Emergence of Metallic Monoclinic States of Electron-Doped VO_2 Films

In order to study the origin of metallization of VO_2 induced by electron injection, we deposited K atoms onto the surface of VO_2 films and investigated the change in the electronic and crystal structures using *in situ* photoemission spectroscopy and X-ray absorption spectroscopy. K deposition onto the surface of insulating monoclinic VO_2 led to a phase transition to metal, in which the V-V dimerization characteristic to monoclinic VO_2 still existed. These results indicate the existence of a novel electronic phase, that is, a metallic monoclinic phase in the case of electron-doped VO_2.

Vanadium dioxide (VO_2) exhibits the metal–insulator transition (MIT) accompanied by a structural phase transition due to the dimerization of V ions at nearly room temperature [1]. Recently, it has been reported that the MIT in VO_2 can be controlled by application of a gate voltage using a field-effect transistor structure. However, the mechanism of the electric-field-induced MIT is still under debate [2, 3]. To understand the origin of the MIT induced by electrostatic injection of charge, it is crucial to obtain information on how the electronic and crystal structures of VO_2 change through the MIT phenomena. In this study, we performed electron doping of a VO_2 surface via *in situ* deposition of K atoms [4, 5], and investigated the change in the electronic and crystal structures via *in situ* photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS), respectively.

The experiments were performed using the *in situ* PES–laser molecular beam epitaxy (MBE) system installed at BL-2A MUSASHI. The oxide-film growth, K deposition, and subsequent spectroscopic measurements were performed without exposing the samples to air by transferring the samples among the chambers connected under ultrahigh vacuum.

Figure 1(a) shows the temperature dependence of the valence-band PES spectra of the VO_2 films (MIT temperature T_{MIT} ~ 295 K) before and after K deposition. For the bare VO_2 films before K deposition, the spectral change across the MIT is in excellent agreement with the results of previous studies [6]. When K atoms are deposited on the surface of the insulating VO_2 films at T = 250 K, a distinct Fermi-edge profile appears, indicating the metallization of VO_2 films induced by electron doping upon K deposition. In addition, the temperature-induced MIT also occurs in K/VO_2, while the T_{MIT} value of VO_2 films is suppressed to within 150–250 K by K deposition. The nearly unchanged peak position of the lower Hubbard band in the insulating K/VO_2 from that of insulating bare VO_2 films suggests that the ground states of K/VO_2 are the same as those of VO_2 films. These results suggest that the carrier-induced MIT is realized by surface carrier injection from K into VO_2 films.

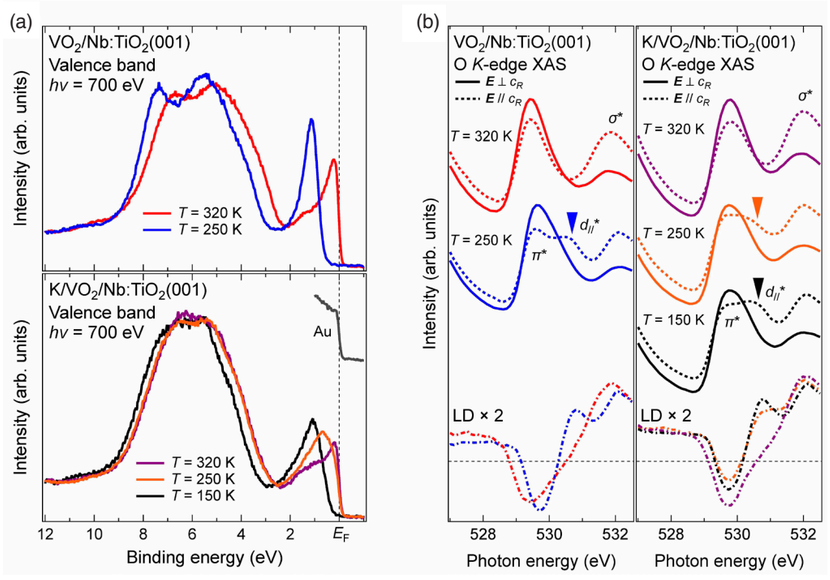

Figure 1: Temperature dependence of **(a)** valence-band PES spectra and **(b)** O *K*-edge XAS spectra with different polarizations and their LD spectra for VO_2/Nb:TiO_2(001) films before and after K deposition.

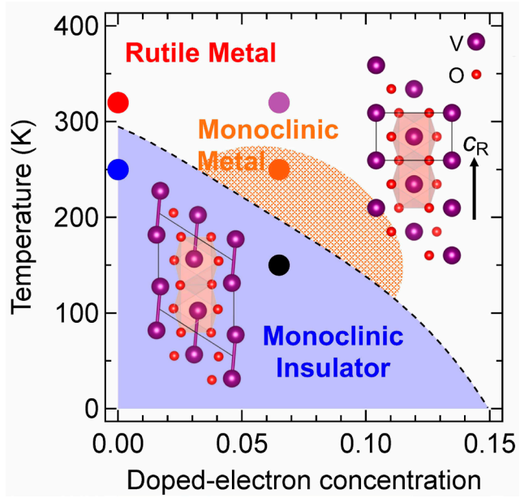

Figure 2: Possible electronic phase diagram of electron-doped VO_2(001) films. Colored solid circles represent spectroscopic measurement points. The inset shows the crystal structure of rutile and monoclinic VO_2. The c_R axis is defined as the *c* axis of the rutile structure.

On the other hand, when the measurement temperature is raised to 320 K, the coherent states at the Fermi level (E_F) evolve into a sharp peak structure reminiscent of that in the metallic rutile phase of VO_2. This means that the metallization states of K/VO_2 at 250 K might be different from the metallic phase of bare VO_2, as well as the high-temperature phase of K/VO_2. These results suggest that a certain different metallic phase exists at the phase boundary near the MIT in the electron-doped K/VO_2. In order to further investigate the metallization state in K/VO_2 from the viewpoint of crystal structures, we carried out polarization-dependent XAS measurements.

Figure 1(b) shows the temperature dependence of the oxygen *K*-edge XAS spectra with different polarizations and their linear dichroism (LD) of VO_2 films before and after K deposition. Additional shoulder structures at 530.8 eV can be identified with the $d_{//}^*$ state by inferring the polarization dependence of the XAS spectra, which is used as a fingerprint of the monoclinic structure with the V-V dimer in VO_2 [6]. The $d_{//}^*$ state is clearly observed in the XAS spectra of the insulating monoclinic VO_2 at 250 K, while the state disappears in the metallic rutile phase at 320 K. Intriguingly, the $d_{//}^*$ state indicative of dimerization of V ions in VO_2 is also observed for K/VO_2 at 250 K, although it showed a metallic behavior in the PES spectra [**Fig. 1(a)**]. These results indicate that the carrier-induced metallic phase in K/VO_2 can be categorized as a novel metallic phase maintaining the dimerization characteristic to the monoclinic phase of VO_2, termed the *metallic monoclinic phase*. Furthermore, the monoclinic metal undergoes a transition to the monoclinic insulator with decrease in temperature (150 K), and to the rutile metal with increase in temperature (320 K). These spectroscopic results suggest that the metallic monoclinic phase exists at the boundary between the insulating monoclinic and metallic rutile phases in the case of electron-doped VO_2 (see **Fig. 2**) [7].

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D. Shiga[1, 2], M. Minohara[2], M. Kitamura[2], R. Yukawa[2], K. Horiba[2] and H. Kumigashira[1, 2] ([1]Tohoku Univ. -IMRAM, [2]KEK-IMSS-PF)