Structural transition and temperature-driven conductivity switching of single crystalline VO$_2$(A) nanowires

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Single crystalline VO$_2$(A) nanowires were synthesized by a facile hydrothermal method. The structural transition and temperature-driven conductivity switching of the VO$_2$(A) nanowires were investigated. Our experimental results show that VO$_2$(A) nanowires exhibit a distinct structural transition accompanied with an order of magnitude change in resistance, and a clear temperature-dependent current switching hysteresis. In order to analyze experimental results, theoretically, the electrical conductivity behavior was found to be consistent with Mott’s small polaron model, the first-principles calculations also indicated that the apical V–O bond changes were mainly responsible for the band gap evolution and hence led to the conductivity switching.

Introduction

Over the past decades, transition metal oxides have attracted great academic interest due to their fascinating properties, such as high-$T_c$ superconductivity, piezo/ferroelectricity, colossal magnetoresistance and nonlinear optical behavior, thus indicating a wide range of prospective applications.$^{1,4}$ Among these oxides, vanadium dioxide (VO$_2$) is a typical representative exhibiting fruitful structural transition behaviors and distinct structure-related properties. In particular, it contains two kinds of first-order transition polymorphs, VO$_2$(M) and VO$_2$(A). VO$_2$(M) has a monoclinic–rutile phase transition near room temperature ($\text{i.e.}$, $\sim$340 K).$^2$ Accompanied with this structural transition, VO$_2$(M) undergoes gigantic changes in resistivity and optical transmittance. As a consequence, VO$_2$(M) has been recently extensively studied with the aim of developing novel sensors and switching devices.$^{4,7}$ Meanwhile, VO$_2$(A) also exhibits an analogous structural phase transition.$^{4,10}$ Nevertheless, presently VO$_2$(A) has been received much less attention compared with VO$_2$(M), although a comprehensive study of VO$_2$(A) phase transition is scientifically important to understand the exact physical mechanism of the first-order structural phase transition which has been debated for decades.$^{7,11}$

In the literature, VO$_2$(A) was synthesized by Théobald$^{12}$ when studying the hydrothermal process of VO$_2$–V$_2$O$_5$–H$_2$O system. It was decades later then Oka et al.$^{16}$ investigated the crystal structure and transition mechanism of VO$_2$(A). They found that the phase transition is a structural transition from a low-temperature tetragonal structure ($A_{1t}$, $P4/ncc$) to a high-temperature body-center tetragonal structure ($A_{1h}$, $I4/m$) and occurs with a shift along the $c$-axis of V atoms. Subsequently, thermally induced electrical and optical properties of macroscopic VO$_2$(A) were studied.$^{11-16}$ The studies showed that VO$_2$(A) undergoes a reversible structural phase transition around 345 K and is probably used as cathode, electron emission, and optical switch materials. The electrical properties on powders-pressed VO$_2$(A) has been investigated.$^{11}$ However, the resistivity is rather high and the hysteresis is not remarkable. Li et al.$^{16}$ investigated the electrical transport properties of an individual nanobelt and calculated the low-temperature phase activation energy, but there is no result in $A_{1t}$. Modern electronic devices are developing to be more miniaturized and smart. It is necessary to study one-dimensional (1D) VO$_2$ to accommodate the development of advanced electronic nanodevices. One-dimensional single crystalline nanowires have been of considerable interest for their significantly different properties and potential applications compared with its bulk counterpart owing to the unique dimensionality and finite size effects.$^{17,18}$ However, a complete study of physical properties of VO$_2$(A) nanowires, especially electrical and electronic properties across the phase transition, is lacking.$^7$ In addition, the orders-of-magnitude change in conductivity accompanied with the

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structural transition is the salient feature of first-order phase transition and the basis for development of advanced electronic nanodevices.\textsuperscript{28} Up to now, it is still unclear for VO\textsubscript{2}(A).

For the above reasons, a further investigation including experimental on conductivity switching and theory of electronic properties in single crystalline VO\textsubscript{2}(A) nanowires is urgently needed. In this letter, we synthesized crystalline VO\textsubscript{2}(A) nanowires by a facile hydrothermal method. The temperature-driven structural transition and accompanied conductivity switching properties were investigated. The electrical conductivity behavior of single crystal nanowire during the phase transition was studied by small polaron model. In order to explore the nature of the conductance change across the phase transition, we carried out the first-principle calculations and studied the densities of states (DOS) as well as electronic bands of \( A_L \) and \( A_T \).

