### **3 Oxide Heterostructure Project**

 Observation and control of novel quantum phenomena in superstructures of strongly-correlated oxides –

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#### **3-1 Introduction**

The goal of this project is to design novel physical properties appearing at the heterointerface of strongly correlated oxides. The physical properties arise from strong mutual coupling among the spin, charge, and orbital degrees of freedom in the interface region between two different oxides [1]. To control such properties, it is necessary to clarify the interfacial electronic, magnetic, and orbital structures. We are therefore using synchrotron radiation spectroscopic techniques that have elemental selectivity to probe these structures in the nm-scale region at the oxide heterointerface. For example, the electronic structure at the interface is determined by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS), the magnetic structure by magnetic circular dichroism of XAS, and the orbital structure by linear dichroism (LD) of XAS. Furthermore, the electronic band structures near the Fermi level  $(E_{\rm F})$ , which dominate the novel physical properties of oxide nanostructures, are investigated by angle-resolved PES (ARPES). We aim to design and create novel quantum materials by optimally combining sophisticated oxide growth techniques using laser molecular beam epitaxy (MBE) and advanced analysis techniques that use quantum beams.

# **3-2 Construction of new beamline for surface and interface studies of oxide superstructures**

Our developed system "*in-situ* photoelectron spectrometer – laser MBE" had been installed at the new undulator beamline MUSASHI (<u>Multiple</u> <u>Undulator</u> beamline for <u>Spectroscopic</u> <u>Analysis</u>



**Fig. 1**: Photograph of (a) BL-2A MUSASHI beamline and (b) *"in-situ* ARPES – Laser MBE system" which is installed as an endstation of BL-2A MUSASHI.

on <u>S</u>urface and <u>HeteroInterface</u>) as an endstation (Fig. 1). At the new BL-2A MUSASHI, we performed both vacuum ultraviolet (VUV: 30–300 eV) and soft X-ray (SX: 250–2000 eV) spectroscopic measurements at the same time, for the same grown sample, with the same experimental setup. This approach guarantees the quality of the experimental data, and offers numerous benefits to

the field of surface science: The newly developed system enables us to obtain complete information on the electronic and chemical structures of oxide nanostructures fabricated by laser MBE with high reproducibility. For example, the chemical states and band lineup of heterostructures are characterized by XAS and PES using SX light, confirming the quality of the heterostructures; afterwards, their band structures are investigated by ARPES using VUV light.

## 3-3 Science topic: Emergence of metallic monoclinic states of electron-doped VO<sub>2</sub> films

Metal-insulator transitions (MITs) are one of the most fascinating physical phenomena to be observed in strongly correlated oxides [2]. MIT is accompanied by an orders-of-magnitude change in conductivity that is induced by external stimuli, and this phenomenon has formed a central topic in modern condensed matter physics for its potential application in future electronic devices [3,4]; further, the phenomenon provides an opportunity to better understand the fundamental physics of strongly correlated oxides. Among the MITs exhibited by strongly correlated oxides, the MIT of vanadium dioxide (VO<sub>2</sub>) [5] is particularly intriguing because both the structural transition and the electron correlation contribute to the MIT: The structural phase changes from metallic rutile (P4<sub>2</sub>/ mnm) to insulating monoclinic  $(P2_1/c)$  across the MIT at nearly room temperature (see Fig. 2) [6]. As shown in the inset of Fig. 2, tilting and pairing of V ions along the  $c_{\rm R}$  axis, which is defined as the c axis of the rutile structure in the monoclinic phase, mark this structural change. Because the distances between paired ions and between ion pairs are different, the V ions in VO<sub>2</sub> are dimerized along the  $c_{\rm R}$  axis in the insulating monoclinic phase [6,7]. Although the MIT that is concomitant with the dimerization of V atoms is reminiscent of the Peierls transition [8], the importance of strong electron correlations in VO2 has also been evident for this MIT in a large number of experimental and theoretical investigations [9-11]. Therefore, the mechanism of the MIT in VO<sub>2</sub> is now mainly understood as a collaborative Mott-Peierls (or Peierls-Mott) transition [11].

This type of MIT driven by the cooperation of the two instabilities has motivated researchers to control the phenomenon via external stimuli.



