Hall voltage reversal and structural phase transition in VO₂ thin films

Cite as: Appl. Phys. Lett. 116, 082106 (2020); doi: 10.1063/1.5143548
Submitted: 24 December 2019 · Accepted: 16 February 2020 · Published Online: 28 February 2020

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ABSTRACT

In this work, we investigated the nanoscale conduction and charge transport characteristics of epitaxial VO₂ thin films around the metal-insulator transition (MIT) using the Hall transport measurement and conduction atomic force microscopy. Unlike the conventional oxides, the VO₂ thin films show unique transport characteristics. First, the dominant carrier type shows a critical change from electron to hole during the MIT sequence (cooling sequence) or from hole to electron during the reverse MIT sequence (heating sequence). Second, the carrier density measured during the MIT sequence is higher than that measured during the reverse MIT sequence, evidenced with a clear thermal hysteresis. Third, the volume fraction (area percentage) of the nanoscale high-conduction phase also shows a thermal hysteresis, evidenced with a larger volume fraction of the high-conduction region in the MIT sequence than the reverse MIT sequence. The first-principles calculations indicate that the dominant carrier is the hole in the monoclinic phase, while it is the electron in the rutile phase, suggesting that the unique charge transport characteristics are attributed to the structural phase transition. Our work provides a deep insight into the nanoscale conduction and charge transports in VO₂ thin films.

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Mott insulators are the strongly correlated electronic materials receiving continuous attention in the past few decades.1,2 The metal-insulator transition (MIT) as the core character of these materials has been highly concerned, while the associated mechanisms can be very fascinating, bringing us to challenges due to the strong electron correlation characteristics. Nevertheless, challenges also exist owing to the coupling of complicated structural ingredients, such as structural defects3 and structural phase transition.4,5 It is known that VO₂ is a typical Mott insulator that offers the d-band electrons with strong electron-electron correlations.6,7 The MIT character of VO₂ has been particularly attractive not only because it occurs around room temperature and offers possible application potential but also due to its role as a core platform for studying strongly correlated electron physics and materials.

In the past few decades, two controversial mechanisms (following the Peierls scenario11,12 and the Mott scenario13,14) have been proposed to explain the MIT effect of VO₂. The Peierls mechanism indicates that a change in the electronic structure will be induced by the structural phase transition (SPT) from the monoclinic phase (insulating phase) to the rutile phase (metallic phase) near the temperature of \( T = T_c \approx 341 \, \text{K} \), where \( T_c \) is called the MIT point. The chemical bonding in VO₂ includes the hybridization of O 2p orbitals with V 3d orbitals.15,16 The band structure changes with the SPT, leading to the variation of the Fermi level.15-19 On the other hand, the Mott mechanism indicates that the MIT is of the first-order feature and can be attributed to a change in the Coulomb energy between the outermost electrons.10-12 This means that the first-order MIT may be owing to the correlation effect instead of structural transition.20,21 Recently, the Peierls-Mott synergistic phase transition mechanism was proposed and extensively discussed. It was believed that the SPT would occur earlier than the reverse MIT and the filling of the d-band would be later than the rearrangement of atoms in the high-T rutile phase, if photons are injected into VO₂ in the low-T monoclinic phase.22 It was also suggested that the SPT and MIT are basically simultaneous by probing the torsion angle variation of the nearest V-V chain coordinates.23 Therefore, it seems that the first-order MIT in VO₂ emerges as...
a consequence of both the electron-lattice interaction and electron-electron interaction,\textsuperscript{26} exhibiting complexity to be further exploration.

One of the recent discoveries on VO\textsubscript{2} is the coexistence of metal and insulating regions evidenced by using near-field scanning microwave microscopy.\textsuperscript{10,26} The area fraction (or volume fraction in the three-dimensional microstructure) of the nanoscale high-conduction and low-conduction phases shows a remarkable \( T \)-dependence.\textsuperscript{7} Nevertheless, it is still unclear what is responsible for such \( T \)-dependences. An investigation of this issue would be interesting for fundamental physics and nanoscale device applications. In the earliest times, Mott believed that the MIT is driven by the change in carrier density, the classical scenario for MIT.\textsuperscript{28,29} When the carrier density is lower than a critical value, a semiconducting or insulating state is favored due to the on-site Coulomb interaction. Otherwise, a high-conductive or even metallic conduction phase ensues.\textsuperscript{28,29} Given this scenario, more complexity would be expected if one further considers the microstructural and electronic inhomogeneities such as electronic phase separation that is intrinsically associated with transition metal oxides.\textsuperscript{30,31} This is the reason why the transport behavior of VO\textsubscript{2}, which has been investigated for many years, remains to be a hot topic to date.

