

References
[1] J. Li, B. D. Gauntt, E. C. Dickey, submitted.
[2] C. Hebert et al., *Eur. Phys. J.* B 28 (2002) 407.
[3] J. B. Goodenough, *Physical Review B* 5 (1972) 2764.
[4] A. D. Rata, *Physical Review B* 69 (2004) 075404.
[5] A. Recnik, J. Bruley, W. Mader, et al., *Philos. Mag. B* 70 (1994) 1021.
[6] This research was sponsored by the U.S. Army Research Office and U.S. Army Research Laboratory under Cooperative Agreement Number W911NF-0-2-0026.

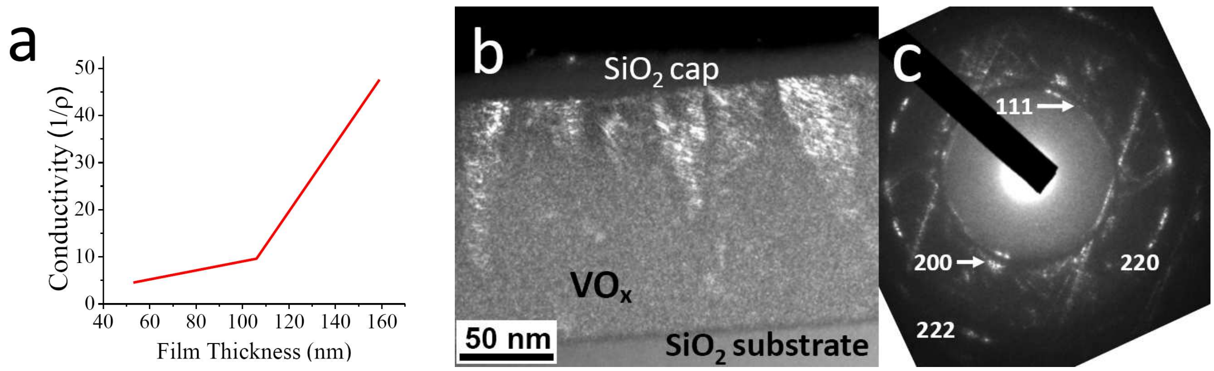

Fig. 1. (a) Increased conductivity with increasing film thickness (ρ: resistivity). (b) TEM DF image of VO_x film (cross section), showing microtwinned nanocrystals with cone shape. (c) SAED pattern of microtwinned nanocrystals, showing fine structure characteristic of the microtwins.

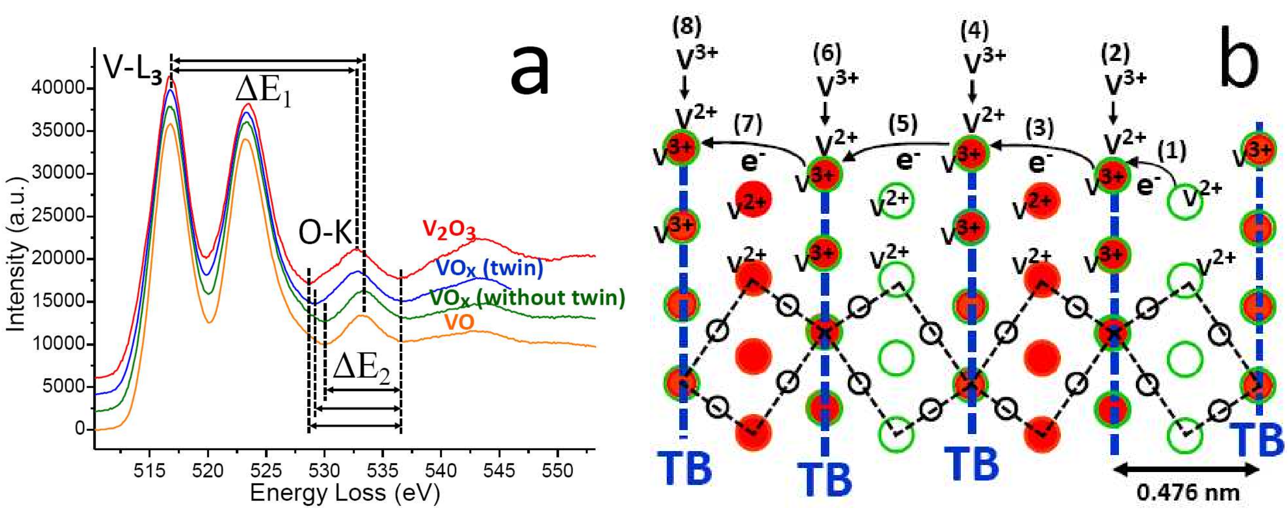

Fig. 2. (a) EEL spectra of VO_x film (for microtwins and nanocrystals without twin feature) and VO, V_2O_3 standards. (b) A structure model ($[01\bar{1}]$ projection) based on f.c.c. rocksalt-structured, micro-twinned VO_x nanocrystals with nonstoichiometry, showing that the period TB [(111) plane] can act as a chain to allow the electrons hopping from V^{2+} to V^{3+} to be easier.