**Experimental**

Single crystallized VO\textsubscript{2}(A) nanowires were synthesized by reduction of V\textsubscript{2}O\textsubscript{5}.\textsuperscript{29} The oxalic acid (H\textsubscript{2}C\textsubscript{2}O\textsubscript{4}.H\textsubscript{2}O) was working as a reducing agent and polyethylene glycol 6000 (PEG-6000) was acting as surfactant. In a typical synthesis, 200 mg of V\textsubscript{2}O\textsubscript{5} powder was dispersed in 17 mL of deionized water and heated up to 85 °C. Subsequently, 200 mg of oxalic acid and 100 mg of PEG-6000 were slowly added to this dispersion under vigorous stirring until a clear black blue transparent solution formed. Then the resulting solution was poured into a 25 mL Teflon-lined autoclave with stainless steel shell and heated in an oven at 220 °C for 48 h. After naturally cooled to room temperature, the products were washed with ethanol and deionized water several times, and finally dried in an oven at 80 °C for 8 h.

The morphology and crystallization of as-synthesized VO\textsubscript{2}(A) nanowires was characterized by a scanning electron microscope (SEM, Quanta 400F), transmission electron microscope (TEM, FEI Tecnai G2 F30) and X-ray diffraction (XRD, Rigaku D-MAX 2200 VPC). X-ray photoelectron spectroscopy (XPS, ESCA-Lab250) was used to confirm the valence state of vanadium. The phase transition temperature was examined by differential scanning calorimetry (DSC, Netzsch DSC-204) with repeated heating-cooling cycles at a heating rate of 10 K min\textsuperscript{-1}. \( I-V \) curves were measured by Keithley 4200 semiconductor characterization system combined with a self-designed shielding box and temperature controlled probe stage (PE95/T95) purchased from Linkam Scientific Instruments.

**Results and discussion**

**Characterization of the VO\textsubscript{2}(A) nanowires**

The morphology and structural properties of VO\textsubscript{2}(A) characterized by SEM, TEM and XRD are presented in Fig. 1. As shown in Fig. 1(a), there are a large number of nanowires with different widths range from tens to hundreds nanometers and their lengths vary from several micrometers to tens of micrometers. Fig. 1(b) and (c) show representative TEM images of an individual nanowire. It can be seen from the images that the spacing between the lattice fringes is 5.95 Å (Fig. 1(c)), which is corresponding to the distance between two (110) crystal planes of VO\textsubscript{2}(A) and the selected area electron diffraction (SAED) pattern in the lower left. Significantly, the whole nanowire is single crystalline because the SAED pattern remains unchanged when the electron beam is moved along the nanowire. Fig. 1(d) shows a typical XRD pattern of the as-synthesized VO\textsubscript{2}(A) nanowires, which is identical with JCPDS 42-0876.\textsuperscript{21,22} No characteristic peaks of any other phases or impurities are indexed in the diffraction pattern, which confirms that the nanowires are pure and highly crystalline. Besides, the VO\textsubscript{2}(A) nanowires grow with a preferential growth direction owing to the most striking peaks belonging to the (110) family.

**XPS spectra of as-synthesized VO\textsubscript{2}(A) nanowires**

Chemical element’s valence state of the as-synthesized VO\textsubscript{2}(A) investigated by XPS is presented in Fig. 2. The survey spectrum in Fig. 2(a) marks three elements of C, O and V. The peaks for C
could be ascribed to the carbon dioxide or oxalic acid absorbed on the surfaces of the powder samples. According to the core-level spectra in Fig. 2(b), the peaks at 516.67 eV, 524.40 eV and 530.59 eV are V 2p3/2, V 2p1/2 and O 1s, respectively, which indicates that the valence of vanadium is +4 and corresponds with the values of VO2(A) reported in previous literatures. It has been proposed that the difference of binding energy between the O 1s and V 2p3/2 peaks could also be used for determining the oxidation state of the vanadium oxides. As for our measurement, the energy (O 1s−V 2p3/2) value is 13.92 eV, which is well consistent with the oxidation state of vanadium reported in earlier studies and further confirms that the valence of vanadium is +4.

**DSC curve of VO2(A) nanowires**

Fig. 3 shows the phase transition temperature of the as-synthesized nanowires. It shows an endothermic peak at 438.1 K and an exothermic peak at 391.8 K during heating and cooling processes, which are similar to the previous reports. The endothermic peak can be attributed to the transition from Al to Ah, while the exothermic peak can be assigned to the reverse transition. It is noticeable that the exothermic peak is less remarkable than the endothermic peak. This is mainly ascribed to the weaker structural transition from Ah to Al. In the heating and cooling cycle, a noticeable thermal hysteresis can be observed, and the hysteresis width ΔTh is 46.3 K. The large and reversible hysteresis implies the characteristic temperature-driven first-order structural transition in the VO2(A) nanowire.

