

Tunable strongly correlated oxide semiconductors revealed by hard X-ray photoemission spectroscopy

Transition metal oxides with strongly correlated electron systems are attracting considerable interest as one of the best candidates for constructing novel electronic devices owing to their rich functionalities such as high- T_C ferromagnetism, perfect spin polarization, and huge metal-insulator transition. Among them, vanadium dioxide (VO_2) exhibits electronically attractive properties, showing orders of magnitude changes in resistivity at its metal-insulator transition temperature (T_{M-I}) of 340 K. The Mott-Hubbard or Peierls transition mechanism has been discussed as one of the origins of these phenomena. From a practical viewpoint, an abrupt change of resistivity is expected to be applied to an uncooled bolometer because their temperature coefficient of resistance (TCR), defined as $(1/\rho)(d\rho/dT)$, becomes huge above room temperature (RT). The TCR of VO_2 is usually over 70%/K; however, the maximum TCR (TCR_{max}) is obtained only in a narrow range of high temperatures around 340 K. This makes VO_2 unsuitable for application in practical devices working at room temperature (RT). Control of the physical features, especially metal-insulator transition, of VO_2 by doping is a promising method of utilizing this attractive functionality at RT. T_{M-I} is reduced by doping with transition metal elements, especially W. Therefore, information on the electronic structures and chemical states of W-doped VO_2 is quite important for understanding the origin of its excellent functionality. We investigated the electronic structures as above and chemical states of $\text{V}_{1-x}\text{W}_x\text{O}_2$ (VWO) thin films by hard X-ray core-level photoemission spectroscopy (HAXPES). HAXPES reveals the true bulk electronic structure up to a depth of about 10 nm, although conventional PES is surface-sensitive and sometimes yields contradictory results concerning the physical properties of the bulk.

HAXPES experiments were performed at beamline BL15XU, and HAXPES spectra were taken at $h\nu=5.95$ keV. The W 4d core-level spectra of VWO and the V 2p core-level spectra of VO_2 and VWO were measured in the metal phase at 360 K [1].

Figure 1 shows the schematic illustration of the crystal structure of VWO and the temperature dependence of the resistivity for VO_2 and VWO films. As shown in Fig. 1(b), the resistivity rapidly decreased, changing VWO from a metallic state in a high temperature region to an insulating region crossing T_{M-I} . Doping a small amount of W effectively shifts T_{M-I} and the temperature of the maximum TCR toward RT, while maintaining a high TCR of about 20%/K, as

shown in Fig. 1(c). Figure 2(a) shows the W 4d core-level spectrum of the VWO film. The W 4d_{5/2} peak is located at $E_B = 246.9$ eV and the single fitting curve is in excellent agreement with the experimental spectrum, indicating that the valence of doped W takes the 6+ state without any other valence numbers. This implies that neighboring V^{4+} ions around the site of W^{6+} dopants change to V^{3+} ions to maintain charge neutrality in accordance with the formula $[\text{V}^{4+}]_{1-3x}[\text{V}^{3+}]_{2x}[\text{W}^{6+}]_x\text{O}_2$.

