

Vanadium Dioxide and Its Applications

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Abstract — Vanadium dioxide is material that has transition is occur from metal to insulator and insulator to metal and this material is dark blur solid. Above 68° C, this material behaves as a conductor and at the room temperature this material behaves as a insulator. Metal to insulator transition and insulator to metal transition is not only the property of vanadium dioxide, it is used in selector devices. and Vanadium dioxide is a material that could be used in many application such as smart windows and ultrafast transistors, etc. In this paper, we discuss about the metal to insulator and insulator to metal transition, specification, switches characteristics of vanadium dioxide and the application of vanadium dioxide.

Key Words — Vanadium dioxide, MIT, IMT, etc.

I. INTRODUCTION

Vanadium dioxide (VO₂) is a smart material that has recently begun to receive a lot of attention. Vanadium dioxide is material showing a metal to insulator transition (MIT) and insulator to metal transition (IMT) with formula VO₂. It is a dark blue solid. This material behaves as an insulator at the room temperature and it works as a conductor above the 67°C. And in the MIT, At the transition temperature, the resistivity of the vanadium dioxide changes by up to 4 orders of magnitude. At the same temperature, a structural transition takes place and the material changes from a low temperature monoclinic structure to high temperature rutile phase. In unstrained material the transition temperature is about 70°C. MIT is not only the property of vanadium dioxide, it is used in selector devices. VO₂ has a high work function of ~5.2eV. In the insulating state VO₂ is a semiconductor and it has been reported to be either n or p type self-doped.

And in the insulator to metal transition, temperature above 67° C large-amplitude, nonlinear lattice vibrations lead to a tetragonal crystal structure with mobile electrons indicating that the vanadium dioxide is a metal. At lower temperatures, the electrons are localized in the atomic bonds in the distorted monoclinic crystal structure indicating that the vanadium dioxide is an insulator. Vanadium dioxide is a material that could be used in many application such as smart windows and ultrafast transistors, etc. This paper shows the more information about the metal to insulator transition, insulator to metal transition and specification of

vanadium dioxide and various application of vanadium dioxide.

II. PROPERTY OF VANADIUM DIOXIDE

Temperature above 68° C, this material behaves as a conductor and at the room temperature, this material behaves as a insulator.

III. INSULATOR TO METAL TRANSITION OF VANADIUM DIOXIDE

When heated to just above room temperature, the electrical conductivity of vanadium dioxide abruptly increases by a factor of 10,000. Unusually large lattice vibrations, which are the oscillations of atoms about their equilibrium positions, stabilize this highly conductive metallic phase. Changes in the crystal structure and electronic properties of vanadium dioxide occur during its insulator to metal phase transition (V blue; O red). Above 67° C (right), large-amplitude, nonlinear lattice vibrations (phonons) lead to a tetragonal crystal structure with mobile electrons (yellow) indicating that the vanadium dioxide is a metal. At lower temperatures (left), the electrons are localized in the atomic bonds in the distorted monoclinic crystal structure indicating that the vanadium dioxide is an insulator.

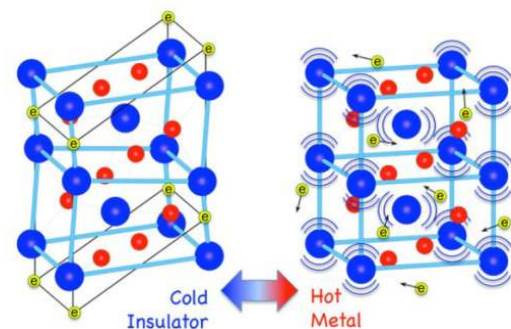


Fig : Transition from insulator to metal

When heated to just above room temperature, the electrical conductivity of vanadium dioxide (VO₂) abruptly increases by a factor of 10,000. Experiments coupled with high-

performance computation reveal how the unusually large lattice vibrations, which are the oscillations of atoms about their equilibrium positions, stabilize this highly conductive metallic phase. Achievement of a quantitative description of phase competition and functionality in metal oxides could pay great dividends in the quest to predictively design materials with unique properties.