Besides, because the MIT in VO\textsubscript{2} is of first-order, one expects a remarkable hysteresis effect in terms of the transport behavior. Therefore, the physics of electrical transport could be path-dependent if one checks the cooling and heating sequences passing through the MIT point separately. At least there are two issues deserving attention here. First, how does the transport behavior change if the low-\( T \) insulating phase and high-\( T \) conductive phase have different dominant carriers? In fact, earlier calculations proposed some hint on this issue and a clarification would be needed.\textsuperscript{26,32} Second, due to the SPT and the MIT, one wonders if the two phase coexistence around the MIT would add more complexity to the transport behavior. Earlier investigations focused on the macroscopic transport of VO\textsubscript{2}, and these issues have been less touched.\textsuperscript{26,32} In our previous work, the one-to-one correspondence between the macroscopic transport and the microscopic transport mapping using conductive atomic force microscopy (CAFM) was established.\textsuperscript{27} It provides a platform on which we can address the two issues mentioned above.

In this work, we investigate in detail the electrical transport behaviors of epitaxial VO\textsubscript{2} thin films upon the heating-cooling cycle across the MIT point \( T_{\text{c}} \), including the longitudinal and transverse (Hall) transport behaviors as well as the CAFM mapping of the microstructures. It was found that the structural phase transition (SPT) and MIT occur simultaneously over a broad \( T \)-range, and surprisingly, the dominant carriers do change from hole to electron or vice versa. The nanoscale two-phase coexistence during the heating-cooling cycle allows the unusual transport behaviors.

In our experiment, the VO\textsubscript{2} thin films were epitaxially deposited on (0001) sapphire (\( \alpha-\text{Al}_{2}\text{O}_{3} \)) substrates using chemical solution deposition and the details of the fabrication process can be found in earlier work.\textsuperscript{29} The micro-structures of the VO\textsubscript{2} thin films have been investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM), and the results can be found in Fig. S1 in the supplementary material. For the transport measurement, the samples were carefully fabricated and the longitudinal electrical resistivity \( \rho \) and Hall voltage \( V_{H} \) were measured using a standard Hall bar with the physical property measurement system (PPMS9, Quantum Design). Figures 1(a) and 1(b) show a schematic configuration of the Hall measurement and the actual photo of the fabricated Hall bar used in this work, respectively. The nanoscale conductivity imaging was carried out using the CAFM technique (CAFM apparatus, Asylum Research Cypher). The CAFM tips used in this work have a curvature radius less than 25 nm, which can guarantee the nanoscale \( dc \)-impedance measurement. The as-measured VO\textsubscript{2} thin films are \( \sim 40 \) nm in thickness determined using cross-sectional transmission electron microscopy.

Figure 1(c) depicts the \( \rho-T \) curves of the VO\textsubscript{2} thin film in one heating-cooling cycle. During the heating process, the resistivity decreases with increasing \( T \) and it begins to drop sharply around \( T \sim 333 \) K. Up to \( T \sim 340 \) K, the resistivity decreases by three orders of magnitude, marking the reverse MIT sequence. Beyond \( T \sim 340 \) K, a further decrease in \( \rho \) can be seen with increasing \( T \). In the cooling sequence, the resistivity shows an increase with decreasing \( T \). The MIT occurs in-between 330 and 340 K, evidencing a marked hysteresis with a \( T \)-window of \( \sim 10 \) K. These results are well consistent with earlier reports.\textsuperscript{14,26}

The Hall measurements were carried out to check the carrier type and carrier density with varying \( T \) values across the MIT point. The geometry for the Hall measurement is illustrated schematically in Figs. 2(a) and 2(b) with the vertically applied magnetic field of \( B \sim -3.0 \) T. Upon heating-up from the low-\( T \)-side where the sample is in the monoclinic phase, as shown in Fig. 2(c), the observed Hall voltage is negative in the low \( T \) end and the voltage magnitude decreases gradually with increasing \( T \) before a rapid decrease back close to zero at \( T \sim 332 \) K. A zoom-in of the data unveils surprisingly the sign reversal of the Hall voltage from the negative sign to the positive one, occurring at \( T = T_{\text{in}} \sim 334 \) K, as shown clearly in the inset of Fig. 2(c). Here, the subscript “\( \text{rh} \)” with \( T_{\text{in}} \) refers to the temperature for the sign reversal during the heating sequence. Further increasing \( T \) beyond \( T_{\text{in}} \), the Hall voltage remains positive although its magnitude is much smaller than the Hall voltage far below \( T_{\text{in}} \). This is reasonable since the low-\( T \) range below \( T_{\text{in}} \sim 334 \) K is dominated with the monoclinic insulating phase and the Hall voltage must be much larger than that in the high-\( T \) range in which the dominant phase is the metallic rutile phase.
The sign reversal at $T_{rh}$ suggests the change of dominant carrier type from hole to electron. As a complementary evidence, we also check the variation of Hall voltage in response to the cooling sequence from the high-$T$ end ($>$ 360 K) where the sample is occupied with the metallic rutile phase. The results are plotted in Fig. 2(d). Again, one sees the sign reversal of the Hall voltage from the positive sign to the negative one at $T_{rc} \sim 324$ K, indicating the change of dominant carriers from electron to hole. It is seen that the Hall voltage vs $T$ curves for the heating and cooling sequences are very similar although $T_{rh}$ and $T_{rc}$ are different, suggesting that the measured data are reliable and the MIT and reverse MIT are nicely reproducible. It should be noticed that the kinks were observed in the Hall voltage curves at temperatures around $T_{rh}$ and $T_{rc}$, which are assumed to be due to an inhomogeneous composite of VO$_2$ with mixed monoclinic and rutile phases. These kink phenomena resulting from phase coexistence have also been found by magnetic measurements in VO$_2$ based synthetic multilayers.\(^{34,35}\)

