Photoheat-induced Schottky nanojunction and indirect Mott transition in VO$_2$: photocurrent analysis

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Abstract

In order to elucidate a mechanism of the insulator-to-metal transition (IMT) for a Mott insulator VO$_2$ (3$d^1$), we present Schottky nanojunctions and the structural phase transition (SPT) by simultaneous nanolevel measurements of photocurrent and Raman scattering in microlevel devices. The Schottky nanojunction with the monoclinic metallic phase between the monoclinic insulating phases is formed by the photoheat-induced IMT not accompanied with the SPT. The temperature dependence of the Schottky junction reveals that the Mott insulator has an electronic structure of an indirect subband between the main Hubbard $d$ bands. The IMT as reverse process of the Mott transition occurs by temperature-induced excitation of bound charges in the indirect semiconductor band, most likely formed by impurities such as oxygen deficiency. The metal band (3$d^1$) for the Mott insulator is screened (trapped) by the indirect band (impurities).

Keywords: Mott transition, VO$_2$, Schottky junction, metal–insulator transition

(Some figures may appear in colour only in the online journal)

1. Introduction

A representative Mott-insulator VO$_2$ with a 3$d^1$ half-filled metal band undergoes the insulator-to-metal transition (IMT) or the metal-to-insulator transition (MIT) with a very large resistance change and a structural phase transition (SPT) between the monoclinic and the rutile tetragonal structure near $T_c \approx 340$ K [1–3]. The IMT indicates the disappearance of the direct gap of 0.6 eV in VO$_2$. Its characteristic is that $T_c$ is tunable [2, 3].

The physical problem in VO$_2$ arose from the controversial argument [4, 5] of whether the abrupt resistance change near $T_c$ is caused by the Mott transition induced by electron–electron interaction between free carriers or by the Peierls charge-density-wave (CDW) transition generated by electron-phonon interaction, which underlies the formation mechanism of the energy gap in insulators. The Peierls MIT is accompanied with the SPT not tunable, in which the lattice distortion induced by the CDW disappears; this MIT does not explain the tunable $T_c$. The CDW is generated by a charge imbalance between nearest neighbor sites [6]. The origin of this problem is attributed to an insufficient understanding of the atomic and electronic structures of VO$_2$, specifically between the Mott or Peierls types.

Previous MIT researches for VO$_2$ are provided for proposing unsolved problems. The VO$_2$ structure contained
high-temperature metallic rutile tetragonal R and low-temperature insulating monoclinic M1 structures [3, 7, 8]. The latter was characterized by the presence of vanadium dimers with alternate V–V distance of $C_R \pm 2\delta$, i.e., the CDW structure (figure 1(a)), while the rutile R-structure had unpaired V-atoms equally spaced at distance $C_R$. A second monoclinic insulator M2 phase was then discovered [9–11]. The M2 phase had two kinds of interstructures: the CDW structure with V–V dimers and an equally spaced V insulator chain structure (ICS) (figures 1(b) and (c)). Although the chain structure was fundamentally the metal structure, the ICS was regarded as an Mott insulator, which results in the presence of the strong correlation [5]. M1 was defined by the superposition of two structures in M2 (figure 1(a)) [5]. The well-known Mott MIT (transition) was explained by the ICS between M2 and PseudoRutile (PR) (figures 1(b) and (c)) [5], but, in the Mott MIT process, the SPT, the disapperance of the CDW structure between M2 and PR, was ignored. Thus, the known Mott MIT can be interpreted as the Peierls MIT (figures 1(b) and (c)); this causes a problem.

In order to overcome this problem, the monoclinic metallic phase (MMP) (or M3 [12]) has been proposed and observed by applying pressure, temperature or light [3, 12–21], but the triple point among M1 ↔ R and M2 ↔ R, which can be interpreted as the Peierls transition, was also posited [8]. Additionally, the coexistence of the Mott transition and the Peierls transition was suggested by theoretical calculations [22], which corresponds to the transitions in figures 1(b) and (c). Finally, the controversial MITs are because the relationship between M2 and MMP and the electronic structure of...
the Mott insulator are unclear. To solve these problems will also disclose the reason why the Mott insulator maintains still insulating state below $T_c$.

Moreover, the Schottky junction between semiconductor and metal has been suggested as a good alternative for observation of the MMP and was observed [23–28]. However, providing a clue to resolve the IMT mechanism mentioned above, a structure of the MMP in the Schottky junction remains to be clarified.

