Observation of First-Order Metal-Insulator Transition without Structural Phase Transition in VO$_2$

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An abrupt first-order metal-insulator transition (MIT) without structural phase transition is first observed by current-voltage measurements and micro-Raman scattering experiments, when a DC electric field is applied to a Mott insulator VO$_2$ based two-terminal device. An abrupt current jump is measured at a critical electric field. The Raman-shift frequency and the bandwidth of the most predominant Raman-active $A_g$ mode, excited by the electric field, do not change through the abrupt MIT, while, they, excited by temperature, pronouncedly soften and damp (structural MIT), respectively. This structural MIT is found to occur secondarily.

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Since Mott first predicted an abrupt first-order metal-insulator transition (MIT) without structural phase transition driven by a strongly correlated electronic Coulomb energy [1], the MIT has not been found in experiments [2–7]. Observations of first-order MITs for a Mott insulator [8] have been achieved by temperature and pressure, and are always accompanied with a structural phase transition from the monoclinic structure of an insulator to the tetragonal structure of a metal [4–6]. This complicates the basic mechanism of the Mott transition and divides it into two major mechanisms: the electron-phonon interaction and the electron-electron correlation. Moreover, whether a MIT near a Mott insulator is continuous or abrupt has long been a problem [2,3,8,9].

We have observed a MIT with an abrupt jump of driving current, when an electric field is applied to two-terminal devices with an interval of 5 $\mu$m fabricated on an epitaxial VO$_2$ film [10]. It is thus imperative to investigate whether the abrupt MIT is accompanied by a structural phase transition. To observe a structural change, a micro-Raman scattering experiment rather than neutron diffraction is suitable to obtain experimental data as the size of the neutron beam cannot be reduced within 5 $\mu$m.

In this letter, we report an abrupt first-order MIT, which does not undergo a structural phase transition, observed by current-voltage measurements and micro-Raman scattering experiments with application of a DC electric field to a two-terminal device fabricated on a Mott insulator VO$_2$ film.

Vanadium dioxide, VO$_2$, has been studied extensively because it displays an abrupt MIT at a critical temperature $T_c \approx 340$ K and a slight lattice distortion from a monoclinic structure with space group $C_{2h}$ for the insulator phase to a tetragonal rutile structure with space group $D_{4h}^{14}$ for the metal phase. From the group theory for VO$_2$, five modes ($A_{1g}$, $B_{1g}$, $B_{2g}$, $E_g$, $A_{2g}$ (silent mode)) to the high temperature phase and eighteen modes (nine $A_g$ and nine $B_g$) to the low temperature phase are revealed as Raman active modes [11]. Schilbe found all possible Raman modes of the insulator phase, except one, and also estimated four possible Raman-mode peaks with broad bandwidth of the metal phase above $T_c$ [12].

FIG. 1. (a), Temperature dependence of resistance of VO$_2$ film I. An abrupt MIT at a critical temperature $T_c \approx 340$ K is clearly shown. The inset shows the number of carriers obtained by Hall measurements. A change of carriers from holes to electrons is shown at 332 K. The minus sign indicates that the carriers are holes. (b) Current-density $J$ vs. voltage $V$ curve measured by VO$_2$ based two-terminal device I. An abrupt MIT is shown. The inset is a circuit with 1 K$\Omega$ and a layout of a two-terminal device.
Epitaxial thin films of VO$_2$ have been deposited on (1102) Al$_2$O$_3$ substrates by laser ablation [13,14]. The thickness of the VO$_2$ films was about 900 Å. For two-terminal devices, Ohmic-contacted Au/Cr electrodes on VO$_2$ films with a width of 50 µm and a length of 5 µm (inset of Fig. 1b) were patterned by photo-lithography and lift-off. All devices used in this research had the same dimensions. Raman spectra were measured by exposing an Ar laser beam to VO$_2$ between electrodes. A 17 mW Ar ion laser with a 514.5 nm line in a micro-Raman system (Renishaw 2000) with a spectral resolution less than 2 cm$^{-1}$ was employed. The Raman system was also equipped with an integral microscope (Olympus BH2-UMA). When the Raman spectra are measured, the current after the abrupt MIT was limited to compliance current to prevent the device from possible damage due to excess current. Even though the compliance current was extended from 2 to 100 mA (measurable maximum current of our system), an abrupt current jump was always observed at a MIT voltage $V_{MIT} = 10 \sim 11$ V. Current I vs. voltage V curves were measured by a precision semiconductor parameter analyzer (HP4156B).