**Electrical transport measurement of the single crystalline VO2(A) nanowire**

The temperature-driven conductivity switching in single crystalline nanowire during the phase transition was studied on a two-terminal device (Fig. 4). The device was fabricated by the standard photolithography and lift-off techniques. Ni/Au (20/100 nm) metallization electrodes was deposited by e-beam evaporator to form an ohmic contact with low resistance. Every temperature point was kept three minutes to make the device have the same temperature with the temperature controller and ensure that the phase transition completely finishes. As shown in Fig. 5(a) and (b), a series of linear and symmetric I−V curves are gained at varying voltages from −1.5 V to 1.5 V in the temperature range from 303 K to 473 K. The linearity and symmetry of the lines indicate an ohmic contact between the VO2(A) nanowire and Ni/Au electrodes. During heating process, the resistance always decreases homogeneously with temperature rising until the temperature rises to 444 K shown in Fig. 5(a) and 7(a). At this point, the resistance suffers a sudden change, and a phase transition occurs. Likewise, Fig. 5(b) shows an abrupt change in resistance at 408 K when cooling down. In the whole heating (cooling) process, the resistance decreases (increases) with the increase (decreases) of temperature, which reflects a typical semiconductor property in either Al or Ah. It suggests that the phase transition in VO2(A) is a typical semiconductor to semiconductor transition, which is analogous to the phase transition of M1−M2 in VO2(M).

Fig. 5(c) shows a clear hysteresis and distinct switching in current by one order of magnitude. The transition temperatures during heating and cooling process determined by peaks of d log I/dT versus T plot in Fig. 5(d) are 444 K and 408 K, and the hysteresis width ΔTh is 36 K. The great differences in the transition temperatures and hysteresis width with DSC measurement in Fig. 3 are considered to be caused by size effects, which has been reported that the phase transition temperature can be tuned by dimensions of VO2 nanostructures and exhibits 1/d dependence (d represents the nanostructures’ dimension). Moreover, the device performances a good reversibility when periodically change the temperature and voltage as shown in Fig. 6. After five cycles, the hysteresis curves in Fig. 6(a) keep high coincidence, and the phase transition temperatures on heating and cooling processes presented in Fig. 6(b) and (c) are all unchanged, which further indicates the well reversibility of VO2(A). Accordingly, our studies achieve steady thermally triggered current–temperature hysteresis curve of single crystalline VO2(A) nanowires involving great changes in resistance as that of VO2(M), which can be envisioned that the single crystalline VO2(A) nanowires are explored for advanced electronic applications, such as switches and sensors.

The temperature-dependent electrical conductivity behavior in transition-metal oxides can be described by small polaron theory. Mott has proposed a conduction model of the optical phonon assisted hopping of small polarons between the localized states, where the conductivity at high temperature...
\( T > \theta_D; \theta_D: \text{Debye temperature} \) is given by \( \ln(\sigma T) = \ln(C) - \frac{W}{kT} \). \( \sigma \) is the conductivity of VO\(_2\)(A), \( C \) is a constant, \( k \) is Boltzmann constant and \( W \) is the activation energy, which is an energy barrier that the electrons must surpass in order to hop to another site.\(^{16,33}\) The dc conductivity in the form of \( \ln(T/R) \) as a function of 1000 \( T^{-1} \) is presented in Fig. 7(b). The solid dots are gained from our experiments and the solid lines are linearly fitted to the dots. The plot indicates that our experimental

![Fig. 5](image)

**Fig. 5** Electrical transport measurement of the single crystalline VO\(_2\)(A) nanowire. Temperature dependent \( I-V \) curves at (a) heating and (b) cooling process; (c) temperature–current hysteresis of the VO\(_2\)(A) nanowire; (d) phase transition temperature during heating and cooling process.

![Fig. 6](image)

**Fig. 6** Reversibility of the single VO\(_2\)(A) nanowire, (a) temperature–current hysteresis curves with five cycles, (b) the phase transition temperatures during heating and (c) cooling process.

![Fig. 7](image)

**Fig. 7** (a) A plot of resistance versus temperature when heating up and (b) DC conductivity as a function of 1000 \( T^{-1} \) (green dots), the magenta solid line is the linear fitting of the dots.
results nearly complete fit to Mott’s model. On the basis of the equation and slopes of the linear fitting curve, the activation energy of the nanowires is calculated to be 0.38 eV for \( A_L \) and 0.33 eV for \( A_H \), which are much smaller than the previously reported value of 0.8 eV and 0.65 eV.\(^{13} \) The large disparities may be due to the different measurement objects (a single crystal nanowire vs. pressed-powders). The good agreement with the Mott’s small polaron model implies the multi-optical-phonon-assisted hopping model during the whole phase transition.\(^{32} \)

It is consistent with Hou et al.\(^* \) results indicating that the phonon–electron interaction plays an important role in the phase transition.

