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Doped vanadium dioxide with enhanced infrared modulation

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Defence R&D Canada – Valcartier
Technical Memorandum
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Abstract

The purpose of this memorandum is to investigate the effect of selected dopants (namely tungsten (W) and W-titanium (Ti)) on semiconducting to metallic phase transition of the vanadium dioxide (VO_2) in the longwave infrared (LWIR) range. The specific properties investigated in this study are the transition temperature T_t, the electrical resistivity and the optical transmittance. The fabrication of films was done by magnetron radio-frequency sputtering technique. The results indicated that T_t of our undoped VO_2 films is ~ 65°C and can be brought down to ~ 15°C with ~2.1 at.% of W doping. When the film is in the metallic phase (above the T_t), the electrical resistivity of undoped films drops three orders of magnitude while it drops two orders of magnitude in W-doped films with an electrical hysteresis of less than 10°C in both cases. Co-doping with W (~1 at.%) and Ti (of ~6 at.%) greatly modifies the resistivity slope, the latter showing no abrupt transition but rather a smooth, linear transition over a large temperature range with T_t near 55°C. The resistivity drop upon heating of the co-doped film is less than one order of magnitude but its electrical hysteresis is totally suppressed. Regarding optical transmittance, all films under investigation have high transmission (>75%) at room temperature (RT) in the IR region. In the metallic phase (above T_t), undoped films become nearly opaque with a transmittance in LWIR of less than 5%, less than 20% for W-doped films and less than 35% for those co-doped with W and Ti. The latter films give a barely noticeable optical hysteresis (~2°C). The results of this study show the possibility and efficiency of doping VO_2 to modulate the transmission in the longwave infrared range and vary the hysteresis.

Résumé

Le but de ce mémorandum est d'étudier l'effet de dopants (ici le tungstène (W) et le W-titane (Ti)) sur les propriétés de transition semi-conducteur-métal du dioxyde de vanadium (VO_2) dans le spectre infrarouge lointain. Les propriétés spécifiques étudiées ici sont la température de transition T_t, la résistivité électrique et la transmittance optique. Les films ont été fabriqués par pulvérisation magnétron radio fréquence (RF). Les résultats indiquent que la T_t des films VO_2 non dopés est de ~ 65°C et peut-être abaissée à ~ 15°C avec l'ajout de W (~2.1 at.%). Lorsque la température des films non dopés dépasse T_t, la résistivité électrique diminue de trois ordres de grandeur, tandis que dans ceux dopés au W on observe une diminution de deux ordres de grandeur. Dans les deux cas, l'hystérésis demeure inférieure à 10°C. Le co-dopage W (~1 at.%) –Ti (~6 at.%) change quant à lui significativement l'allure de la courbe de résistivité, laquelle ne montre plus de transition abrupte mais plutôt une transition pratiquement linéaire qui s'étend sur un large domaine de température avec une T_t près de 55°C. La baisse de résistivité lors de la transition est encore moins marquée ici avec un changement de moins d'un ordre de grandeur. Cependant, l'hystérésis électrique est complètement supprimée. En ce qui concerne la transmittance optique, tous les films étudiés ici sont transparents (>75%) dans l'infrarouge à température ambiante. En phase métallique (au-dessus de T_t) la transmission dans l'infrarouge diminue énormément avec moins de 5% de transmission pour les films non dopés, moins de 20% pour ceux dopés au W, et 35% pour ceux co-dopés W-Ti. Dans ce dernier cas, l'hystérésis optique est pratiquement éliminée (~2°C) avec l'ajout du Ti. Cette étude démontre l'efficacité du dopage du VO_2 pour moduler la transmission dans le spectre de l'infrarouge lointain.

Executive summary

In some military surveillance and civilian electro-optical (EO) systems, there is a need to use an optical switch to modulate the incident optical signal. These modulations could be simply an on-off action (digital) or a gradual change of transmission (analog). Vanadium dioxide (VO_2) is identified as a suitable material where modulation is required because of its ability to change its phase from semiconducting to metallic (and, consequently, its electrical and optical properties) in a sudden and reversible way at a specific temperature coined the transition temperature (T_t). The latter (~68°C) is highly convenient for all practical purposes since it lies near room temperature.