To understand the sign reversal of the Hall voltage in both the heating and cooling sequences, a reasonable argument goes obviously to the difference in the dominant carrier type between the low-$T$ insulating and high-$T$ conductive phase. This issue can be qualitatively addressed by looking at the band structures of the two phases. As a reasonable approach, the first-principles calculations of the band structures for the insulating monoclinic phase and conductive rutile phase become the first priority to see the possible carrier type each. The calculations were performed based on the projected augmented wave (PAW) pseudo-potentials using the Vienna ab initio Simulation Package (VASP).\(^{36-38}\) The electronic interactions are described using Perdew–Burke–Ernzerhof (PBE) parametrization of generalized gradient approximation (GGA).\(^{39}\) The plane wave cutoff was set to 550 eV. A $6 \times 6 \times 6$ mesh for the monoclinic phase and an $8 \times 8 \times 8$ mesh for the rutile structure are used for Brillouin-zone sampling.\(^{40}\) Dudarev implementation\(^{41}\) was adopted to add an on-site Coulomb interaction $U_{eff} (=U - J) = 3.0$ eV to the $3d$ orbitals of vanadium. The lattice constants and atomic positions were fully optimized iteratively until the Hellman–Feynman forces converged to less than 5.0 meV/Å. The corresponding lattice parameters used for the calculation can be referred to Table S1 in the supplementary material.

While the bandgap value if any may be slightly underestimated in the present computation scheme, the qualitative characteristics remain similar. The calculated band structures for the two phases are given in Figs. 3(a) and 3(b) where the total and partial density of states (DOS) spectra are plotted. As shown in Fig. 3(a) for the monoclinic phase, the valence band near the Fermi level ($E_F$) is mainly composed of V-$3d$ states, while the V-$3d$ state is dominant at the top of the valence band, implying that the dominant carriers would be holes. The bandgap, as modified by applying $U_{eff}$, is $\sim 0.65$ eV, consistent with
earlier predicted results\textsuperscript{42} and other reported estimated/measured values.\textsuperscript{43,44} Considering the fact that the low-\(T\) region far below the MIT point \(T_c\) would be occupied with the insulating monoclinic phase, one can assume that the low-\(T\) phase prefers holes as the dominant carriers. On the other hand, one looks at the rutile phase, and its band structure plotted in Fig. 3(b) shows again the dominant V-3d state in the conduction band. The Fermi level \(E_F\) enters the conduction band, implying the metallic-like electronic structure. Nevertheless, it is clear that the dominant carrier in this phase is the electron. Similarly, one can assume that the dominant carriers in the high-\(T\) region far above \(T_c\) should be electrons since the rutile phase is dominant in the high-\(T\) region.

Based on the calculated results in Fig. 3, one can explain at least qualitatively the observed sign reversal of the Hall voltage upon heating-cooling cycling. For a qualitative discussion, the MIT sequence is accompanied by the SPT sequence. Therefore, the low-\(T\) region, mainly occupied with the monoclinic phase, must have holes as the dominant carriers. The high-\(T\) region, mainly occupied with the rutile phase, must have electrons as the dominant carriers. In other words, the SPT sequence not only participates in the MIT sequence but also controls the electric transport behaviors more. It is worth noting that in the work by Luo \textit{et al.},\textsuperscript{24} the carriers of VO\(_2\) thin films are electrons no matter in the high temperature or in the low temperature region. The structural phase transition induced carrier type change has not been observed. The reason is that in their work, the VO\(_2\) thin film is grown by magnetron sputtering and contains a lot of oxygen vacancies. In that case, the majority carrier type in VO\(_2\) thin films is dominated by defects like oxygen vacancies within the whole temperature range.\textsuperscript{35–47}