In this paper, we first present photoheat-induced Schottky nanojunctions with the MMP phase between the monoclinic insulating phases through simultaneous nanolevel measurements of photocurrent and Raman scattering for microlevel VO$_2$ devices. From the temperature dependence of the Schottky junction, we deduce that an electronic structure of the Mott insulator includes an indirect band. The IMT (or the Mott transition) mechanism is demonstrated. The relationship between $M_2$ and MMP and the photoinjection effect are discussed.

2. Fabrication of VO$_2$-based devices

The VO$_2$ films were grown on $r$-plane sapphire (Al$_2$O$_3$) substrates using a laser-deposition technique disclosed in a previous paper [29]. The film thickness was typically $\sim$100 nm. Two-terminal VO$_2$ devices were fabricated into linear shapes using a photolithography processes and etched using an ion-beam-assisted milling method. The approximately (500 nm Au)/(30 nm Ti) electrode layer on the etched VO$_2$ film was deposited using an RF-sputtering method and the lift-off technique. The widths of the current channels of the VO$_2$ devices were designed to be narrower than those of the electrodes to avoid a delayed transition of VO$_2$ outside the electrodes.

3. Experimental setup

For nanolevel photocurrent and Raman measurements, in figure 2(a), an Ar-ion laser, with a wavelength of 514.5 nm ($2.41 \text{ eV}$), was chopped at 100 Hz and then focused onto VO$_2$
devices using a 50 × objective lens (N.A. 0.8) to achieve a spatial resolution of 700 nm. The laser power was maintained at 1.5 mW during the measurements. For each pixel, Raman and photocurrent signals were integrated for 3 s and were scanned with a step of 500 nm in the spatial domain. The scattered Raman signal was dispersed using a Jobin–Yvon Triax 550 spectrometer (1200 grooves mm⁻¹) and detected using a charge-coupled device (CCD). The photocurrent measurements were conducted in the 2-probe configuration using the lock-in methods required for a high signal-to-noise ratio. In addition, our Raman and photocurrent measurements were performed at various temperatures and ranged from 303 to 343 K in air. Devices I and II were (L × W) 20 × 10 μm².

4. Photocurrent measurements

To explore on a nanolevel whether the IMT in VO₂ is accompanied by the SPT, we prepared a photo(laser)-induced Schottky nanojunction and examined both the photocurrent, analyzing the electronic structure, and the Raman scattering, analyzing the material structure, through nanolevel measurements reducing inhomogeneity. Figure 2(a) shows a schematic diagram for the Raman and photocurrent measurements. Figure 2(b) shows an intensity map of the monoclinic Raman A_g mode 622 cm⁻¹, measured at 323 K (50 °C) in device I, with L = 20 μm and W = 10 μm, whereas figure 2(c) presents a photocurrent map simultaneously observed using Raman scattering. The Raman map clearly distinguishes the VO₂ channel with a violet area and the Au/Ti electrodes of two black areas at the edges. The violet area indicates that the intensity of the Raman A_g mode is uniform over the measured region. In the photocurrent image, the red and blue regions represent positive and negative currents, respectively [23–28]. We take the positive current as a reference to electrons moving to the right (figure 2(c)). The strong photocurrent near the electrodes is due to the formation of Schottky junctions, which consist of the VO₂ channel as a semiconductor and the electrodes as a metal.

5. Formation of metallic phase

To form an artificial metallic phase on the film channel, we illuminated the VO₂ channel using an additional Ar-ion laser (514.5 nm, 2.41 eV, 2 mW) beam, represented by a green cone with a diameter of 700 nm, for 80 min at 323 K (50 °C) (figure 2(c)). The power density of the focused beam was as high as 500 kW cm⁻², which is sufficient to induce the IMT; however, a part of the power can be transmitted because the sapphire substrate does not absorb the energy. The remaining power energy can remain in the thick substrate as far as the beam is focused [30]. The power energy can heat the substrate and the film, inducing their thermal expansion. Then, when the energy is suddenly removed, the film can undergo rapid contraction, causing a small change in its physical properties due to oxygen emission and can be leaky (more metallic).