An example of application where digital modulation (on/off) is needed and where VO_2 films could be exploited is a digital light valve array in a miniature infrared dispersive spectrometer as in the TIF project 15ea03. In the latter case, the VO_2 windows will act as open or closed valves to multiplex the incoming infrared signal. As a result, the optical throughput can be kept high (multiple slit openings) for improved signal-to-noise ratio while individual narrow slits can still be used for acceptable spectral resolution. Other potential applications for VO_2 films, this time for analog modulation, include smart radiator devices where heat dissipation or exchange for thermal control is needed (such as micro or nanosatellites) and IR signature management for vehicles allowing adaptive camouflage according to environmental or temperature changes throughout the day.

The purpose of this memorandum is to investigate the effect of selected dopants (namely, tungsten (W) and W-titanium (Ti)) on semiconducting to metallic phase transition of the vanadium dioxide (VO_2) in the longwave infrared range (LWIR). The specific properties investigated in this study are the transition temperature T_t, the electrical resistivity and the optical transmittance. The fabrication of films was done by magnetron radio-frequency sputtering technique. The results indicated that T_t of our undoped VO_2 films is ~ 65°C and can be brought down to ~ 15°C with ~2.1at.% of W doping. When the film is in metallic phase (above the T_t), the electrical resistivity of undoped films drops three orders of magnitude while it drops two orders of magnitude in W-doped films with an electrical hysteresis of less than 10°C in both cases. Co-doping with W (~1 at.%) and Ti (of ~6 at.%) greatly modifies the resistivity slope, the latter showing no abrupt transition but rather a smooth, linear transition over a large temperature range with T_t near 55°C. The resistivity drop upon heating of the co-doped film is less than one order of magnitude but its electrical hysteresis is totally suppressed. Regarding optical transmittance, all films under investigation have high transmission (>75%) at room temperature (RT) in the IR region. In the metallic phase (above T_t), undoped films become nearly opaque with a transmittance in LWIR of less than 5%, less than 20% for W-doped films and less than 35% for those co-doped with W and Ti. The latter films give a barely noticeable optical hysteresis (~2°C). The results of this study show the possibility and efficiency of doping VO_2 to modulate the transmission in the longwave infrared range.

The results in this study show that doped VO_2 thin films are promising materials to modulate the transmission in the longwave infrared range. Future work will include pursuing tests of electronically induced transition (electrochromic mode) and conducting additional doping

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tests. A new multispectral and tunable uncooled IR detector design has also been envisaged and a proposal for such a new detector has been recently submitted [1].

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Sommaire

Pour certains systèmes militaire et civils de surveillance électro-optique (ÉO), l'utilisation de commutateurs optiques est nécessaire pour moduler le signal optique entrant. Ces modulations peuvent servir simplement comme mode d'ouverture ou de fermeture (numériques) ou pour des changements graduels de la transmission (analogique). Le dioxyde de vanadium (VO_2) est considéré comme le matériau adéquat à utiliser là où la modulation est nécessaire car il possède la capacité de passer d'une phase semi-conductrice à métallique (suivi par ricochet des changements dans les propriétés optiques et électriques) d'une façon soudaine et réversible à une température donnée appelée température de transition (T_t). Cette dernière (68°C) est très intéressante en vue d'applications pratiques, car elle est située près de la température ambiante. Un exemple d'application où la modulation numérique est requise et où les films de VO_2 seront utilisés est dans la fabrication d'un réseau numérique de valves optiques pour le microspectromètre du projet FIT 15e03. Dans ce cas particulier, les fenêtres optiques VO_2 agissent comme des valves ouvertes ou fermées pour le multiplexage du signal infrarouge entrant. D'autres applications potentielles, cette fois-ci pour moduler de façon analogique le signal, incluent des dispositifs intelligents pour radiateurs (tels que pour les micro ou nanosatellites) lesquels doivent exercer un contrôle thermique par échange de chaleur ainsi que l'adaptation de la signature infrarouge des véhicules pour s'adapter aux changements environnementaux ou climatiques qui se modifient au cours d'une journée.