**Fig. 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.

Recently, it has been reported that the MIT in VO<sub>2</sub> can be controlled by the application of a gate voltage using a field-effect transistor structure [12]. However, the mechanism of the electric-field-induced MIT is still under debate [12–14]. For understanding the origin of the MIT, it is crucial to obtain information on how the electronic and crystal structures of VO<sub>2</sub> change through the MIT phenomena induced by electrostatic injection of charge. Thus, in this study, we performed electron doping of a VO<sub>2</sub> surface via *in situ* deposition of K atoms [15], and we investigated the change in the electronic and crystal structures via *in situ* PES and XAS, respectively [16].

The experiments were performed using the "*in situ* PES–laser MBE" system installed at BL-2A MUSASHI of the Photon Factory, KEK (see Fig. 1). The distinct feature of the present study is that 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 3 shows the temperature dependence of the valence-band PES spectra of the VO<sub>2</sub> films (MIT temperature  $T_{MIT} \sim 295$  K) before and after K deposition. Regarding the bare VO<sub>2</sub> films before K deposition, the spectral change across the MIT is in excellent agreement with the results of previ-





**Fig. 3:** (a) Temperature dependence of valenceband PES spectra measured at hv = 700 eV for VO<sub>2</sub>/Nb:TiO<sub>2</sub>(001) films before K deposition. (b) That after K deposition, wherein the spectrum near  $E_F$  of Au acquired at T = 250 K under the same experimental conditions is shown as a reference of the Fermi-edge cutoff. Note that the colors of each spectrum correspond to those of the solid circles in Fig. 2.

ous studies [11]. When K atoms are deposited on the surface of the insulating VO<sub>2</sub> films at T = 250K, a distinct Fermi-edge profile appears, indicating the metallization of VO<sub>2</sub> films induced by electron doping upon K deposition. In addition, the temperature-induced MIT also occurs in K/VO<sub>2</sub>, while the  $T_{MIT}$  value of VO<sub>2</sub> 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<sub>2</sub> from that of insulating bare VO<sub>2</sub> films suggests that the ground states of K/ VO<sub>2</sub> are the same as those of VO<sub>2</sub> films. These results suggest that the carrier-induced MIT is realized by surface carrier injection from K into VO<sub>2</sub> films.



**Fig. 4:** (a) Temperature dependence of O *K*-edge XAS spectra with different polarizations (upper panel) and their LD spectra (lower panel) of VO<sub>2</sub>/Nb:TiO<sub>2</sub>(001) films (a) before and (b) after K deposition. Filled triangles indicate the position of shoulder structures originating from the  $d_{II}^*$  states. Note that the colors of each spectrum correspond to those of the solid circles in Fig. 2.

On the other hand, when the measurement temperature is raised to 320 K, the coherent states at  $E_F$  evolve into a sharp peak structure reminiscent of that in the metallic rutile phase of VO<sub>2</sub>. This means that the metallization states of K/VO<sub>2</sub> at 250 K might be different from the metallic phase of bare VO<sub>2</sub>, as well as the high-temperature phase of K/VO<sub>2</sub>. These results suggest that a different metallic phase exists at the phase boundary near the MIT in the electron-doped K/VO<sub>2</sub>. To further investigate the metallization state in K/VO<sub>2</sub> from the viewpoint of crystal structures, we carried out the polarization-dependent XAS measurements.

Figure 4 shows the temperature dependence of the oxygen *K*-edge XAS spectra with different polarizations and their LD of VO<sub>2</sub> 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<sub>2</sub> [11]. The  $d_{//}$  state is clearly observed in the XAS spectra of the insulating monoclinic VO<sub>2</sub> at 250 K, while the state disappears in the metallic rutile phase at 320 K. Intriguingly, the  $d_{II}^*$  state indicative of dimerization of V ions in VO2 is also observed for K/VO<sub>2</sub> at 250 K, although it showed a metallic behavior in the PES spectra (see Fig. 3). These results indicate that the carrier-induced metallic phase in K/VO<sub>2</sub> can be assigned as a novel metallic phase maintaining the dimerization characteristic to the monoclinic phase of VO<sub>2</sub>, termed the metallic monoclinic phase. Furthermore, the monoclinic metal undergoes a transition to the monoclinic insulator with a decrease in temperature (150 K), and to the rutile metal with an 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  $VO_2$  [16].

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