

# Modulation of metal-insulator transition temperature in W-doped VO<sub>2</sub> thin films : toward Mott devices

**Hidefumi Takami, Kenichi Kawatani, Teruo Kanki, Shigenori Ueda<sup>1</sup>,  
Keisuke Kobayashi<sup>1</sup>, and Hidekazu Tanaka\***

Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

<sup>1</sup>NIMS Beamline Station at SPring-8, National Institute for Materials Science, Sayo, Hyogo 679-5148, Japan

\*Email address: h-tanaka@sanken.osaka-u.ac.jp

## Introduction

Vanadium dioxide (VO<sub>2</sub>) has electronically attractive property, and shows orders-of-magnitude changes in resistivity at around 340 K. These changes are accompanied by a structural deformation between the monoclinic insulating phase at low temperature and the rutile metallic phase at high temperature [1]. Due to the generally abrupt nature of the metal-insulator transition (MIT), VO<sub>2</sub> has been suggested as a potential candidate for Mott field-effect transistors or high-sensitive bolometers. However, in order to realize such Mott devices working at room temperature (RT), it is necessary to modulate the MIT temperature ( $T_{MI}$ ) to RT. W doping into mother VO<sub>2</sub> materials is promising method to modulate the  $T_{MI}$  because of a high reduction rate of  $T_{MI}$  against a small amount of doping concentration, which is more effective than in the other transition metal dopants. On the other hand, the physical description of the  $T_{MI}$  modulation by doping is still unknown due to a complex mechanism of MIT caused by both electron correlation and structural deformation. In this research, we investigated electronic structures of W-doped VO<sub>2</sub> (VWO) by hard x-ray photoemission spectroscopy (HX-PES) and clarify the modulation mechanism of  $T_{MI}$ . Moreover, we suggest that the VWO thin films are suitable for electronically controllable Mott devices working at RT.

## Experimental

The V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub> thin films were deposited on Al<sub>2</sub>O<sub>3</sub> (0001) single crystal substrates using a pulsed laser deposition (PLD) technique (ArF excimer:  $\lambda=193$  nm). The film thickness was measured by nanoscale hybrid AFM (Keyence VN-8000). The crystallinity was examined by X-ray diffraction measurements (XRD; Rigaku RINT2000), and the electronic properties were measured using a four-probe method in a Physical Property Measurement System (PPMS; Quantum Design). The HX-PES experiments were performed at BL15XU of SPring-8, and the HX-PES spectra were taken at  $h\nu = 5.95$  keV.

## Results and Discussion

Figure 1 shows XRD patterns of VWO films with various doping levels. A peak at  $2\theta=41.7^\circ$  indicates reflection from a (0001) sapphire substrate and a peak at  $2\theta=40.0^\circ$  corresponds to the reflection from the (020) peak of VWO.

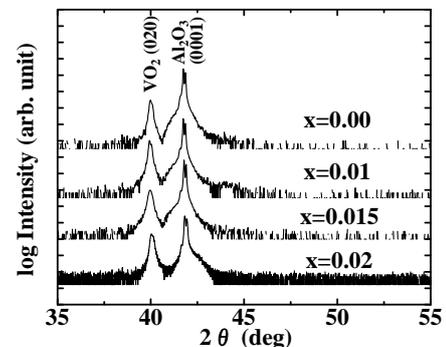


Fig. 1 XRD patterns of V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub> thin films for x = 0 to 0.02.

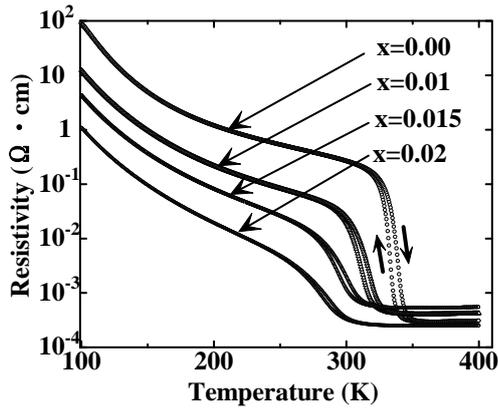


Fig. 2 Temperature dependence of resistivity for  $V_{1-x}W_xO_2$  thin films.

Figure 2 shows the temperature dependence of resistivity for the VWO thin films.  $T_{MI}$  was effectively modulated from 340 K for the  $VO_2$  thin film to 322, 309, and 300 K for VWO with W-dopant concentration of 1.0, 1.5 and 2.0 at %, respectively.

The reduction rate of  $T_{MI}$  against W-content  $x$  ( $dT_{MI}/dx$ ) was about 25 K/%, which is consistent with other reports [2]. This drastic change of  $T_{MI}$  is due to carrier doping effect rather than internal pressure by W-doping [3]. In the evidence of carrier doping, according to the W 4d core level spectra, we find that a valence state of doped W is  $6^+$ . This implies that neighboring  $V^{4+}$  ions around the site of  $W^{6+}$  dopants change to  $V^{3+}$  ions to maintain charge neutrality. This suggests that two electrons are doped into  $VO_2$  and the half-filled  $d^1$  electron configuration is collapsed, which would cause the decrease in the effective Coulomb repulsion energy ( $U_{eff}$ ).

In order to investigate the relationship between carrier doping effects and  $U_{eff}$ , we analyzed the evolution of the spectral weight of the coherent state and the incoherent state against various doping level. Figure 3 shows a valence band spectrum for  $VO_2$  decomposed into the two components, which are coherent peak at the lower energy region and incoherent broad peak at the higher energy region. We

found that the ratio of the coherent state and the incoherent state increases by increasing the dopant level, which means that the  $U_{eff}$  is decreased by doping W in the Brinkman-Rice picture [4]. This is a direct evidence of a modulation of  $U_{eff}$  by W-doping. Therefore, metal phase is more stabilized and  $T_{MI}$  is reduced to RT.

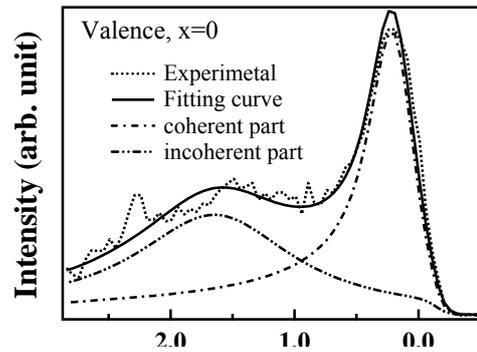


Fig. 3 Valence band spectrum for  $VO_2$  thin film decomposed into coherent part and incoherent part.

## Conclusion

We modulated a metal-insulator transition temperature of  $VO_2$  by W-doping. The doped electrons decrease  $U_{eff}$ . Therefore, the room temperature MIT was achieved, promising characteristics for Mott devices [5].

## References

- [1] J. B. Goodenough, *J. Solid State Chem.* **3**, 490 (1971).
- [2] C. Kim, J. S. Shin, and H. Ozaki, *J. Phys.: Condens. Matter* **19**, 096007 (2007).
- [3] H. Takami *et al.*, *Appl. Phys. Express* **3**, 063201 (2010).
- [4] W. F. Brinkman, and T. M. Rice, *Phys. Rev. B* **2**, 4302 (1970).
- [5] H. Takami *et al.*, *Jpn. J. Appl. Phys.* **50**, 055804 (2011).