Recent development on the understanding and application of Vanadium dioxide: Challenges and Opportunity

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Abstract

VO_2 since the descovery in 1969 by Morine have drawn a great deal of interest due to its ultrafast change in resistivity by heating to 60°C. Change in electronic properties has been attributied to structural as well as electronic driven. In this paper we present a recent development on new polymorphs of VO_2 such as A, B and M phases its electronic properties and its potential application in the field of gas sensing, bolometer and switching devices which is ascribed to VO_2's high temperature co-efficient of resistance.

Introduction

Study of metal-insulator transition in transition metal oxide systems has been important focus in both fundamental and applied research. In the d-electron systems, these transitions are the result of instabilities occuring from complex interplay of spin, charge, orbital and lattice degree of freedom. Among them VO_2, a $3d^1$ system, has attracted a great interest in last few decades for its MIT close to room temperature ($T_{MIT} \sim 340$ K) concomitant with a structural phase transition at

the same temperature. The nature of the band gap opening in the low temperature phase of $VO_2(M)$ is still not fully resolved and recent results suggests that it is phase change as well as electronic driven, and possibly, VO_2 is best described by a explicit case of a Pierels-Mott insulator having e-e dimerization as well as correlations of V atoms both adding to the opening of an insulating gap. The electrical measuremnt of the $VO_2(M)$ and $VO_2(R)$ phases is frequently described by the c_R/a_R ratio correlated to the $VO_2(R)$ phase lattice parameters and its change is correlated with the Vanadium-Oxygen equatorial as well as apical distances as shown [1] in **Figure** 1 (a). The distortion of the octahedra along c_R and along the a_R axis alters the overlap of the orbitals and thus influence the electronic band sturcture [2]. Oxide ligands crystal field divides d orbitals into t_{2g} and e_g orbitals, represented in **Figure** 1 (b). The $d_{3z^2-r^2}$ and d_{xy} orbital related to e_g head directly towards the oxygen ligands which gives rise to e_g^σ and e_g^π states of Vanadium 3d-O 2p orbitals [3]. Contrarory to that, the t_{2g} states are built from the $d_{x^2-y^2}$, d_{xz}, and d_{yz} orbitals. The width and position of d orbital band is subject to both p, d orbital hybridization as well as strongly influence by V-V interactions. The d_{xz} and d_{yz} form a pi* superposition with the oxide ligands which gives rise to π* states. The $d_{x^2-y^2}$ orbital directed along the x-axis, experiences overlap parallel to the rutile c axis giving rise to antibonding $d_\parallel^*$ states with b_{1g} symmetry but are chosen as the $d_\parallel$ bands [4].

In order to understand the effect of edge sharing octaherdas that mediate the metal-metal (V-V) and metal-oxygen (V-O) bonding in the rutile or monoclinic phases on their electronic properties of the VO_2 system we have choosen numerous other phases of VO_2 such as M/R, A, B, which is described to dissimilar V-V and V-O distance [5]. Although structural studies have been