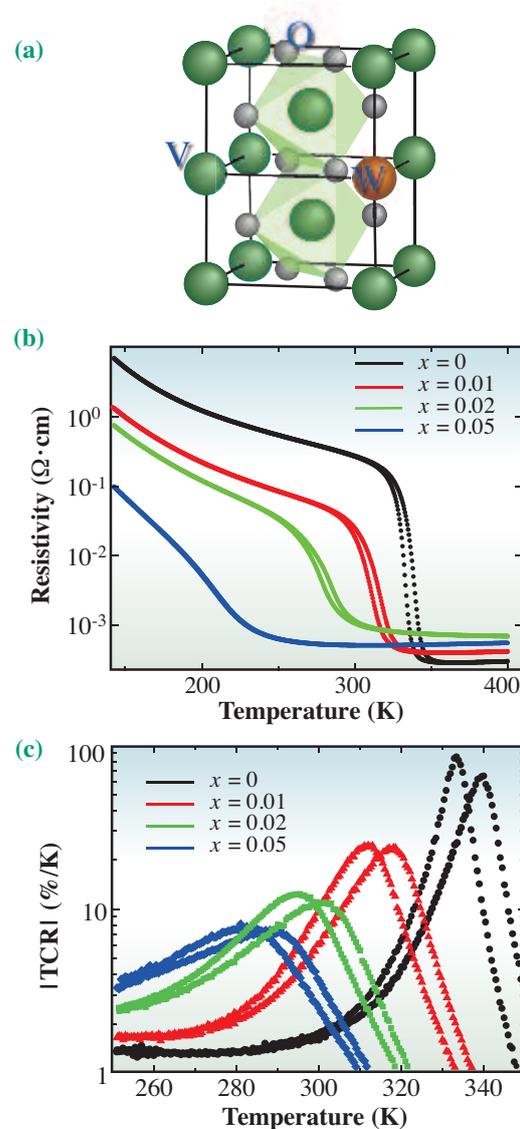


Fig. 1. (a) Schematic illustration of $(\text{V}_{1-x}\text{W}_x)\text{O}_2$ thin films. (b) Characteristics of metal-to-insulator phase transition for different W doping ratios. (c) Characteristics of temperature coefficient of resistivity (TCR).

To clarify this experimentally, Fig. 2(b) shows the V 2p core-level spectra of the VVO films with various W doping levels. Satellite shoulder structures were observed at E_B of 514 eV at the lower binding energy of the V 2p_{3/2} main peak, as shown in the dashed box in Fig. 2(b). It was explained by the well-screened states due to electrons in the vicinity of E_F , as observed only in metallic manganites [2,3] and vanadates [4] and only through the use of HAXPES. This shoulder intensity I_s is related to the density of states of the cohered metallic band around E_F , $D(E_F)$, as expressed by $I_s \propto D(E_F)$. For the VVO film, with increasing W doping ratio, I_s is notably enhanced, indicating the enhancement of the carrier density and suggesting the presence of V³⁺ (3d²) ions, as illustrated in Fig. 3, although the detection of V³⁺ in core-level spectra is difficult because the chemical shift of V 2p_{3/2} between V⁴⁺ and V³⁺ is only 0.15 eV. This effect breaks the half-filled insulating state (V⁴⁺-V⁴⁺ (3d¹-3d¹)) electron configuration. As a result, the increase in carrier from W-doping into VO₂ is a dominant effect for changing T_{M-I}.

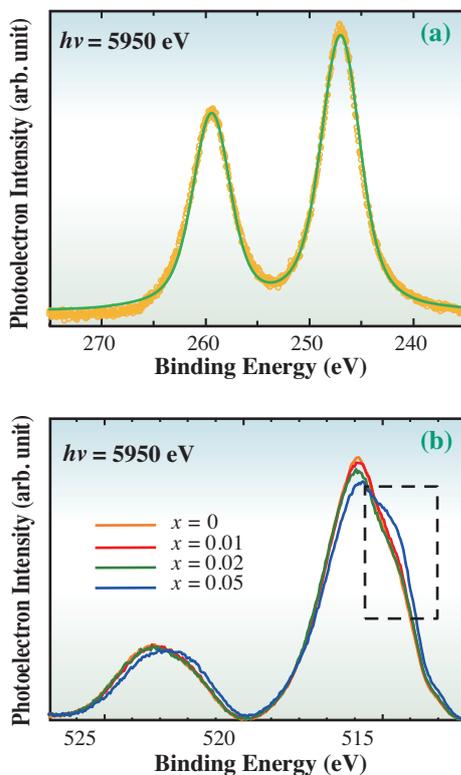


Fig. 2. Hard X-ray photoemission spectra of the (V_{1-x}W_x)O₂ thin films: (a) for W 4d core level (the solid line represents the fitting curve) and (b) for V 2p core level with various W doping levels.

The HAXPES study revealed that electron doping is an effective mechanism for controlling the metal-insulator transition in the (V_{1-x}W_x)O₂ system. Regarding the future significance of this study, the field effect control of transition metal oxides with strongly correlated electrons in heterostructures offers opportunities to create novel functional electronic devices such as electrically tunable colossal magnetoresistance, ferromagnetism, and high-T_C superconductivity devices with controlling interactions between charges with spins [5]; perovskite manganites and high-T_C superconductors are good candidates. The present study demonstrated that VO₂ is a candidate material for constructing functional oxide devices owing to its huge metal-insulator transition.

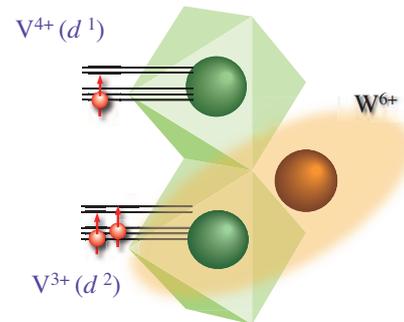


Fig. 3. Schematic illustration of the physical state of (V_{1-x}W_x)O₂ based on the mechanism of tunable strongly correlated oxide semiconductors.

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