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Discovery of nanoscale reduced surfaces and interfaces in VO_2 thin films as a unique case of prewetting

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VO_2 thin films grown on SiO_x/Si substrates have been characterized at the sub-nanometer level by Cs-corrected scanning transmission electron microscopy along with electron energy loss spectroscopy. Reduced transitional regions of 2–3 nm thick were found at both the surface and the interface, where the vanadium valence progressively changes from +4 to +2. The formation of these nanometer-thick surficial and interfacial layers can be interpreted as a unique case of prewetting, and it explains the degradation of metal-to-insulator transition properties in VO_2 thin films.

Keywords: VO_2 thin film; Prewetting; Electron energy loss spectroscopy (EELS); Surface structure; Interface structure

VO_2 exhibits a metal-to-insulator transition (MIT) near room-temperature (68 °C), which causes dramatic changes in both electrical and optical properties [1]. During this transition, the crystal structure of VO_2 transforms from the high-temperature tetragonal rutile phase ($P4_2/mnm$) into the low-temperature monoclinic phase ($P2_1/c$) [2–4]. This transition can be used for various applications, such as thermochromic "smart window" coatings [5,6], memory devices [7,8] and ultrafast switches [9–11]. The binary vanadium–oxygen system consists of four primary oxide phases – VO, V_2O_3, VO_2 and V_2O_5 – as well as two series of the homologous mixed-valence oxides known as the Wadsley ($V_{2n}O_{5n-1}$) and Magnéli phases (V_nO_{2n-1}) [12,13]. These competing phases can be formed during the film deposition process, and can broaden the phase transition, reduce the transition amplitude, and lower the transition temperature [13,14]. Thus, maintaining the stoichiometric VO_2 single phase is crucial. Moreover, surfaces and interfaces in VO_2 can introduce chemical inhomogeneity to affect the MIT behavior. By using atomic resolution electron energy-loss spectroscopy (EELS) analysis, an interfacial V_2O_3-like transition layer was revealed in a well-crystallized VO_2 film grown epitaxially on a sapphire substrate [15]. The determination of the V oxidation states is largely owing to the EELS near-edge structures, which are very sensitive to the chemical environments [15–17]. This study is motivated by the critical need to perform a structural and chemical characterization of VO_2 film deposited on silicon substrate, which is technically more useful than the previous study on the VO_2/sapphire for understanding the MIT properties.

In this study, a single-phase VO_2 film deposited on such a SiO_x/Si substrate was investigated by bright-field (BF) imaging, high-angle annular dark-field (HAADF) imaging and EELS analysis in a Cs-corrected scanning

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transition electron microscope (STEM). Transition layers of 2–3 nm thick with continuous reduction are found at both the surface and the interface, the formation of which can be explained as a unique case of prewetting using a modified Cahn diffuse-interface model [18].

The VO_2 film was deposited by reactive magnetron sputtering on the Si substrate with a ~3 nm thick amorphous native oxide (SiO_x) layer on the top of it (SiO_x/Si). A pure V sputtering target was used while the Ar and O_2 gases were introduced with the required flow ratio of 2.7% for O_2 (O_2 flow rate/total flow rate). The substrate temperature was maintained at 450 °C during the film growth for 200 min [19]. The VO_2 thin film is about 100 nm thick and composed of irregularly shaped grains from around 10 nm to 100 nm without epitaxial relation to the substrate, as seen in Figure 1a. The MIT properties were investigated by measuring the infrared transmittance ($\lambda = 2000$ nm) as a function of temperature on a UV–vis–NIR spectrophotometer (Hitachi U-4100, Japan). As shown in Figure 1b, the transition temperature is around 68 °C and comparable to that of VO_2 single crystal. However, the hysteresis width (ΔH) is about 6 °C and the transition sharpness (ΔT) is about 16 °C, which are wider than those of a VO_2 single crystal ($\Delta H \sim 2$ °C and $\Delta T \sim 0.1$ °C).

The cross-section TEM specimens were prepared by standard mechanical polishing and ion milling. The local structural and chemical investigations were performed in a Cs-corrected STEM (USTEM-200, Nion Co., USA), operated at 100 keV to minimize the beam damage. In HAADF images, V atoms exhibit enhanced intensity as compared with Si atoms. EELS spectrum images are obtained using a sub-angström electron probe, with a typical dwelling time of 0.3 s per pixel and an energy dispersion about 0.06 eV per channel. The optimized pixel size is 0.15 nm, which enables relatively fast acquisition.