reported, the full electronic band structures of the $VO_2(A/B)$ polymorphs are not available. the synthesis by pulsed laser deposition of non-stable phases such as $VO_2(A/B)$, allows to stabilize these polymorphs in the thin film form. Besides their importance to the physics of VO_2 transitions $VO_2(A)$ and $VO_2(B)$ phases may find applications in catalysts, photovoltaics and battery electrode applications.
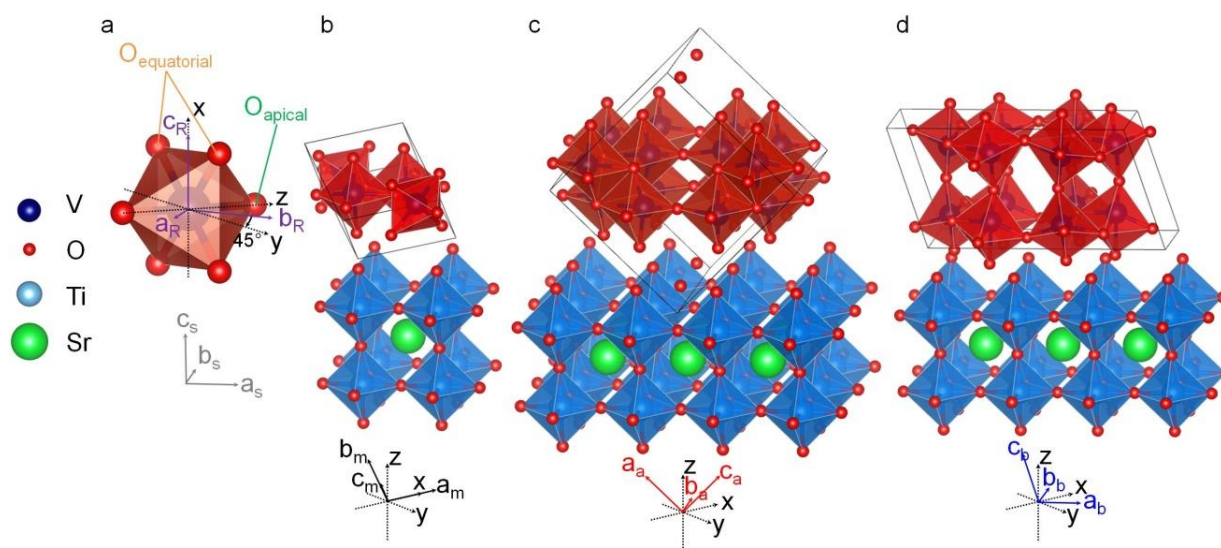
Figure 1 Crystal structure overview and XRD pattern of VO_2 polymorphs. (a) Octahedron is drawn to illustrate various V–O and O-O bond lengths, (b) $VO_2(M)$, (c) $VO_2(A)$, (d) $VO_2(B)$ unit cell arrangement on the $SrTiO_3$.

Based on the relative orbital picture for $VO_2(A/B)$ in comparison with $VO_2(M)$ and $VO_2(R)$, the Hard X-ray Photoelectron Spectroscopy (HAXPES) [5,6] results has been shown in **Figure 3**. While the earlier argument focused on the role of the V-V separation the role of the oxygen in screening the V-V interaction must also be taken in to account. A more detailed study of this screening effect has been reported using XAS measurement [7]. The electronic band structure

modification along the metal-insulator transition in the $VO_2(R/M)$ system, first described by Goodenough, can be qualitatively depicted in term of crystal field environment, i.e., hybridization of the O 2p and V 3d orbitals (p-d overlap) directly correlated to the c_R/a_R ratio. In the metallic state, $VO_2(R)$, depicted in **Figure 1**, the density of state at the Fermi level is a mixture of $d_\parallel$ and π^* orbitals, with a larger contribution of the p-d overlap in the π^* band, which therefore lies at higher energy. Across the MIT, the decrease of the c_R/a_R ratio (**Table** 1), relates to an increase of the p-d orbital overlap, and the V-V dimers leads to a uplift of the π^* band above the E_F and splitting of the $d_\parallel$ band. The electronic band structure in the insulating state $VO_2(M)$, shown in **Figure 3**, results in the cmpletely empty antibonding $d_\parallel^*$ and π^* bands, leading to a band gap of ~ 0.7eV.
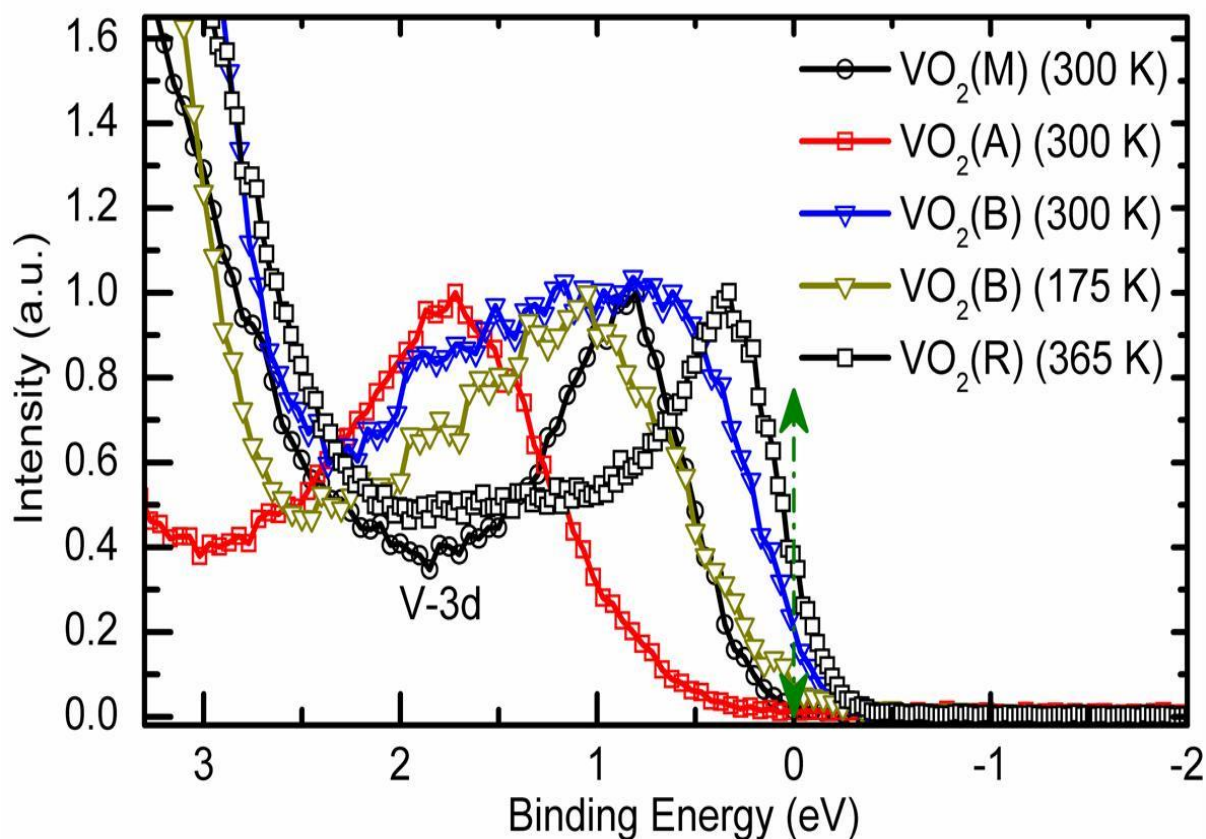
Figure 2 HAXPES spectra taken a photon energy 3.5 keV for VO$_2$ polymorphs grown on STO.