**First-principle calculations results of VO\(_2\)(A)**

To reveal the phase transition mechanism of VO\(_2\)(A), the structural and electronic properties are investigated by the first-principle calculations. The first-principle calculations for VO\(_2\)(A) were carried out in VASP package with the projected-augmented wave (PAW) potentials. We used the framework of Perdew–Burke–Ernzerhof revised for solids (PBEsol) type generalized gradient approximation (GGA). To extract more convincing results, two effects were considered in particular. On-site potential was added to account for the correlated nature of V 3d electron. And the spin–orbital coupling (SOC) was introduced to give precise insights into the electronic structures before and after the phase transition. During the calculation, the kinetic energy cutoff for plane-wave was set to 450 eV and the \( k \)-point grids were taken as \( 4 \times 4 \times 4 \) for \( A_L \) and \( 4 \times 4 \times 8 \) for \( A_H \). The lattice constants and atomic structures were obtained from experiments and optimized self-consistently until force on each atom was less than 0.02 eV Å\(^{-1} \).\(^{10} \)

The structural transition of VO\(_2\)(A) are presented in Fig. 8(a). Both \( A_L \) and \( A_H \) consist of a distorted VO\(_6\) octahedral with V atoms located in off-center, which results in two different V–O distances and two types of oxygen atoms, namely O\(_1\) and O\(_2\). The V–O\(_2\) bonding shows a shorter distance in the distorted VO\(_6\) octahedral, 1.703 Å for \( A_L \) and 1.695 Å for \( A_H \) displayed by the thin black dash lines. Across the phase transition, the V–V distance along \( c \) axis changes from an alternate distances of 3.041 Å and 2.944 Å (\( A_L \)) to an even distance of 3.055 Å (\( A_H \)). The electronic structure of VO\(_2\)(A) is investigated by calculating the partial density of states (PDOS) and the band structure shown in Fig. 8(b) and (c). Either \( A_L \) or \( A_H \), the valence band maximum (VBM) is mostly dominated by \( d_{xz} \) and \( d_{yz} \), while the conduction band minimum (CBM) is mainly composed of \( d_{x^2−y^2} \) (usually designated as the \( d_{1g} \) bands\(^{34} \)). The band structure of \( A_L \) and \( A_H \) shows many differences. For the low temperature phase \( A_L \), VBM is situated at \( \Gamma \) point, while CBM is located at \( M \) point, resulting in an indirect band gap of 1.12 eV. As for \( A_H \), the VBM is situated at \( M \) point, and the CBM is located at \( X \) point, showing an indirect band gap of 0.75 eV. Obviously, both \( A_L \) and \( A_H \) show a semiconductor behavior. It is in agreement with our experimental results and previous report.\(^{14} \) The visualized illustration is presented by molecular orbital scheme in Fig. 9. From the figure we can see that the band gap decreases when changing from \( A_L \) to \( A_H \), which is resulted from the increase of \( \pi^* \) orbitals and decrease of \( d_{1g} \) orbitals. The changes of the orbitals are owing to the decreases of the apical V–O\(_2\) bond length and consequently increase the energy level of the \( \pi^* \)
orbitals relative to those of the d_{3z^2} orbitals. The decrease of the energy band gap during the phase transition suggests that VO_{2}(A) has a better electrical conductivity when the phase transition occurs, which is consistent with the experiment results.

Conclusions

In summary, VO_{2}(A) nanowires have been successfully synthesized by a facile hydrothermal treatment. Temperature-driven conductivity switching and electronic properties of single crystalline nanowires are studied, experimentally and theoretically. Our results show that VO_{2}(A) exhibits a distinct structural transition accompanied with an order of magnitude change in resistance, which is promisingly used for sensors and switches. During the phase transition, the electrical conductivity behavior is found to be completely fit to Mott’s mode and the activation energy is calculated to be 0.38 eV and 0.33 eV for AL and AH. Furthermore, the first-principle calculations results indicate that VO_{2}(A) possesses indirect band gaps and the band gaps are 1.12 eV for AL and 0.75 eV for AH. The crystal lattice in particular the apical V-O bond changes play a crucial role in the band gap evolution and then lead to the conductance change. Further studies related to diameter effects of VO_{2}(A) nanowires should be progressed to clarify the intrinsic influences on first-order phase transition caused by size effects.

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Notes and references