Figure 1a shows the temperature dependence of resistance of VO$_2$ film I. An abrupt MIT and hysteresis are shown near $T_c \approx 340$ K ($68^\circ$C). This is consistent with previous measurements [15,16]. It was proposed that this abrupt MIT arises from the structural phase transition from monoclinic below $T_c$ to tetragonal above $T_c$ [4,6]. Hall measurements reveal that the number of hole carriers increases with increasing temperature by $T_c \approx 340$ K, and that electron and hole carriers coexist near $T_c$ (inset of Fig. 1a). Owing to mixing of an electron Hall voltage and a hole Hall voltage, the number of carriers at temperatures from 332 to 340 K cannot be exactly determined. The number of hole carriers at $T_c$ is expected to be $n_c \approx 3 \times 10^{18}$ cm$^{-3}$ (0.018% of d-band charges) from the Mott criterion causing the first-order MIT [1], based on an exponential decrease of resistance (increase of carrier) with increasing temperature. In the metal regime above 340 K, the major carriers are electrons (inset of Fig. 1a). Fig. 1b shows a current density J vs. voltage V curve measured by two-terminal device I fabricated on VO$_2$ film II. An abrupt jump at 21.5 V and Ohmic behavior (metal characteristic) above 21.5 V are exhibited. The current density after the current jump is about $J \approx 6 \times 10^5$ A/cm$^2$ measured in a circuit with 1 KΩ, which corresponds to a value obtained in a dirty metal. These are typical characteristics of a first-order MIT.
tures between 45 and 85°C during a cooling cycle with VO\textsubscript{2} based two-terminal device II. The spectra are superimposed on the contribution of the Al\textsubscript{2}O\textsubscript{3} substrate with sharp peaks near 376, 415, 574, 641, and 746 cm\textsuperscript{-1} (bottom of Fig. 3a). The polarized directions of incoming and outgoing light propagating to the direction of [1102] are all the same. The Raman spectra display: (i) features of a distorted monoclinic rutile structure with narrow line shapes below 50°C, (ii) a typical characteristic in the coexistence of semiconductor and metal phases in the range of 50~60°C, and (iii) a broad peak around 570 cm\textsuperscript{-1} as a Raman active mode of metal phase of VO\textsubscript{2} above \( T = 60°C \) (dash-and-dotted line in Fig. 2). Although there have been some reports where Raman active modes are not observed in a VO\textsubscript{2} film above \( T_c \) [17,18], our result is consistent with that of previous investigations in a bulk VO\textsubscript{2} [11,19]. Compared with the previous measurement [12] of VO\textsubscript{2} at 83 K, we can resolve almost all allowable Raman active modes (6 \( A_g \) and 4 \( B_g \)) at room temperature, except for a very weak \( A_g \) mode near 595 cm\textsuperscript{-1} and a strong \( A_g \) mode near 149 cm\textsuperscript{-1}, which is suppressed by a cutoff filter in our measurement system. Both peak position and assignment of the symmetry modes are denoted at the bottom of Fig. 2. All \( B_g \) modes were weakly measured in our polarization configuration to satisfy the Raman selection rule. As temperature increases, the intensities of narrow and strong \( A_g \) mode peaks decrease and bandwidths seem to broaden, while a new broad Raman peak near 570 cm\textsuperscript{-1} appears. Above \( T = 66°C \), Raman active modes of the monoclinic phase are not shown; instead, two broad Raman peaks superimposed on the sharp Al\textsubscript{2}O\textsubscript{3} modes, strong near 570 cm\textsuperscript{-1} and weak near 400 cm\textsuperscript{-1}, appear and are clearer with increasing temperature (top of Fig. 2). These broad peaks were assigned to phonon modes with \( A_{1g} \) and \( E_g \) symmetries, respectively [11,12]. In particular, the broad \( A_{1g} \)-mode peak near 577 cm\textsuperscript{-1} becomes obvious with increasing temperature from 58°C. This may be attributed to simultaneous changes of the crystal structure and the conductivity. 

Figure 3a shows the compliance-current dependence of Raman spectra observed at the current jump of a MIT voltage \( V_{MIT} = 10 \sim 11V \) for VO\textsubscript{2} based two-terminal device II. With increasing of the compliance current, \( A_g \) and \( B_g \) modes in the spectra vanish without any change in their peak positions and bandwidths, which indicates that the features of the monoclinic phase do not change. From \( I = 16 \) to 30 mA (blue lines in Fig. 3a), the peaks of Raman active mode of VO\textsubscript{2} are not found. The ratio of background levels of Raman spectra near 1000 cm\textsuperscript{-1} for the metal phase at \( I = 16 \) mA to the insulator phase at \( I = 0 \) mA is about 1.23, which is quite close to the value of 1.20 obtained from the temperature dependence by considering the Boltzmann correction between 26°C at room temperature and 68°C near \( T_c \) in Fig. 2. This indicates that the measured phase has already become metal. Moreover, the ratio at \( I = 100 \) mA (Fig. 3b) is as high as 3.11, which is due to the increase of the number of conduction carriers excited by the electric field. In particular, the spectra of \( I = 50 \) and 70 mA measured at 15V and 19V in the Ohmic regime (over \( V_{MIT} = 10 \sim 11V \)), respectively, show a broad peak near 570 cm\textsuperscript{-1} (arrow in Fig. 3a). The broad peak is a secondary effect produced by Joule heating due to high conduction after MIT, as described in a following section. Note that the residual resistance is about 250 Ω in the Ohmic regime and the current density is about \( J \approx 1.1 \times 10^7 \) A/cm\textsuperscript{2} at \( I = 50 \) mA. Moreover, the spectrum of 100 mA was also measured at \( V = 25V \).