Aetukuri et al.[8] recently reported that a reduction in apical V-O distance, related to an increase of c_R/a_R ratio, in the VO$_2$(R/M) system effects the metallic phase to convert into more insulating phase and the vice-versa respectively. In the metallic phase, VO$_2$(R), with the increase in p-d overlap due to larger c_R/a_R, electrons are transferred from the π^* to $d_\parallel$, leading to shift of π^* band towards higher energy with respect to $d_\parallel$, hence making system more insulating. On the contrary, the increase of the c_R/a_R ratio in the insulating phase VO$_2$(M) up shifts the π^* band towards higher energy while it decreases the $d_\parallel$ band splitting making the system more metallic.
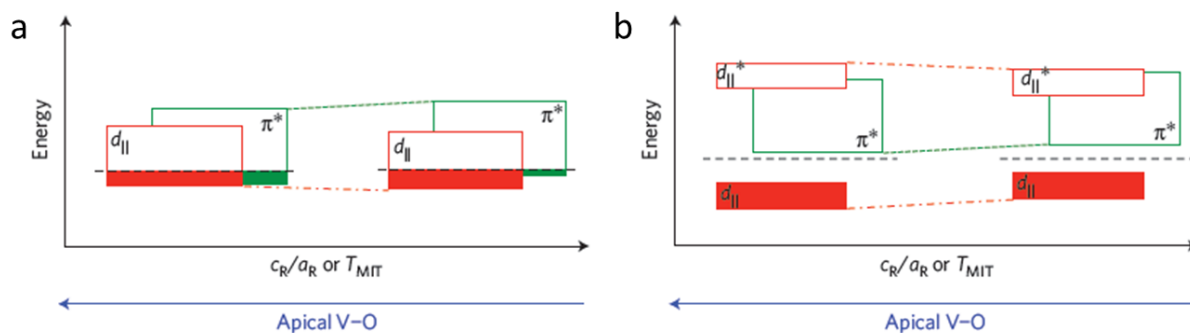

Figure 3 Strain-dependent orbital-occupation changes. The valence electron states in the metallic state (a) and the insulating state (b) [8].

Table 1 V-V and apical V-O distances for VO$_2$ polymorphs related to c_R and a_R values and evaluated c_R/a_R ratio.