6. Schottky nanojunction with the monoclinic metallic phase

After irradiation, Raman and photocurrent measurements were again performed in the same region of device I (figures 2(d) and (e)). A new photocurrent emerged around the
irradiated spot, due to the formation of an additional Schottky nanojunction with a MMP between monoclinic insulating phases (red and blue in figure 2(f) correspond to the semiconductor), which is distinct from the previous junction near the electrodes (figure 2(c)). The intensity of the photocurrent measured near 323 K is not high, which is shown in figure 2(d). This emergence indicates that a metallic region is formed by laser illumination even below the bulk $T_c$. The simultaneously measured Raman image reveals the uniform intensity of the monoclinic peak (figure 2(e)). Specifically, the corresponding Raman spectra, measured near the new photocurrent nanospot (figure 2(f)), remains monoclinic, although the intensities at spots ‘D’ and ‘E’ slightly decrease (figure 2(g)). This finding demonstrates the presence of the MMP, resulting in the Schottky nanojunction, which differs from the expected situation for the rutile structure and also supports the concept of the mechanism being unaccompanied by the SPT. In addition, after laser illumination on two different spots in VO$_2$ device II at 353 K (80 °C), the measured temperature dependence of the photocurrent is observed with two Schottky junctions (figure 2(h)). The temperature dependence of Raman scattering measured for device I shows the disappearing phonon peak near 200 cm$^{-1}$ representing the monoclinic mode and the broadness of the A$_1g$ mode near 525 cm$^{-1}$ of tetragonal (figure 4(b)) [31], indicating the SPT to be between monoclinic and tetragonal at $T_{SPT} \approx 341$ K (−68 °C). This finding is in agreement with the SPT measured by a change of coherent phonons [13]. The junction spots were persisted for a few days at room temperature; this was confirmed by measurements of photocurrent at the junction. This result provides a way to create and control this transient MMP by prolonged laser illumination with moderate intensity.

Figure 3(a) shows the temperature dependence of the photocurrent and the Schottky nanojunction measured for device I. The magnitude of the photocurrent in the photocurrent images is displayed (figure 3(b)). Schottky peaks are presented near electrodes. The Schottky nanojunctions are exhibited between 16 and 17 μm in position and their magnitudes at 333 K and 338 K are smaller than those at lower temperatures (inset in figure 2(d)). The Schottky junctions at 333 K and 338 K are very dim (figure 3(a)). The size of the metallic phase in the Schottky nanojunction is less than 1 μm, suggesting a nanolevel MMP below $T_c$.

The Schottky peaks near 3 μm and 23 μm in position increase with increasing temperature and rapidly rise over 333 K (figure 3(b)). The peak values of the photocurrent are extracted and the inverse peak values are drawn with temperature (figure 4(a)). Since the inverse photocurrent is proportional to resistance, the temperature dependence of the inverse photocurrent has the same behavior as the temperature dependence of resistance with activation energies of $\Delta_{act \, \text{left \, \, electrode}} \approx 77$ meV and $\Delta_{act \, \, \text{right \, \, electrode}} \approx 86$ meV; this is the typical characteristic of VO$_2$. Near $T_c$, the magnitude of jump is less than two orders and the broadness is very large. This suggests that the sample is highly leaky. In this case, because the IMT occurs by small heat energy, the Schottky junction can easily be formed by the focused Ar-ion laser generating heat energy. The cause of the rapid rise in photocurrent is attributed to the IMT. We confirmed that a diffusion of an Au electrode into VO$_2$ had no influence on the photocurrent value through measurements of the temperature dependence of the work function.
7. Discussion on temperature dependence of the Schottky junction

In order to explain the IMT phenomenon in the Schottky junction, we consider the temperature dependence of resistance in VO$_2$ undergoing the IMT near $T_c$ (figure 4(a)). Below $T_c$, resistance exponentially decreases with temperature, which is the characteristic of the extrinsic semiconductor [3, 32–35] and can be formed by impurities such as oxygen vacancies [36, 37]. This suggests that heat induces the IMT, which is regarded as indirect transition excited by thermal phonon, and that the Mott insulator has an indirect band. The indirect band should exist between the main Hubbard band formed by the on-site Coulomb energy $U$ between free electrons in 3$d^1$ of VO$_2$. Therefore, the electronic band structure of the Mott insulator for the IMT is predicted, as shown in figure 4(c). The band structure reveals that the IMT occurs by excitation of bound charges in the main $d$-band ($a_{1g}$ or $d_{1z}$ band) [38, 39] when bound charges $N_{stem,c}$ in the indirect semiconductor band are excited at the IMT point; resistance $\propto 1/N_{ex}^{5,6}$. The total carrier density, $N_{semi,c} \equiv \max(N_{ex}) \approx 3 \times 10^{18}$ cm$^{-3}$, at the transition point was measured by the Hall effect [40, 41] and theoretically analyzed on the basis of Mott’s criterion [42]. We briefly mention the IMT in VO$_2$ that has two kinds of energy gaps of $\Delta_{act} \approx 0.15$ eV (generally, indirect gap $= 2\Delta_{act}$ according to a definition used here) and $\Delta_{direct} \approx 0.6$ eV (direct gap) which are proportional to $T_c$. When $\Delta_{act} \propto T_c$ and $\Delta_{direct} \propto T_c$, they are given, $\Delta_{act} \propto \Delta_{direct}$ is deduced. Thus, as temperature increases, $\Delta_{act}$ and $\Delta_{direct}$ decrease, and, at the IMT point, two gaps simultaneously disappear (figure 4(c)). Moreover, as evidence supporting this suggestion, previous researches suggested the generated metallic carriers with long life time [24–27], and that the IMT occurs when energy is absorbed [43]. These are previous signs for the heat-induced IMT. Note that Mott also mentioned the impurity-induced MIT in Ti$_3$O$_7$ [44, 45].