Vanadium dioxide (VO_2), a "functional material" that could be used in applications such as smart windows and ultrafast field effect transistors, exhibits an [insulator](#) to metal transition upon heating to just above room temperature. At the transition temperature, its electrical conductivity abruptly increases by a factor of 10,000 and the atomic lattice rearranges from a monoclinic to a tetragonal structure (see figure). A fundamental description of the physical and electronic properties during the transition in VO_2 has remained controversial for over 50 years. Researchers at Oak Ridge National Laboratory employed advanced neutron and x-ray scattering experiments at DOE user facilities, coupled with large-scale first-principles calculations with super computers, to determine the detailed mechanism for the transition. Their studies, published in *Nature*, revealed that the thermodynamic force driving the insulator-to-metal transition is dominated by the lattice vibrations (phonons) rather than electronic contributions. In addition, a direct, quantitative determination of the phonon dispersions was achieved, as well as a description of how changing occupancies in the atomic orbitals participate in the phase transition.

The low-energy phonons were found to change the bonds between atoms (i.e., electron orbitals), allowing some electrons to travel freely at higher temperatures leading to a metallic state. This research demonstrates that an harmonic lattice dynamics play a critical role in controlling phase competition in metal oxides, and provides the complete physical model vital for the predictive design of new materials with unique properties.

IV. METAL TO INSULATOR TRANSITION IN VANADIUM DIOXIDE

Since the discovery of the metal to insulator transition in vanadium dioxide, there has been a lot of interest in this kind of phase transition, as it is accompanied by a large change in the electrical resistivity and optical properties. This transition occurs at $T_t = 340$ K. In single crystals, the resistivity change reaches a factor of 10^5 over a temperature range of 0.1K. Hysteresis associated with this transition is of about 2K. The conductivity jump and the narrowness of the hysteresis loop is a very good indication of a how close the stoichiometry is to vanadium dioxide. Small deviations destroy the sharpness of the transition and increase the

hysteresis width. The crystalline state of the material has an influence too: polycrystalline material will have a broader transition than single crystals. The transition temperature also depends on the crystalline state and oxygen non-stoichiometry. As a rule, the MIT in vanadium dioxide is to a certain degree suppressed in thin films as compared to single crystals. At high temperatures, vanadium dioxide has a rutile-type structure with vanadium atoms equally spaced along the corresponding *cr*-axis. At the transition to the low temperature state, these vanadium atoms pair along the *cr*-axis with a slight twist which leads to a monoclinic symmetry. The gap in the insulating low-temperature phase is about 0.7-1.0 eV (depending on stoichiometry and other factors).

Despite the many efforts made towards obtaining an understanding of their electronic behavior, the vanadium oxides still pose many open questions. This fully applies to vanadium dioxide as far as the nature of transition is concerned. Some authors related its phase transition to a Mott-Hubbard scenario, whereas others attributed it to electron-phonon coupling (a Peierls mechanism) on the basis of the crystal symmetry change. In the recent monograph, it is stated that the metal insulator transition in vanadium dioxide has a combined nature, having the features of both Mott and Peierls transitions. Nonetheless, many experimental facts indicate that the transition might be initiated by an increase in the free charge carrier density (without heating to $T = T_t$ and without affecting the lattice, i.e. not under, for example, doping or pressure) under photo-generation, injection, or high-field generation at switching. These results evidence that the electron-electron interaction is of importance for a correct description of the transition. This is supported by studies of the MIT in thin films of amorphous vanadium dioxide obtained by anodic oxidation.

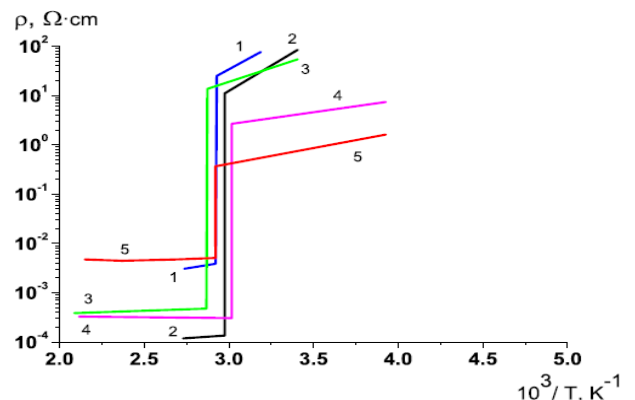


Fig : Resistivity of VO_2 single crystals along the *c* axis as a function of reciprocal temperature.

It should be emphasized however that the question about the MIT mechanism in vanadium dioxide, posed as "either

Mott or Peierls transition", has no sense because, actually, this mechanism is essentially dual. Meanwhile, one should be aware of the fact (and take this fact into account when analyzing the capabilities of vanadium dioxide - based electronic devices) that the initiating mechanism is still the correlation-driven electronic Mott transition. In two-terminal MOM devices with vanadium dioxide, electrical switching due to MIT is Observed. This switching effect is described in terms of the current-induced Joule heating of the sample up to $T = T_t$, which has been confirmed by the direct IR-radiation measurements of the switching channel temperature. In these early works, switching has been observed in single crystals, planar thin-film devices, as well as in vanadate glasses, vanadium dioxide - containing ceramics, V₂O₅-gel films and anodic oxide films on vanadium. When as-prepared samples do not consist of pure vanadium dioxide, preliminary electroforming is required, resulting in the formation of the vanadium dioxide containing channel. For such samples the threshold voltage decreases with temperature and reaches zero.

at $T \sim T_t$.