Now, there remain two more issues to be discussed. The first issue deals with the dramatic difference in the Hall voltage difference between the low-\(T\) region and the high-\(T\) region. The second issue is related to the microstructural characteristics during the MIT sequence. For the first issue, it is seen from Figs. 2(c) and 2(d) that the Hall voltages at, e.g., \(T \approx 300\) K (low-\(T\) region end) and \(T \approx 350\) K (high-\(T\) region) differ by more than two orders of magnitude, implying the dramatic difference in the carrier density between the two regions. Such a big difference in the carrier density, no matter holes or electrons, is the reason for the difference in the Hall voltage. The Hall voltage also shows a difference at the same \(T\) during the heating and cooling process, which is also attributed to the difference in carrier density. To confirm this argument, one can estimate the carrier density hysteresis from the measured Hall data, and the results are plotted in Fig. 4, where the carrier density \(n\) on the log-scale is plotted against \(T\) in the heating and cooling cycle. Clearly, one sees the big difference in the carrier density between the two phases, as expected.

Interestingly, the magnitude of the carrier density in the heating-cooling cycle also shows \(T\)-dependent hysteresis, similar to the \(p-T\) curves shown in Fig. 1(b). Starting from the low-\(T\) end, the carrier density is \(\sim 10^{19}\) cm\(^{-3}\) on the order of magnitude, and it increases gradually with increasing \(T\), reaches up to \(\sim 10^{21}\) cm\(^{-3}\) upon the insulating to metal transition around 330 K, and becomes saturated at \(6 \times 10^{21}\) cm\(^{-3}\). It is worth noting that the carrier density as a function of \(T\) shows a kink at \(T \sim 332\) K, the point at which the dominant carrier type changes from hole to electron, according to the Hall data. In the cooling sequence from the high-\(T\) end, the carrier density decreases gradually with decreasing \(T\), reaching the point at which a kink-like feature appears, corresponding to the switching of the carrier type from electron to hole. Beyond this point, the carrier density further falls and reaches down to \(2 \times 10^{19}\) cm\(^{-3}\) at \(T \sim 300\) K.

Considering that VO\(_2\) is a strongly correlated electron system, the observed phenomena described above can be understood without surprising. It is well known that transition metal oxides often show inhomogeneities in electronic states and transport behaviors. In our previous work,\textsuperscript{27} the nanoscale high-conduction and low-conduction regions coexist in a broad \(T\)-window covering the nominal MIT point, suggesting the coexistence of the monoclinic phase and rutile phase. In addition, the area (volume) fraction of the high-conduction region changes gradually with varying \(T\) in the heating-cooling cycle, consistent with the claim that the conductive rutile phase and insulating monoclinic phase coexist over a broad \(T\)-range.

In order to further confirm this claim, we performed a set of CAFM imaging of the sample used for the Hall voltage measurement, by addressing the one-to-one correspondence between the CAFM imaged microstructure and the carrier density/type. CAFM imaging was performed onto a \(2\ \mu\text{m} \times 2\ \mu\text{m}\) square area upon the heating and cooling cycle. The details of the measuring setup and procedure for the CAFM imaging were given in our previous work.\textsuperscript{27} Here, the bright contrast represents the highly conductive region and the black contrast marks the weakly conductive region.

Apart from the carrier density data plotted in Fig. 4 for the heating-cooling cycle, we insert a set of probed CAFM images for illustrating the evolution of the conductive phase and insulating phase on the nanoscale during the cycle. The area (volume) fraction of the conductive regions as a function of \(T\) in the cycle shows the one-to-one correspondence with the carrier density loop. This correspondence between the CAFM imaging and carrier density against temperature in the heating-cooling cycle suggests that the two phase coexistence has twofold scenarios. On one hand, the electronic phase coexistence over the broad \(T\)-range is identified, where the low-\(T\) insulating phase with the carrier density as low as \(10^{19}\) cm\(^{-3}\) and the high-\(T\) metallic phase with the carrier density as
high as $\sim 10^{22} \text{ cm}^{-3}$ were confirmed to coexist by the CAFM imaging and transport measurement. On the other hand, the structural phase coexistence over the $T$-range is also identified, where the hole-dominant monoclinic insulating phase and electron-dominant rutile conductive phase were confirmed to coexist by the Hall voltage measurement.

In summary, the Hall effect and CAFM measurements were carried out to investigate the nanoscale conduction and charge transport characteristics of VO$_2$ thin films. The dominant carrier phase were confirmed to coexist by the Hall voltage measurement. The present results prove that the structure phase transition cycles are critical in their nanoscale conduction and unique charge transport behaviors of VO$_2$ thin films.

See the supplementary material for XRD and AFM measurement results and relevant VO$_2$ lattice parameters used in the first-principles calculations.

This work was supported by the National Key Research Project of China (Grant No. 2016YFA0300101). X.B.L acknowledges the support of the Project for Guangdong Province Universities and the Colleges Pearl River Scholar Funded Scheme (2016).

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