Polymorphs	c_R	Apical distance	Average (a_R)	c_R/a_R
VO$_2$(M)(LTP)	V-V=2.6542 Å	V-O=1.7618+2.0509 Å	V-O=1.90635 Å	1.3923
VO$_2$(A)(LTP)	V-V=2.7696 Å	V-O=1.6446+2.2685 Å	V-O=1.95655 Å	1.4155
VO$_2$(R)(LTP)	V-V=2.8509 Å	V-O=1.9630+1.9630 Å	V-O=1.96300 Å	1.4523

| VO$_2$(B)(HTP) | V-V=3.0053 Å | V-O=1.9347+2.0643 Å | V-O=1.99950 Å | 1.5030 |
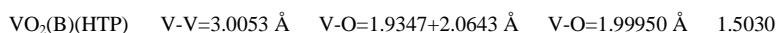
Infrared detection and bolometer:

There is a ever growing demand for highly sensitive photodetcor in the infrared (IR) range for the use in a varity of viable applications, such as transportation, millitary & security [9], industrail machine, waste and toxic pollutant detection, medical imaging[10,11], night vision devices, missile guiding sensors, incursion alarms and reconnaissance. Infrared radiations are part of the electromagnetic spectrum ranging from 0.70 μm (equivalent to frequency 430 THz or photon energy 1.7 eV) to 1000 μm (equivanet to frequency 300 GHz or photon energy 1.24 meV). The infrared transmission permissible by the atmosphere are in the range from mid wave infrared (MWIR) (3-5 μm wavelength). The 8-14 μm wavelength region are under long wave infrared, LWIR region. There are basically two types of IR detectors-photon and thermal. Thermal photodectors, such as bolometers, have emerged as technology of choice, as they do not need cooling. The largets cryogenically cooled detectors, pyroelectric devices, room temperature uncooled detectors, thermopiles and bolometers, offer decreased unit, cost, reduced power utilisation, smaller size, reduced weight, improved reliability, operational convenience. The key parameter that affects the performance of bolometer is linked to its temperature coefficient of resistance (TCR, 2-4 %/ K for state-of-the-art materials), low resistivity to reduce thermal noise (1/f) and joule heating. In the class of Vanadium oxide the VO$_2$ has a large absorbance in mid-far infrared spectrum. Morover, it also has high TCR near its metal insulator transition. W -doped VO$_2$ thin films showed a high TCR 10 %/K with continious sensitivity across MIT. The resistivity of insulating phase was also lower by an order of magnitude (0.1 Ω-cm) [12]. Though

a lot of work has been reported on the fabrication and general properties of the different vanadium oxides, the literature on the use of vanadium oxide in bolometers has been limited. The first report published on using vanadium oxide as the bolometer material was in 1988 by Wood et al at Honeywell Inc.. Wood and Stelzer later revealed that 500 Å thick mixed vanadium oxide (VOx) films had no phase transitions near room temperature but still had a TCR of up to -3 %/K. In 1993, Jerominek et al showed that dc sputtered stoichiometric V_2O_5 films exhibited a TCR of up to 4% and hence could be used for bolometric applications [13].

Flexiable Breath Sensors:

Breath sensing and investigation which is a new field of medical devices, has showed an impending applications in infection diagnose, metabolic monitoring. There are indication that modifications in respiratory rate can be used to guess serious clinical procedures such as cardiac failure. The Feiyi Liao et al; [14] in his paper shows, by utilizing a flexible skin like breath, the real-time monitoring of breath by transfering vanadium dioxide (VO_2) thin films on PDMS substrates. It can easily be covered on the skin under the nose and operate at different temperatures. This is attributed to VO_2's high temperature coefficient of resistance. It shows improved response time and recovery time as fast as 0.5 s. The fast response time suggest that it is feasible to constract a sensor device based on VO_2 for monitoring breath for prevention of apnea syndrome.

Conclussion:

In conclusion, we have shown that the VO_2 may exist in many polymorphs such as VO_2(A, B, and M). The the HAXPES measurements studies suggests that B is semi-metallic, A is

insulating, while M is semiconducting. Thus by controling cationic and anionic atomic arrival rates growth of novel functional polymorphic materials can be achieved. Ultrafast switching speed of VO_2 and its change in resistivity by an order of 4 by temperature, light, chemical and gas stimulli makes it a promising material for sensing and switiching devices.

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