In this case, the switching mechanism is well described by a simple thermal model often termed as the "model of critical temperature", provided that the ambient temperature T is not much lower than T_t :

$$V_{th} \sim (T - T_t)^{1/2}$$

that is, the squared threshold voltage linearly tends to zero at $T \rightarrow T_t$,

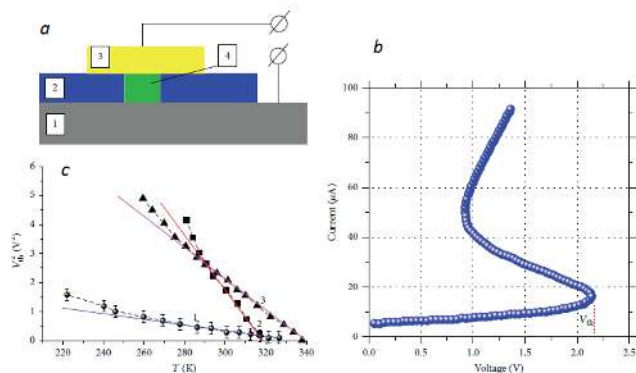


Fig.2. (a) The sandwich switching structure based on anodic vanadium oxide.

(b) the I - V characteristic after electroforming for one of the samples at room temperature.

(c) Squared threshold voltage as a function of temperature for vanadium oxide based switch: 1, 2, 3 – three different samples.

However, at a sufficiently low temperature, and in sandwich thin-film nanostructures (that is, in high electric fields), the possible influence of electronic effects on the MIT should be taken into account. A field-induced increase in charge carrier density will act to screen Coulomb interactions, leading to the elimination of the Mott-Hubbard energy gap at $T < T_t$. This non-thermal (electronic) mechanism of switching in vanadium dioxide is considered in the next section.

Finally, it should be noted that although the switching effect in vanadium dioxide has long been known, recently this problem has received considerable attention once again, primarily due to the promising potential applications in emerging oxide electronics.

V. SPECIFICATION OF VANADIUM DIOXIDE

Chemical formula	VO ₂
Molar mass	82.94 g/mol
Melting point	1,967° C
Boiling point	2,727° C
Density	4.571 g/cm ³ (monoclinic) 4.653 g/cm ³ (tetragonal)
Magnetic susceptibility	+270.0.10 ⁻⁶ cm ³ /mol
Appearance	Deep blue powder
Crystal structure	Distorted rutile (<70° C, monoclinic) Rutile (>70° C, tetragonal)

VI. VANADIUM DIOXIDE SWITCHES CHARACTERISTICS

Devices with just VO₂ between electrodes display symmetric I-V characteristics around zero bias. As the applied bias increases and the current density exceeds approximately 5×10^4 A/cm², volatile switching is observed (Fig.).

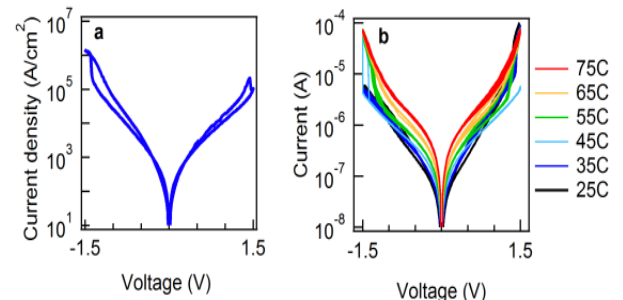


Fig. a. Current density as a function of bias voltage for a 60×60 nm² device with ~ 8 nm VO₂ between TiN electrodes. b. Current as a function of bias measured at ambient temperatures increasing every 10°C from room temperature to 75°C. Note that the hysteresis disappears at 75°C (red line).

the observed volatile switching is consistent with a Joule heating induced MIT. We have reported on the Joule heating induced MIT in two terminal devices with VO_2 .