Le but de ce mémorandum est d'étudier l'effet de dopants (ici, le tungstène (W) et le W-titane (Ti)) sur les propriétés de transition semi-conducteur-métal du dioxyde de vanadium (VO_2) dans le spectre infrarouge lointain. Les propriétés spécifiques étudiées ici sont la température de transition T_t, la résistivité électrique et la transmittance optique. Les films ont été fabriqués par pulvérisation magnétron radio-fréquence (RF). Les résultats indiquent que la T_t des films VO_2 non dopés est de ~ 65°C et peut être abaissée à ~ 15°C par l'ajout de W (~2.1 at. %). Lorsque la température des films non dopés dépasse T_t, la résistivité électrique diminue de trois ordres de grandeur, tandis que chez ceux dopés au W on observe une diminution de deux ordres de grandeur. Dans les deux cas, l'hystérésis demeure inférieure à 10°C. Le co-dopage W (~1 at.%) –Ti (~6 at.%) change quant à lui significativement l'allure de la courbe de résistivité, laquelle ne montre plus de transition abrupte mais plutôt une transition pratiquement linéaire qui s'étend sur un large domaine de température avec une T_t près de 55°C. La baisse de résistivité lors de la transition est encore moins marquée ici avec un changement de moins d'un ordre de grandeur. Cependant, l'hystérésis électrique est complètement supprimée. En ce qui concerne la transmittance optique, tous les films étudiés ici sont transparents (>75%) à température ambiante. En phase métallique (au dessus de T_t), la transmission dans l'infrarouge diminue énormément avec moins de 5% de transmission pour les films non dopés, moins de 20 % pour ceux dopés au W, et 35 % pour ceux co-dopés W-Ti. Dans ce dernier cas, l'hystérésis optique est pratiquement éliminée (~2°C) par l'ajout du Ti. Cette étude démontre l'efficacité des dopants étudiés pour moduler la transmission dans le spectre de l'infrarouge lointain du VO_2. Les travaux à venir incluent des tests (présentement en cours) de transition de phase induite de façon électronique (mode électrochrome) ainsi que la poursuite d'ajustement des propriétés de transition du VO_2 par

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dopage. Un nouveau concept pour un détecteur non refroidi multibande et ajustable dans l'IR a été envisagé et une proposition de projet pour un tel détecteur a été soumise récemment [1].

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1. Introduction

In some military surveillance and civilian electro-optical (EO) systems, there is a need to use an optical switch to modulate the incident optical signal. These modulations could be simply an on-off action (digital) or a gradual change of transmission (analog). A few examples are optical fiber switches for telecommunications and a digital light valve array in a miniature infrared dispersive spectrometer as in the TIF project 15ea03. In the latter case, the VO_2 windows will act as open or closed valves to multiplex the incoming infrared signal. As a result, the optical throughput can be kept high (multiple slit openings) for improved signal-to-noise ratio while individual narrow slits can still be used for acceptable spectral resolution. Multispectral and tunable uncooled IR detector development could also benefit from optical modulation enhancement capability.

Some of the current and emerging technologies propose novel solutions on optical switching such as micro-shutters, liquid crystal based and microelectromechanical systems (MEMS) based devices. Nevertheless, there are limitations in these technologies. Piezo-electric based micro-shutters are mechanical components that are subject to mechanical failure. They also have limited switching speed and require high voltage for the actuation. Liquid crystal technology is mature but, it suffers the constraints of low switching speed in the sub-millisecond range and relatively high infrared (IR) absorption [2] that is disadvantageous in IR systems. In the case of MEMS based devices (e.g. micro-mirror devices), a good on/off contrast at modest speed could be achieved. However, the design complexity at device level (microstructures surrounding the mirrors), system level (overall system design and optical alignment challenges due to reflective configuration only), and final device packaging are some of the challenges preventing a wider use of this technology.