FIG. 4. (a) Temperature (filled symbol and black line) and compliance-current (open symbol and red line) dependence of a Raman \( A_g \) mode near 622 cm\textsuperscript{-1}. A single Lorentzian shape, taking into account the linear background contribution of Al\textsubscript{2}O\textsubscript{3} substrates, was assumed to fit the peak position (square and black line) and the bandwidth (circle and red line) of the Raman mode. BW means the bandwidth. (b) Temperature dependence of the abrupt MIT observed at VO\textsubscript{2} based two-terminal device III in a cryostat above room temperature. Near \( T_c \), the abrupt MIT disappears and Ohmic behavior appears. The MIT voltage decreases with increasing temperature.

To compare the abrupt MIT excited by temperature with that by an electric field in detail, we investigate changes of the peak position and bandwidth of the predominant \( A_g \) mode near 622 cm\textsuperscript{-1}. When the \( A_g \) mode is assumed to be only a single Lorentzian shape, the shape spectra contain both the contributions of the Al\textsubscript{2}O\textsubscript{3} substrates, showing linear dependence (bottom of Fig. 3a), and the new \( A_{1g} \) mode near 570 cm\textsuperscript{-1} (top of Fig. 3a).
Fig. 4a shows the temperature and the compliance-current dependence of the position and bandwidth of the A$_g$-mode peak of 622 cm$^{-1}$. With increasing temperature, the peak position of the A$_g$ mode downshifts and the A$_g$ mode changes to the A$_{1g}$ mode (black filled square in Fig. 4a), and the initial bandwidth of 65 cm$^{-1}$ broadens (black filled circle in Fig. 4a). Furthermore, for Lorentzian-fitting results of temperature behaviors of A$_g$ modes near 195 cm$^{-1}$ and 222 cm$^{-1}$ below $T = 60^\circ$C, it was found that the change of peak positions ($<2$ cm$^{-1}$) and bandwidths ($<3$ cm$^{-1}$) was slight, except for an increase from 11 cm$^{-1}$ to 20 cm$^{-1}$ of bandwidth of the A$_g$ mode near 222 cm$^{-1}$. Note that, in the metal phase above $T_c = 60$ K, these A$_g$ modes should vanish and feasible B$_{1g}$ mode could be active (B$_{1g}$ near 240 cm$^{-1}$ may be screened here) [12].

Meanwhile, for a MIT excited by an electric field, the position and bandwidth of the A$_g$-mode peak near 622 cm$^{-1}$ is nearly unchanged (open square and open circle with red lines in Fig. 4a, respectively). At most, the bandwidth of the A$_g$ mode becomes only 8 cm$^{-1}$ wide, and the peak position shifts by only 3 cm$^{-1}$ to the high frequency side. This indicates that the abrupt MIT is basically independent of the structural phase transition, although the MITs by temperature and pressure accompany the structural phase transition [4–6].

Figure 4b shows the decrease of the transition voltage of the abrupt MIT with increasing temperature and Ohmic behavior without a current jump near $T_c \approx 400$ K and over. If a structural phase transition resulting from Joule heating occurred during the Raman measurement, the abrupt current jump should disappear or the transition voltage should also be remarkably decreased. Thus, although the broad peak near 570 cm$^{-1}$ at $I = 50$ and 70 mA in Fig. 3a is a sign of a structural phase transition by temperature, the peak is a secondary effect because the spectra at I = 50 and 70 mA were also measured at $V_{MIT} = 10 \sim 11$V.

Since the electric field excitation can induce an abrupt MIT from a Mott insulator by reducing only the repulsive Coulomb potential between electrons as suggested by the Brinkman-Rice (BR) picture [20] and extended BR picture [21], it is thought that carriers move like cold electrons on the Fermi surface without lattice heating. This might cause a significant difference in the field excitation from the thermal excitation and intense photo-excitation, inevitably incurring a structural phase transition via hot electron and/or hot phonon generation [22–24].

In conclusion, by analysis of the behaviors of predominant A$_g$-Raman-active modes, it was revealed that the abrupt first-order MIT of VO$_2$ by a DC electric field occurs without a structural phase transition, in contrast with that by temperature. Thus, the MIT in strongly correlated materials occurs abruptly due to a decrease of the on-site critical Coulomb interaction by an excitation such as an electric field. Furthermore, the abrupt MIT will provide very important clues for solving ongoing debates on metallic characteristics near the MIT [2,8,9] and for future device applications.

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