A simple check of the Joule heating induced MIT is I-V characterization at increasing ambient temperature (Fig). The onset of the switching takes place at lower bias as the ambient temperature increases and above T_C the switching and hysteresis disappear. In the current devices this happens at about $65\text{--}75^\circ\text{C}$ —orange and red curves in Fig. In these simple devices, the current density at 1.5V is higher than $106\text{A}/\text{cm}^2$. Pulsed measurements show device turn-on times shorter than 10ns . The on/off current ratios are approximately 200 when estimated at 1.5V vs. 0.8V making these devices interesting as selectors. We evaluate their performance in full memory cells further in this article.

The MIT enhances the on/off current ratio. By improving the quality of the materials to have a larger magnitude of transition, the on/off current ratios are expected to increase further. However, the downside is the dependence on temperature of the opening voltage of the selector. It is also important to emphasize that these selectors are current not voltage controlled and a certain current density is needed to induce the MIT. However, this current density could be decreased by isolating the devices thermally.

VII. APPLICATIONS OF VANADIUM DIOXIDE

[1] Thermochromism :

Thermochromism in vanadium oxide materials represents another possibility for smart coating in energy efficient buildings. Thin film of VO_2 is one of the most durable thermochromic materials undergoing IMT at 65°C , which is close to its bulk value. However, several techniques such as (a) doping with suitable materials such as tungsten(W), Molybdenum (Mo), Niobium (Nb) and Rhenium (Re) (b) fluorination: replacement of some oxygen atoms by fluorine (c) mechanical stress induced by an over layer, can lower the transition temperature making it quite suitable as a window coating. Figure shows the normal transmittance spectra for VO_2 film at temperatures below and above T_C , measured in the wavelength range of 0.3 to $2.5\ \mu\text{m}$. For higher wavelengths (the near infrared region, greater than $\sim 0.7\ \mu\text{m}$), the transmittance is modulated considerably as a function of temperature as compared to the low wavelength region, which is central to an efficient, energy controlling smart window. It means, for wavelengths near infrared, temperature dependent modulation of transmission spectra is observed while maintaining transparency to visible light. At the same time, the near infrared reflectance increases appreciably above T_C inline with the decrease in corresponding transmittance. For use of materials in glazing technology, transmission of light and

also the reflectivity (in most applications) are very important. Ideally, a glazing material transmits solar radiation from exterior to interior when the “window” conducts heat out of the building during daytime in the winter and reflects solar radiation when it conducts heat into the building during daytime in the summer.

Later, in an attempt to improve the material performance, Granqvist studied the transmittance spectra by replacing some of the oxygen with fluorine at various temperatures as shown in Figure.

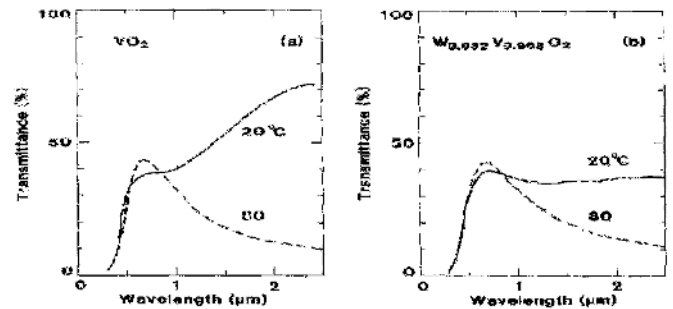


Fig : Transmittance spectra for (a) VO_2 and (b) w-doped VO_2 films at temperature below and IMT

The transition temperature T_C of W-doped thin film of VO_2 drops almost linearly when the level of doping increases. Sobhan et al. showed that W-doped film, with the composition of $\text{W}_{0.032}\text{V}_{0.968}\text{O}_2$, undergoes IMT at $\sim 32^\circ\text{C}$ and the normal transmittance for this structure varies as shown in Figure. While doping decreases T_C to a comfort temperature, the thermochromic modulation of infrared transmittance, on the other hand, becomes small for the doped sample making it less useful for the energy control in smart windows.

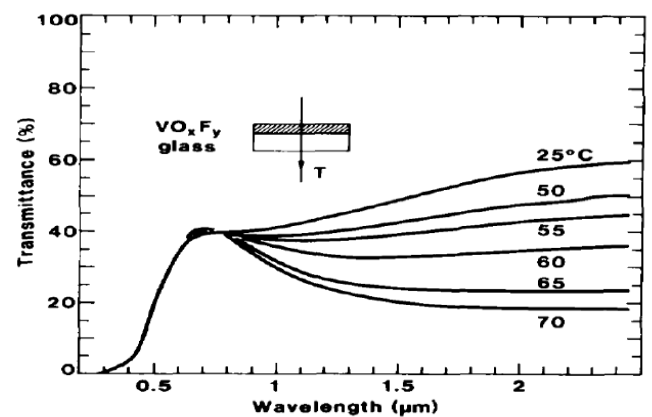


Fig : Normal transmittance spectra for vanadium oxyfluoride film at various temperatures