In the meantime, an attractive technology is being studied with increasing attention: the chromogenic materials based devices for optical switching applications. In the case of vanadium oxide, it possesses potentially suitable spectral characteristics, optical contrast, modulation linearity, and switching speed with proper design.

The purpose of this memorandum is to investigate the effect of selected dopants (namely tungsten (W) and W-titanium (Ti)) on VO_2 semiconducting-metallic transition capability in the longwave infrared range (LWIR). Such tailoring of the intrinsic properties increases the number of potential applications for VO_2 films as a functional component in electro-optic systems. The specific properties investigated in this study are the T_t, the electrical resistivity and the optical transmittance. Experiments were designed and performed on various film composition to extract this information.

In the following, the properties of VO_2 and considerations on device design and configuration will be discussed in Chapter 2. In Chapter 3, the experiment details will be presented followed by results and conclusion. The work was supported under Work Breakdown Element 15ea03 entitled “Miniature IR spectrometer”. The information in this document presented some of the work performed on the project at DRDC Valcartier between March 2004 and November 2006.

2. Properties of vanadium oxide and device configurations

2.1 Properties of vanadium dioxide

The chromogenic material family encompasses many different materials that have the capability of reversibly modifying their optical properties upon specific stimulation whether it is temperature, pressure, electric field or ion injection. Materials whose optical changes are triggered by temperature and electric field are called thermochromism and electrochromism, respectively. Among all these materials, vanadium dioxide (VO_2) has drawn a lot of attention since its semiconducting-to-metallic phase transition was first observed by Morin in 1959 [3]. The particularity of VO_2 with respect to other chromogenic materials is that the mechanism responsible for its optical modulation is a phase transition triggered at a transition temperature T_t close to room temperature (RT): T_t ~68°C for undoped single crystal. VO_2 has a monoclinic lattice and an energy band gap of ~0.7eV in semiconducting state. The energy gap is mainly determined by the crystal structure and not by electron correlation [4]. At temperature above the transition threshold, this energy band gap vanishes as the lattice becomes tetragonal and the film behaves as metal. When temperature is brought back below T_t, thermal hysteresis is observed in VO_2 polycrystalline films [5]. Since it is problematic to operate a device in this hysteretic region (less predictable performance), the device would operate at either semiconducting or metallic state, or one could tailor the film with minimum hysteretic effect.

The semiconductor-to-metal transition of VO_2 can also be triggered at $T<T_t$ if a critical electron density is achieved in the VO_2 film. The required charge density for the electrochromic transition of VO_2 is related to a critical electron density similar to the classical Mott metal-insulator transition given by $(n_c)^{1/3}\ \alpha_H \approx 0.25$ where n_c is the critical electron density. α_H is the Bohr radius in the cases of doped semiconductors and high-temperature superconductors while this term is equal to the coherence length ξ in the case of compounds of transition and rare-earth metals such as VO_2 where $\xi=4\pi\varepsilon_o\varepsilon\hbar^2/m^* e^2$ [6]. ε is the dielectric constant, ε_o is the permittivity of free space, $\hbar$ is the reduced Planck's constant, m^* is the effective mass of electron and e is the charge of an electron. In the case of VO_2, ε is ~100 and $m^*=3m$ where m is the electron rest mass [6]. This leads to ξ = 17.7Å. With this value, this results in $n_c \approx 10^{18}$ cm^{-3}. The value n_c was experimentally proven [7].

The critical electron density can be established by mechanisms such as electrostatic charge accumulation or electron injection under deep depletion in the VO_2 film (both in electrochromic mode). Coulomb screening of electron-electron interactions is induced at the critical electron density state and this screening is sufficient to shield the effect of the ionic core leading to no bound state. The energy gap will disappear and the film becomes metallic. If the density falls below this critical value, the Coulomb screening will be weakened and electrons again will interact with the ionic sites. As a result, the film returns to semiconducting state.

