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Filling-controlled Mott transition in W-doped VO_2

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We investigated valence band spectra of VO_2 and W-doped VO_2 thin films by using bulk-sensitive hard x-ray photoemission spectroscopy. The observed spectra transfer from the incoherent part to the coherent part with increasing W-doping level, enhancing the photoelectron intensity at the Fermi level. These results show that an increase of the carriers by a small amount of W dopants significantly changes the strength of the effective Coulomb repulsion energy, causing stabilization of a metallic state with decreasing metal-insulator transition temperature.

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I. INTRODUCTION

Strongly correlated electrons play a crucial role in fascinating phenomena such as high-Tc superconductivity in cuprates[1–3] and colossal magnetoresistance in manganites.[4–7] It is well known that the transition points can be tuned by controlling either the band filling or the bandwidth.[8,9] Even now, the investigation still lies as challenging theme to realize exotic electronic phase control for interest in condensed matter physics and future Mott devices.[8,9] A series of vanadium oxides with huge metal-insulator transitions (MIT) have provided a proper example for this area. In longstanding studies of this material, bandwidth control of the Mott transition points by applying pressure has been experimentally achieved[10–13] based on Mott's original ideas, that is, controlling the ratio of Coulomb repulsion energy U to bandwidth W. On the other hand, dopant control of MITs in vanadium oxides has been experimentally reported for many impurity elements, including W, Cr, Ti, Ga, Fe, and Al.[14–16] In particular, W-doping leads to a drastic change in the MIT temperature ($\Delta T_{\mathrm{MI}} = 21$–$28$ K/at%).[14,17–19] In our previous report,[20] we showed that the chemical state of doped W takes only a $6+$ valence state according to a photoemission spectrum of the W $4d$ core level, which suggests an increase of two V^{3+} ($3d^2$ electron configuration) ions and a decrease of three V^{4+} ($3d^1$) ions per one W^{6+} substitution in terms of charge neutrality in the system. This indicates a collapse in the half-filled $3d^1$ electron configuration of V^{4+} ions. The stoichiometric increase of the averaged $3d$ configuration becomes $1+x$ against the ratio of W^{6+} substitution x in $[V^{4+}]_{1-3x}[V^{3+}]_{2x}[W^{6+}]_xO_2$. There has, however, been no experimental study of the physical description of filling control related to effective U (U_{eff}) and the metal-insulator transition. Here, we investigated the relationship between changes in the MIT temperature by tungsten (W) doping in VO_2 and changes of the band filling with modulation of U_{eff}.

II. EXPERIMENTAL METHODS

W-doped VO_2 thin films with a thickness of 110–186 nm were deposited on an $Al_2O_3(0001)$ substrate using a pulsed laser deposition technique (ArF excimer: $\lambda = 193$ nm) described elsewhere.[14] The hard x-ray photoemission spectroscopy (HX-PES) experiments ($h\nu = 5.95$ keV) were performed in an ultrahigh-vacuum chamber equipped with a temperature-controlled stage and a high-resolution hemispherical electron analyzer at the undulator beamline BL15XU of SPring-8. The total energy resolution was set to 230 meV. The binding energy (E_B) was referred to as the Fermi energy of an Au thin film. The valence band spectra were normalized by the integrated intensity of V $2p$ spectra and the chemical composition of V after subtracting an integrated-type background and O $2p$ component.[21]

III. RESULTS AND DISCUSSION

The temperature dependence of the resistivity in various W-doped VO_2 (VWO) thin films is shown in Fig. 1. The reduction rate of T_{MI} is 19.5 K/at%, which is in good agreement with the values obtained in a previous study.[22] In the metallic state at $T > T_{\mathrm{MI}}$, VWO has a tetragonal structure with equally spaced V atoms, while in the insulating state, it has a monoclinic structure with the Peierls gap originating from dimerized V atoms. To better understand the relationship between dopant effect and U_{eff} by HX-PES, therefore, it may be useful to consider the metallic state, which has a simpler Mott's description based on the Fermi liquid theory with strongly correlated electrons. Figure 2 shows the valence band spectra in various W-doped VO_2 thin films in the metallic states at 360 K. The spectra consist of the quasiparticle component (the coherent part) and the satellite component (the incoherent part). The incoherent component is a residual part arising from the self-energy by the electron-electron interaction.[23] In order to decompose the experimental spectra into the two components, we compared the experimental spectra with the calculated density of states (DOS) based on density functional theory (DFT) combined with the local density approximation (LDA). As the DFT calculations reproduced only the coherent part, a residual part after subtracting the calculated spectra[24] (red dashed lines in Fig. 2) from the experimental spectra (solid lines) is expected to be the incoherent spectra (blue dotted lines). The calculated DOS employed to the fitting was multiplied by the Fermi-Dirac distribution at 360 K, and peak intensities of the calculated spectra were fitted to the experimental spectra. The coherent state is a main peak observed at $E_B = 0.20$ eV, and the incoherent state corresponds to the broadening region in the range of $E_B = 0.9$–2.2 eV. As the W-dopant concentration increased, there was a notable

