Thickness Dependence of Electronic and Crystal Structures in VO₂ Ultrathin Films

The relative role of Mott and Peierls instabilities is responsible for a unique metal-insulator transition of VO₂. Through in situ photoemission spectroscopy, we investigated the change in the electronic and crystal structures of dimensionality-controlled VO₂ films, where the balance between the two instabilities is controlled as a function of thickness. Spectroscopic results reveal that VO₂ in the thin thickness limit becomes a novel electronic phase, that is, a rutile-type Mott insulating phase without the V-V dimerization characteristic of bulk VO₂, as a result of the superiority of the Mott instability over the Peierls one.

Vanadium dioxide (VO₂) exhibits an abrupt metal-insulator transition (MIT) near room temperature accompanied by structural phase transition due to the dimerization of V ions. Through the MIT, the conductivity of VO₂ changes by a few orders of magnitude. Thus, VO₂ is regarded as one of the most promising candidate materials for future Mott electronics [1]. The mechanism of the MIT in VO₂ is now mainly understood as a transition driven by the cooperation of Mott instability (i.e., strong electron correlation) and Peierls one (i.e., V-V dimerization) [2]. However, it is not yet clear how both of them contribute to the electronic behavior in the channel region during device operation. For designing the VO₂ channel layer with the desired performance, it is crucial to obtain information on the size-dependent characteristics of nanostructured VO₂, because the properties of devices based on strongly correlated oxides commonly vary in a scale of a few nanometers [3]. Against this backdrop, we investigated the change in the electronic and crystal structures of thickness-controlled VO₂ films via in situ photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) measurements and determined the electronic phase diagram of VO₂ ultrathin films.

The experiments were performed using an in situ PES-laser molecular beam epitaxy system installed at BL-2A MUSASHI. The ultrathin-film growth and subsequent spectroscopic measurements were performed without exposing the samples to air by transferring them among the chambers connected under ultrahigh vacuum.

![Figure 1](image)

Figure 1. Thickness dependence of the valence-band spectra for VO₂ films measured at 320 and 250 K. For the thick 10-nm films (MIT temperature $T_{\text{MIT}}$ = 250 K), the spectral changes characteristic of the temperature-driven MIT in VO₂ [2, 4] are observed. The line shapes of these spectra remain almost unchanged even when the film thickness is reduced down to 2 nm, suggesting the invariance of the physical properties of VO₂. Meanwhile, for $t$ ≤ 2 nm, the density of states at the Fermi level ($E_F$) for the 320-K spectrum is steeply reduced and eventually disappears completely at 0.5 nm. A closer look reveals that a Fermi edge profile exists down to $t$ = 1.5 nm, indicating the occurrence of thickness-dependent MIT at a critical thickness of 1.0–1.5 nm. In addition, focusing on the line shapes below the critical thickness, the characteristic temperature-induced spectral changes considerably weaken. These results strongly suggest that another insulating phase emerges in the thin thickness limit. To further investigate this insulating nature in terms of crystal structures, polarization-dependent XAS measurements have been performed.

![Figure 2](image)

Figure 2. Electronic phase diagram of VO₂(001) ultrathin films. Circles indicate $T_{\text{MIT}}$ determined from transport measurements [5], inset shows the crystal structures of corresponding rutile and monoclinic VO₂.

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