The speed of phase transition of VO_2 has been experimentally measured to be in the order of nanoseconds [7] and even 100 femtosecond [8] under photoexcitation. Undoped thin film VO_2

in semiconducting state is fairly transparent between 1 μm (~40% transmission) and 12 μm (~80% transmission) and it is nearly opaque (few % transmission) from 1 to 12 μm in metallic state, covering the main IR spectrum of military interests.

2.2 Design consideration of VO_2 based optical switch: thermochromic and electrochromic

As described above, semiconducting-to-metallic transition in VO_2 can be used for optical switching. In thermochromic mode, a simple IR optical switch may consist of a VO_2 film deposited on a Si substrate which has an average optical transmission of 40% between 1.1 and 12.0 μm. An external heater can be used to raise the VO_2 film temperature to T_t. "Heaterless" schemes can be achieved as well by passing an electrical current through the VO_2 film through external electrodes made to the silicon and the VO_2 film. It is understood that thermally induced transition is relatively slow and the switching speed depends on the heater power and the thermal mass. The time required for heating up and cooling down could be reduced by reducing the thermal mass around the VO_2 film. For example, a VO_2 film could be fabricated on a suspended SiO_2 or Si_3N_4 microbridge, similar to microbolometer design. Due to the reduced thermal mass and increased thermal isolation, millisecond switching or faster is possible.

In electrochromic mode, electronically induced transition could allow microseconds and even nanoseconds switching speed. This higher response speed is more favorable in many applications. An electronically switching device typically consumes less power than a thermally switching device and is more energy efficient. VO_2 phase transition triggered by pure electrochromic effect has been demonstrated with configurations of two-terminal electronic switch and three-terminal transistor device [7]. There were other reports claiming optical switching demonstrations by pure electrochromic induced transition. The fact is that, unfortunately, it is less trivial to realize an optical switching device operating in electrochromic mode. The main reason is that it is difficult to isolate thermochromic and electrochromic effects in electrochromic experiments where, for example, Joule heating could play a role within the presence of leakage current under strong electrical field. Electrochromic tests are currently under investigation in the Micro Systems Laboratory of DRDC Valcartier and results should be available shortly.

In a stand point of pure applications, it is considered successful if an optical switch possesses the required speed, spectrum characteristics, on-off contrast, transition voltage, regardless if the transition is caused by effects of thermochromic, electrochromic, or both. With an understanding of the properties of VO_2, a proper switch design can maximize the device performance while avoiding triggering the inherent problems mentioned above. For example, an electrochromic/thermochromic optical switch is useful with sufficient switching speed, throughput and contrast as long as its IR self-emission due to heating is either negligible or could be subtracted. One design strategy is to tailor the phase transition point and the electrical-optical properties by impurity doping of VO_2 films. This approach will be discussed in the following section.

2.3 Doping of vanadium dioxide

Impurity doping of donors or acceptors can influence the semiconducting-metallic transition properties of VO_2 films. Studies [9-14] showed that doping VO_2 films with impurities such as Nb, Ta, Mo, W (n-type doping) will lower T_t while doping with Al, Cr, Fe, Ti (p-type doping) will rise T_t. In an n-type doped VO_2 film, the electron critical density n_c could be achieved at lower electron injection level or weaker electric field due to the elevated electron concentration. Among various n-type dopants, W was chosen because it is the most effective to decrease T_t: only one atomic percent of W is needed to decrease T_t by 23°C. However, the use of n-type doping will degrade the IR transmission in semiconducting state as the film becomes more conductive and metallic. A balance must be reached between the lowest acceptable transmission and the highest acceptable T_t or voltage.

Consequently, to address this point, we are exploring the effects of W doping VO_2 on phase transition and electrical-optical properties. Another interesting avenue for tailoring VO_2 properties is codoping. Dr Mohammed Soltani (INRS-EMT) recently showed [14] that Ti-W codoping suppresses both the optical (at λ=2.5 μm) and electrical hysteresis with a T_t at ~60°C. This feature is desired in analog sensors such as pressure and temperature sensors where zero hysteresis is needed. The Micro Systems Laboratory of DRDC Valcartier is investigating codoping as well.