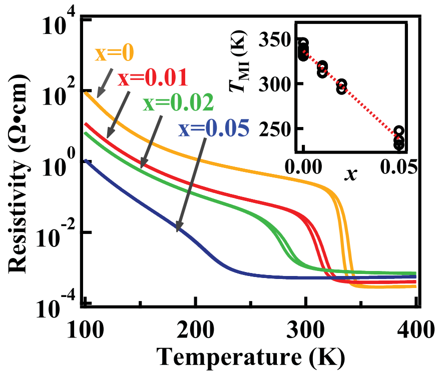

FIG. 1. (Color online) Temperature dependence of resistivity for VO_2 and $V_{1-x}W_xO_2$ thin films. Inset shows the x dependence of the metal-insulator transition temperature $T_{\rm MI}$.

transfer of the V 3d spectral weight from the incoherent part to the coherent part.

We now consider the spectral weight transfer in terms of the carrier-doping effect. The renormalization factor Z, namely, the weight of the quasiparticle pole, would therefore be a good index for the quantitative estimation of the strength of $U_{\rm eff}$ in various VWO thin films. In the case of small self-energy, the spectral function $A(E)$ derived from Green's function can be decomposed into the coherent and incoherent terms using Z[23] as follows:

$$A(E) = ZA_{\rm coh}(E) + (1 - Z)A_{\rm inc}(E), \qquad (1)$$

where $A_{\rm coh}(E)$ and $A_{\rm inc}(E)$ are the spectral functions of the coherent and incoherent parts, respectively. The spectral integral in experiment in Fig. 2 can be represented as,

$$\int I(E)dE = \int I_{\rm coh}(E)\,dE + \int I_{\rm inc}(E)dE, \qquad (2)$$

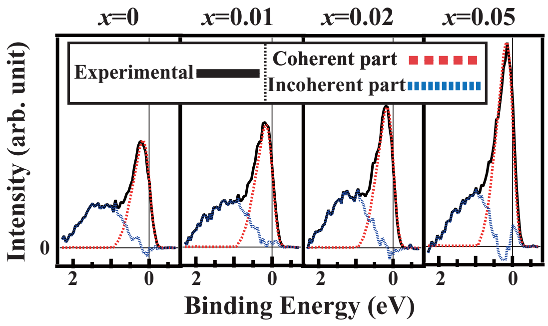

FIG. 2. (Color online) Decomposition of the valence band spectra into the coherent part (red dashed line) and the incoherent part (blue dotted line) taken at 360 K for hν = 5.95 keV.

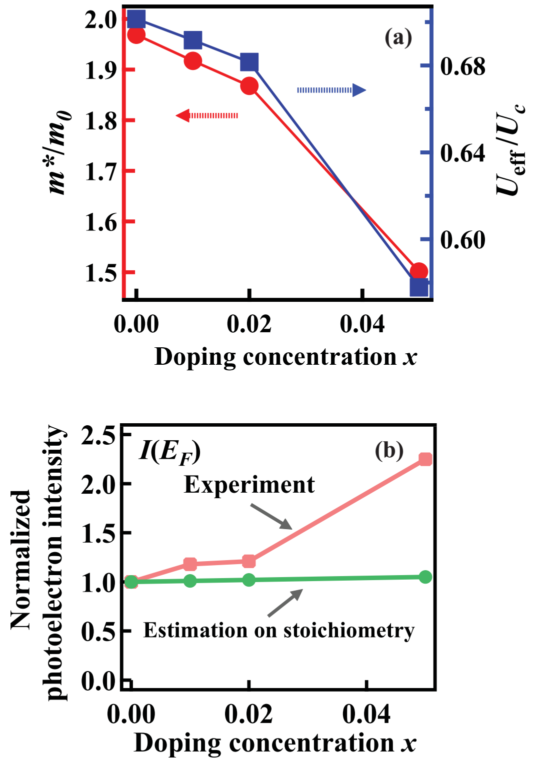

FIG. 3. (Color online) (a) Relationship between the doping concentration x and m^*/m_0 in the left red axis and $U_{\rm eff}/U_C$ in the right blue axis obtained using Eq. (4). (b) The doping concentration x versus experimentally obtained $I(E_F)$ (red filled square) and estimated $I(E_F)$ (green filled circle) based on the stoichiometry. We calculated the latter one by assuming that each W ion replaces a V site and introduces one extra charge carrier into the system.