Transition layers are found at both the surface and the interface of the single-phase, polycrystalline VO_2 film on SiO_x/Si substrate, as shown in Figure 2. At a typical facetted grain surface, the first 1.0–1.5 nm thick layer (denoted as L-1 in the following text) is observed to be structurally different from the grain interior in the BF image, which is further confirmed in the HAADF image by the absence of transgranular lattice fringes within this layer (the absence may be caused by either a poorer crystalline form, a smaller fringe spacing or lattice misalignment). The interface between the VO_2 grains and the ~3 nm thick amorphous SiO_x layer exhibits more structural variations, a typical case also

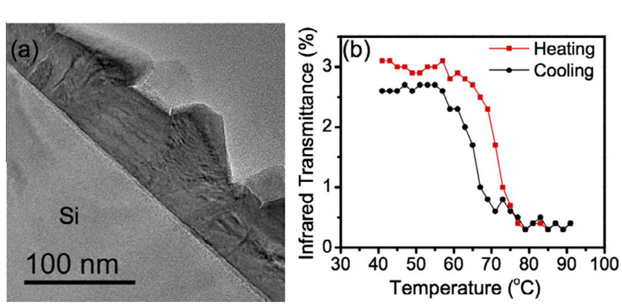

Figure 1. (a) TEM image and (b) thermal hysteresis loops of the infrared transmittance at wavelength 2000 nm for VO_2 thin film.

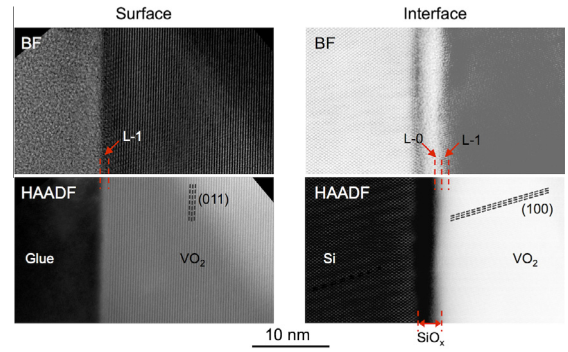

Figure 2. BF and HAADF images for the surface (left) and interface (right) of the VO_2 thin film. The fringes are indexed referring to the VO_2 monoclinic phase.

appearing in Figure 2. By comparing the simultaneously recorded BF and HAADF images, V-related contrast was found to extend beyond the edge of the VO_2 grain by about 1.0–1.5 nm into the amorphous SiO_x, indicating a significant diffusion of V ions into the SiO_x layer (denoted as L-0). Adjacent to this diffuse layer is a transition layer, again 1.0–1.5 nm thick (L-1), showing lattice fringes in the BF image but not in the HAADF image, which is similar to the surface transition layer.

Spatially resolved EELS reveals the local chemical characteristics of these extended transition layers on the VO_2 film, thanks to the strong hybridization of vanadium unfilled 3*d* bands with oxygen 2*p* bands, which induces significant changes on the V-$L_{2,3}$ white lines located at 515 and 522 eV. From V_2O_5, VO_2 and V_2O_3 to VO, successive chemical shifts of around 0.2, 1.2 and 0.6 eV on the V-$L_{2,3}$ lines towards lower energies indicate the successive reductions of the valence state [15–17]. Furthermore, a clear shoulder is visible on the V-L_3 edge for the VO_2 phase. On the other hand, the O2*p*–V3*d* hybridization causes the transition of O1*s* electrons to the vacant anti-bonding t_{2g} and e_g states in the VO_6 octahedral environment, which correspond to the pre-peaks of the O-*K* edge at around 530 eV, thus also reflecting the change in V valence [20,21]. With the decreasing oxidation state of V, the 3*d* electrons tend to preferentially fill the t_{2g} lower state, which lowers the relative weight of unoccupied t_{2g}/e_g and gives rise to the characteristic O-*K* features: two well separated peaks for VO_2; overlapping but still recognizable for V_2O_3 and V_2O_5; and overlapping into one broaden peak for VO. Therefore, such fine structures of the V-$L_{2,3}$ and the adjacent O-*K* edges can be used to monitor the local chemical change and the non-stoichiometry distribution in the VO_2 film.

EELS spectrum imaging is performed across these transition layers of this VO_2 film, as shown in Figure 3(a–d for the surface and e–h for the interface). HAADF images acquired synchronously are also shown as references (Fig. 3a and e). The energy shift maps (Fig. 3b and f) are extracted from the maximum of the V-L_3 line at each pixel, with the energy position for VO_2 being set to zero; drifting during acquisition to the right-hand side is also detected. Across both the surface and interface, the energy shift decreases continuously towards VO_2 over a width of 3 nm or more,