The Schottky nanojunction is made at a given temperature lower than $T_c$ by the focused laser beam (figures 2(h) and 3); the state around the Schottky nanojunction formed by the IMT is still semiconducting. The IMT occurs in the IMT condition $\Delta N = 0^\circ$, which is elucidated by the temperature-assisted photoinduced IMT, when the excited carrier density, $N_{exc}(T)$, is determined at the given temperature and the carrier density $N_{ex}$ excited by the focused laser light is defined. That is, at $\Delta N = 0$, the constant value $N_{semi,c} = N_{exc}(T)$ (at the given temperature, $T$) $+ N_{ex}$ (heat generated by the focused laser light, i.e. phototherm) is defined. This reveals that $N_{ex}$ (phototherm) decreases as $N_{exc}(T)$ increases. Thus, the presence of the Schottky nanojunction at a temperature below $T_c$ is demonstrated (tunable concept).

Moreover, we find the photoinduction effect measured at chopping frequencies of over 2 kHz by Argon laser 457.9 nm in a previous research [27]. The direct photoinduction effect, in which carriers are doped in the direct band (0.6 eV) by photons, is not considered for the laser wavelength. Because, at over 2 kHz, the sample becomes a thermal equilibrium state which maintains a constant temperature, the photocurrent measured by the photoinduction effect can corresponds to that obtained by contribution of $N_{ex}$ at the given temperature discussed above. For example, in the case of the Schottky nanojunction measured at 313 K (figures 3(a) and (b)), at the condition $N_{semi,c} = N_{ex}$ (313 K) $+ N_{ex}$ (phototherm) $\approx 3 \times 10^{18}$ cm$^{-3}$, it can be interpreted that the region except the Schottky-nanojunction part at 313 K in figures 3(a) and (b) comes from the photoinduction effect.

8. Mott transition

As for the Mott transition, the relationship between M2 and M3 is discussed. The observation of the MMP, called the M3 phase [12], has the physical meaning that the present IMT transparently occurs between the monoclinic insulator M1 and the MMP in the same monoclinic structure (figure 1). An MIT between M2 and the MMP can be the Mott transition induced by the breakdown of the critical Coulomb interaction, when it is assumed that the equally spaced V-zigzag-chain structure in M2 (spin = 1/2 Heisenberg antiferromagnetic insulating chains regarded as the Mott insulator (ICS)) [5] also exists in the MMP (figures 1(d) and (e)). This assumption is natural because the chain structure is presented in both M2 and PR [7] and the MMP exists above the rutile structure. As a supporting evidence of this suggestion, a zigzag chain T(tetragonal)-like structure (distorted M1 structure) below $T_c$ was observed in thick film deposited on TiO$_2$ substrate [46]. We note that the SPT occurs between MMP and PR (figures 1(c) and (e)) [21]. Moreover, the diverging effective mass near $T_c$ was analyzed as evidence of a strong correlation [40, 47]. This Mott MIT (figures 1(c) and (e)) differs from the previous Mott MIT transparently undergoing the SPT between M2 and PR (figures 1(b) and (c)) [5, 7]. The IMT speeds of below 60 fs [16] and 40 ± 8 fs [37] shorter than the suggested phonon (or structural) bottleneck of 80 fs support the presence of the MMP.

9. Conclusion

The MMP in the Schottky nanojunction below $T_c$ for VO$_2$ can be evidence of Mott’s electronic transition and is revealed by the tunable IMT induced by excitation of bound charges in the main $d$-band induced by excitation of bound charges in the indirect band of the Mott insulator with impurities. Furthermore, the metal band of 3$d^1$ (VO$_2$) as the Mott insulator is screened (trapped) by the extrinsic indirect band (impurities) formed by such as oxygen deficiency.
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