where $I_{\rm coh}(E)$ and $I_{\rm inc}(E)$ are the decomposed spectra as shown by red dashed and blue dotted lines in Fig. 2, respectively. The equational correspondence relations between Eq. (1) and Eq. (2) are $\int I(E)dE = \int A(E)dE$, $\int I_{\rm coh}(E)dE = Z\int A_{\rm coh}(E)dE$, and $\int I_{\rm inc}(E)dE = (1-Z)\int A_{\rm inc}(E)dE$, respectively. The three spectral integrals of $\int I(E)dE$, $\int I_{\rm coh}(E)dE$, and $\int I_{\rm inc}(E)dE$ can be derived from experimental spectra and decomposed spectra in Fig. 2. Thus, Z can be experimentally determined as following equation:

$$Z = \int I_{\rm coh}(E)dE \Big/ \left(\int I_{\rm coh}(E)dE + \int I_{\rm inc}(E)dE\right), \qquad (3)$$

when only the spectral weight changes in the constant spectral integral. According to the Brinkman-Rice picture,[25] the relative $U_{\rm eff}$, which is given as $U_{\rm eff}/U_C$ (where U_C is the critical Coulomb energy at which the effective mass $[m^*/m_0]$ of a quasiparticle diverges and at which an MIT of first order occurs), can be determined using Z as follows:

$$Z = \left(\frac{m^*}{m_0}\right)^{-1} = 1 - \left(\frac{U_{\rm eff}}{U_C}\right)^2. \qquad (4)$$

Figure 3(a) shows the W-doping concentration dependence of $U_{\rm eff}/U_C$ and m^*/m_0 estimated by Eq. (4). $U_{\rm eff}/U_C$ and m^*/m_0 decrease with increasing x, suggesting disruption in the d^1 configuration because the shift from an integer number for the 3d electron configuration causes a drastic reduction of $U_{\rm eff}$.[4,26,27] In Fig. 3(b), we evaluated relative changes of the DOS reflecting the number of carriers (red filled squares) by the spectral intensities at the Fermi level and of doped carriers estimated using the stoichiometry of $V_{1-x}W_xO_2$ (green filled circles) against the amount of doping level x. With increasing x, the experimental spectral intensity at the Fermi level drastically increases in comparison with estimated carrier-

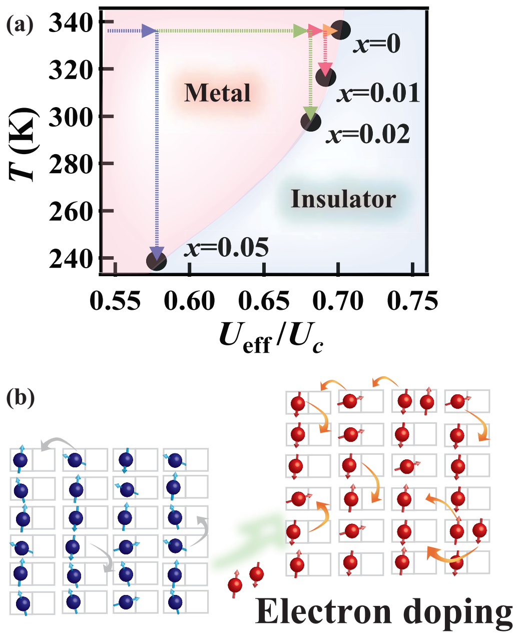

FIG. 4. (Color online) (a) Metal-insulator phase diagram of VO_2 expected from our experiment showing temperature and effective Coulomb interaction. (b) The schematic image of filling control in VO_2. Drastic changes of the electronic states are induced by doped carriers, which break a half-filled state in a strongly correlated electron system.

doping ratios represented as $1 + x$ in $V_{1-x}W_xO_2$. Judging from the reduction of m^*/m_0 with increasing x, these results provide strong evidence of changes in band filling with modulation of U_{eff}. In contrast, W-doping induces an internal pressure of 0.1–0.3 GPa per at%.[20,28] However, the changes in T_{MI} (denoted by ΔT_{MI}) due to pressure are quite weak according to past reports[29] and are expected to be approximately 0.8 K per GPa, instead of the actual changes of $\Delta T_{\mathrm{MI}} = 21$ K due to W-doping at 1 at%. Therefore, the influence of internal pressure is almost negligible with variation in T_{MI}.

Finally, Fig. 4(a) shows the phase diagram for T and U_{eff} obtained from the experiment. It is clear that the transition temperature can be modulated by changing U_{eff}/U_C. The synergistic effect on reduction of U_{eff}/U_C and increase in carriers cause stabilization of the metallic state, as shown in Fig. 4(b). As a result, T_{MI} shifts to lower temperature by W-doping.

In summary, we investigated valence band spectra of VO_2 and W-doped VO_2 thin films by using bulk-sensitive hard x-ray photoemission spectroscopy, and elucidated that changes in the metal-insulator transition temperature by W-doping in VO_2 result from changes in the band filling, with drastic change of U_{eff}. This is the same characteristic feature that results in drastic changes of transition temperature observed in cuprates having high-Tc superconductivity and in manganites having large magnetoresistance.

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