Photoemission spectroscopy measurements for phase-separated TiO_2-VO_2 films on mica substrates

Yuji Muraoka[a], Takanori Wakita[a] and Takayoshi Yokoya[a]

[a]*Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushima-naka, Tsushima, Kita-ku, Okayama 700-8530, Japan*

Keywords: Photoemission spectroscopy, TiO_2, VO_2, Film, Phase separation, Mica substrate

Spinodal decomposition is a phase-separation process in which a material spontaneously decomposes into two phases with distinct composition [1]. This results in the spontaneous formation of microstructures with nanosized compositional fluctuations that have been observed in many oxide systems. A rutile-type TiO_2-VO_2 system is known to exhibit spinodal decomposition in bulk [2], where VO_2 exhibited a metal-insulator transition (MIT) at 340 K upon cooling, accompanied by a structural change from a high-temperature rutile-type tetragonal form to a low-temperature monoclinic form (M1). The TiO_2-VO_2 system showed a characteristic phenomenon, that is, anisotropy in decomposition. Solid solution of $Ti_{0.4}V_{0.6}O_2$ bulk was firstly prepared and annealed below 800 K. The system showed spinodal decomposition along the *c*-axis direction, and a nanometer-scale lamellar structure with alternating stacking of tetragonal Ti-rich and monoclinic V-rich phases was formed while retaining a coherent interface.

The anisotropy in decomposition has been applied to form multilayer structures in TiO_2-VO_2 films, and horizontally, diagonally, and vertically aligned multilayer films have been obtain by using single crystal and glass substrates [3-5]. Such self-organized multilayer structures via phase separation are attracted interest as a bottom-up technology for the fabrication of nanostructured devices. A, challenging research for the self-assembled multilayer structures is to form them on flexible substrates such as a mica substrate. The obtained multilayered films could be used as flexible electronics for applications. So far there is no repot on the formation of multilayer structures via the phase decomposition in TiO_2-VO_2 films on flexible substrates. In this study we prepare the spinodally decomposed TiO_2-VO_2 films on mica substrates and study the electronic states by using photoemission spectroscopy in order to examine the occurrence of the phase decomposition in the films.

The TiO_2-VO_2 films were fabricated on mica substrates using a pulsed laser deposition technique with a YAG laser (λ = 355 nm). To induce spinodal decomposition, thermal annealing was performed at 673 K under an oxygen pressure of 1.3 Pa for 24 h. Photoemission spectroscopy (PES) measurements were carried out on the beamline BL-5, at the Hiroshima Synchrotron Radiation Center in Hiroshima University. The excitation photon energy $h\nu$ of 150 eV was used for measurements and valence band spectra were taken at 300 K and 370 K to examine the occurrence of metal-insulator transition. Before measurements, the films were annealed at 393 K under ultrahigh vacuum (~10^{-6} Pa) for 10 min to clean the film surface.

Figure 1(a) shows the valence band spectra of annealed TiO_2-VO_2 films on mica substrates taken at 300 K. No intensity at the Fermi level was seen, indicating that the film is insulating. On the other hand, the finite intensity at the Fermi level is observed in the spectrum taken at 400 K, showing that the film is metallic. This clearly shows that the annealed film exhibits a metal-insulator transition as increasing temperature from 300 to 400 K. Since the metal-insulator transition originates from the V-rich phase, the PES results indicate the emergence of spinodal decomposition in the annealed TiO_2-VO_2 films on mica substrates.

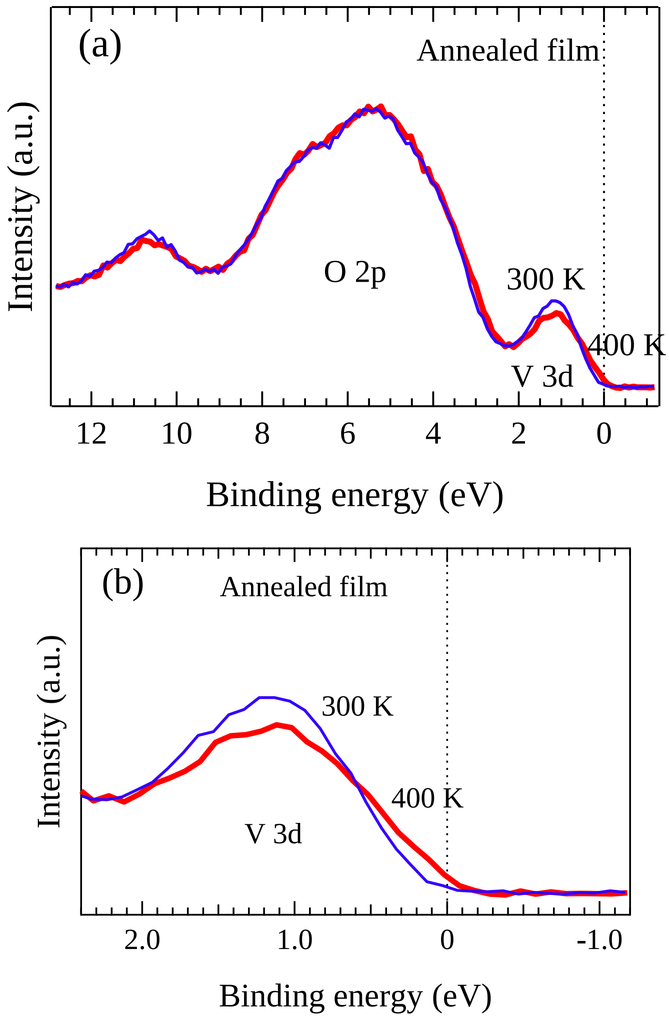

FIGURE 1. (a) Valence band spectra and (b) Near Fermi level spectra of the annealed TiO_2-VO_2 films measured at 300 and 400 K.

REFERENCES

1. J.W. Cahn, *Acta Met.* **9,** 795 (1961).
2. Z. Hiroi *et al.*, *Chem. Mater.* **25,** 2202 (2013).
3. Z. Chen *et al.*, *ACS Nano* **10,** 10237 (2016).
4. G. Sun *et al.*, Sci. Rep. **8,** 5342 (2018).
5. Y. Muraoka *et al.*, *Thin Solid Films* (2023) accepted.