For a $0.13\ \mu\text{m}$ thick VO_xF_y coating, the T_C was found to decrease to 52°C and the near infrared transmission was found to be strongly temperature dependent. In this case, visible transmittance was found to be 28% , irrespective of

the temperature and the solar transmittance was noticed to be ranging from 35% at room temperature to 28% at 70°C. The decrease in T_c and increase in transmittance in the visible spectrum show that VO_2 can be a very good candidate for thermochromic smart window application.

[2] Resonance tuning using vanadium dioxide :

The capacity of a metamaterial to interact with radiation of certain frequencies in a strong and a special manner is known as its so called resonant behavior. Scientists have been able to device metamaterials working at a single frequency or narrow band in the microwave or infrared regions of the spectrum, terahertz domain and even in the lower end of the visible spectrum. Recently, research in metamaterials is progressing by overcoming the limitations of bandwidth and the dynamic control of metamaterial's properties in real time has been achieved either through non linear responses or externally tunable components. Particularly, after Pendry et al. introduced the concept of split ring resonator (SRR), scientists have constructed metamaterials using SRR and further research has been conducted towards the creation of tunable metamaterials using SSR. It is the dynamically controllable metamaterial that allows us to take advantage of the full potential of its peculiar properties. Shadrivov et al. "took the first step towards the creation and study of fully controlled, tunable nonlinear metamaterial systems through the study of the tunability and self-induced nonlinear response of a single SRR." In his study, Shadrivov used a specially doped p-n junction diode: the variation of diode capacitance led to the change in resonance conditions of the SRR in microwave region. Significant progress has been made towards the study of tunable metamaterials and has been core research in modern science and technology.

Particularly, Driscoll et al. have achieved dynamic tuning, with a tuning range of at least 20%, in the near infrared region by using a device made of a 100nm thick gold SRR array and 90nm thick VO_2 film grown on sapphire substrate. Both the gold and VO_2 layers are much thinner than the periodicity of SRR array (20 m) and are said to form an effective (single) material layer. This structure is now considered as a hybrid metamaterial since it has the combined property of both SRR and VO_2 . It is well established that VO_2 undergoes insulator metal phase transition (IMT), on a sub-picosecond timescale, as a result of some external stimuli. At the onset of the phase transition, nanoscale (5 -10nm) metallic rains or "puddles" emerge from the insulating host of VO_2 . The percolative nature of the phase transition causes divergent permittivity. This drastic change in optical behavior has a strong effect on the resonance frequency of the SRR metamaterial - the local electromagnetic fields of the SRR gets modified as if a tunable dielectric were inside a capacitor. It is found that the

resonance frequency of the hybrid system varies inversely with the change in permittivity of VO_2 . Furthermore, the decrease in metallic puddles damps the resonance amplitude.

Wen et al. have proposed VO_2 cut-wire fabricated on silica-glass substrate as a terahertz metamaterial. The advantage of cut-wire resonator over SRR is that it exhibits simple yet broad band response. Furthermore, cut-wire resonators are easy to design and fabricate. Motivated by the 4 orders of magnitude change observed in the dielectric properties of VO_2 during IMT, researchers are rigorously busy to find out whether the same order of magnitude change in extinction can be obtained in metamaterials. Furthermore, due to the pronounced hysteresis present in phase transition, scientist are interested in designing memory metamaterials where the metamaterial tuning persists even if triggering stimulus for IMT disappears. A wide variety of structures based on VO_2 phase transition have been studied in recent years due to the versatile properties of VO_2 . More interestingly, some researchers have identified VO_2 as a natural disordered metamaterial.

VIII. ADVANTAGES OF VANADIUM DIOXIDE

- Layer of a vanadium dioxide is thinner
- Transition switching of this material is faster
- Due to the IMT and MIT property, it is used in many applications

CONCLUSION

This paper is on a vanadium dioxide material and their applications. we noted that above 67° C vanadium dioxide is behaves as a conductor and at the room temperature it behaves as a insulator. From the characteristics , we noted that Joule heating induced metal to insulator transition in a devices with VO_2 and If we improve the quality of a material we have got larger magnitude of transition And this transition is ocure on a sub-picosecond and thermochromism in vanadium dioxide is useful for smart coating in energy efficient buildings. Resonant tuning is possible by using the vanadium dioxide.

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