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 (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 KVO$_2$, 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 KVO$_2$ from that of insulating bare VO$_2$ films suggests that the ground states of KVO$_2$ 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.

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 KVO$_2$ at 250 K might be different from the metallic phase of bare VO$_2$, as well as the high-temperature phase of KVO$_2$. These results suggest that a certain different metallic phase exists at the phase boundary near the MIT in the electron-doped KVO$_2$. In order to further investigate the metallization state in KVO$_2$ 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 $d_{xy}$ 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 $d_{xy}$ 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 $d_{xy}$ state indicative of dimerization of V ions in VO$_2$ is also observed for KVO$_2$, 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 KVO$_2$ can be categorized as a novel metallic phase maintaining the dimerization characteristic to the monoclinic phase of VO$_2$, termed the metallic monoclinic phase. Further more, 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 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].

REFERENCES

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