

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(A) shows the thickness dependence of the valence-band spectra for VO₂ films measured at 320 and 250 K. For the thick 10-nm films (MIT temperature

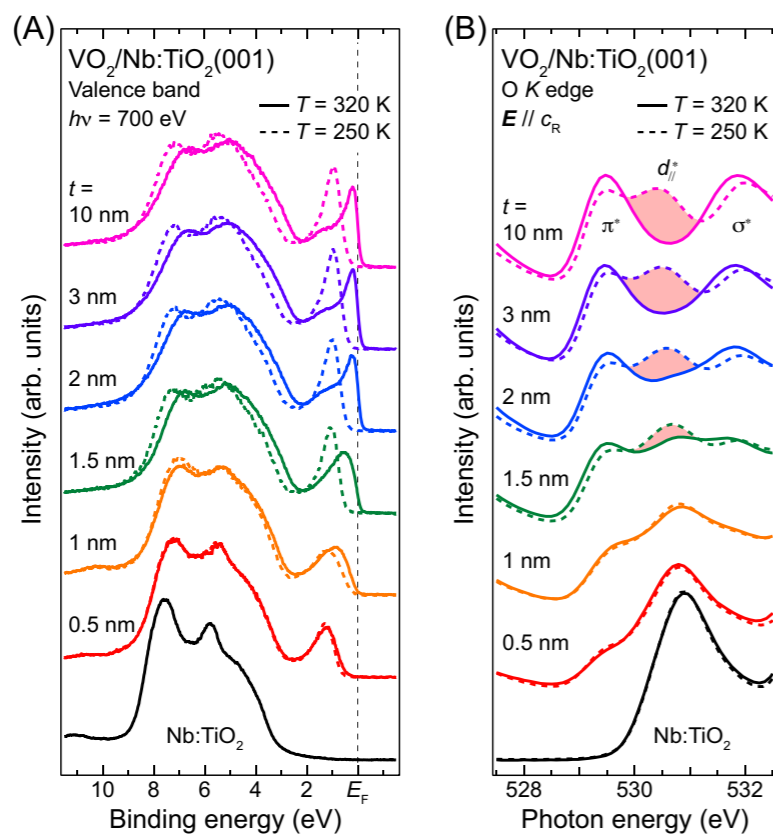


Figure 1: Thickness dependence of (A) valence-band PES and (B) O K-edge XAS spectra measured at 320 and 250 K for VO₂/Nb:TiO₂(001) films. Polarization vector \mathbf{E} is parallel to the c_R axis, which is defined as the c axis of the rutile structure.

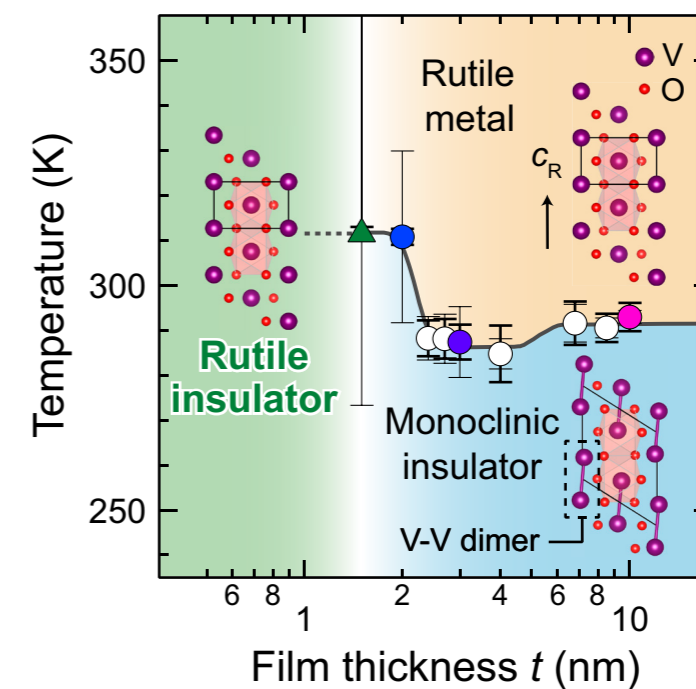


Figure 2: Electronic phase diagram of VO₂(001) ultrathin films. Circles indicate T_{MIT} determined from transport measurements [5]. Insets show the crystal structures of corresponding rutile and monoclinic VO₂.

$T_{\text{MIT}} \sim 293$ 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 t 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 1(B) shows the thickness dependence of the oxygen K-edge XAS spectra for VO₂ films measured at 320 and 250 K. An additional peak appears around 530.6 eV only for the insulating monoclinic phase. This peak can be identified with the d'' state, which is used as a fingerprint of the V-V dimerization in VO₂ [2]. Indeed, the d'' peak is clearly observed in the 10-nm spectra. With decreasing t , the d'' states begin to weaken and eventually disappear completely below the critical thickness ($t < 1.5$ nm), indicating that the V-V dimerization no longer occurs for VO₂ films in the two-dimensional limit wherein insulating ground states are stabilized [Fig. 1(A)]. Furthermore, in comparison with the electronic phase diagram (Fig. 2) determined from

transport measurements [5], it is concluded that VO₂ in the two-dimensional limit exhibits a *rutile-type Mott insulating nature*, owing to the dominance of the Mott instability over the Peierls one [5]. The present determination of the complicated electronic phase diagram of ultrathin VO₂ films may offer valuable insight into the long-standing problem surrounding the MIT of VO₂, which is the relative role of the two instabilities. In addition, it provides important information for designing the VO₂ channel layer of future Mott transistors.

REFERENCES

- [1] M. Nakano, K. Shibuya, D. Okuyama, T. Hatano, S. Ono, M. Kawasaki, Y. Iwasa and Y. Tokura, *Nature (London)* **487**, 459 (2012).
- [2] T. C. Koethe, Z. Hu, M. W. Haverkort, C. Schüßler-Langeheine, F. Venturini, N. B. Brookes, O. Tjernberg, W. Reichelt, H. H. Hsieh, H.-J. Lin, C. T. Chen and L. H. Tjeng, *Phys. Rev. Lett.* **97**, 116402 (2006).
- [3] K. Yoshimatsu, T. Okabe, H. Kumigashira, S. Okamoto, S. Aizaki, A. Fujimori and M. Oshima, *Phys. Rev. Lett.* **104**, 147601 (2010).
- [4] D. Shiga, M. Minohara, M. Kitamura, R. Yukawa, K. Horiba and H. Kumigashira, *Phys. Rev. B* **99**, 125120 (2019).
- [5] D. Shiga, B. E. Yang, N. Hasegawa, T. Kanda, R. Tokunaga, K. Yoshimatsu, R. Yukawa, M. Kitamura, K. Horiba and H. Kumigashira, *Phys. Rev. B* **102**, 115114 (2020).

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