3. Experimental procedure

In general, a film of ~0.1 to 0.2 μm is sufficient to provide significant optical modulation. The contrast also depends on the composition and the microstructure of the films that are very much related to the fabrication techniques.

3.1 Thin film fabrication & characterization

3.1.1 Thin film structure

The device configuration used in our experiments consists of a sandwiched configuration of silicon-silicon oxide-VO_2. The silicon bottom layer consists of a 500 μm-thick lightly n-doped (1-10 Ω-cm) silicon wafer, so that electrically it behaves like a metal, but is still transmissive in IR. The middle layer is a 100 nm-thick thermally grown (dry) oxide that provides electrical isolation and finally the VO_2 layer is the semiconducting part. The device was fabricated on a ~1 cm^2 wafer piece.

3.1.2 Deposition

All VO_2 thin films were deposited by reactive radio frequency (rf) magnetron sputtering technique. For undoped VO_2 films, a 2-inch vanadium target (99.7% purity) was used. Same size W-doped and W-Ti co-doped targets were purchased from Plasmaterials Inc. with a composition (starting material) of 98.5 at.% of vanadium and 1.5 at.% of tungsten for W-doped vanadium target and 86.5 at.% of vanadium, 12 at.% of titanium and 1.5 at.% of tungsten for W-Ti co-doped vanadium target. All three were mounted on a planar magnetron gun. A substrate was positioned on a substrate holder equipped with heating element. The substrate temperature was kept at 500°C during deposition.

High purity Ar gas was used as the ion supplier gas for the plasma formation and O_2 gas as the reactive gas. The gases were introduced through separate mass flow controllers. The partial pressure of O_2 strongly affects the stoichiometry of VO_2 and must be controlled precisely. Using our sputtering facility, the gas flow for undoped VO_2 films flow is set at 1.29 Standard Cubic Centimeter per Minute (SCCM) and 82.6 SCCM, respectively, for O_2 and Ar. For the doped films, the optimized gas flow remains the same for Ar but becomes 1.8 SCCM for O_2 for W-doped films and 2.0 SCCM for W-Ti co-doped. A significant phase transition and contrast could be observed and characterized with these gas parameters. Other parameters will lead to films with no phase transition, insulating films, or metallic films. It is important to note that the oxygen gas flow rates might need to be adjusted slightly when some environmental conditions (such as the moisture content of the air) vary slightly. The chamber pressure during deposition was maintained at 10mTorr and the magnetron power was set at 50 W. The typical deposition rate is 9 nm per min for VO_2 films and half this value for doped films. After deposition, the as-deposited film was cooled down in ambient atmosphere. The grain orientation of the VO_2 films was measured by XRD at an external facility. The crystallographic plane (011) was found to be parallel to the surface of the film.

The doping concentration of the deposited this films was estimated from X-ray photoelectron spectroscopy (XPS) at room temperature on an Axis-Ultra system from Kratos at University

Laval equipped with an Al monochromatic source. Etching of the film surface with an argon ion beam was done in order to remove the naturally formed carbon contamination layer (~10 nm thick). These carbon atoms, often found as hydrocarbide molecules, are not doped elements in the atomic structure of the VO_2 and therefore removal of the contamination layer enhances the precision of spectroscopy quantification. $W4p_{3/2}$ bands and Ti_{2p} were used for concentration calculations. Other peaks were not used due to either their smallness or their interference with other elements' peaks.

3.1.3 Thickness & resistivity measurements

The film thickness was determined by surface profilometry (Dektak 3030) instrument and was typically ~ 0.12-0.15 μm. The electrical resistivity was measured using the standard four-point probe technique (Lucas Lab, model 302). The change in resistivity was recorded every second for both heating and cooling cycles from RT to 100°C. Gradual and constant incrementation of temperature is not easily achieved. The heating and cooling rates varied typically as follows: 12°C/min near RT and 6°C/min at high temperatures. Similarly, the cooling rate was typically of 2°C/min at high temperatures and to 0.3°C/min near RT.

3.1.4 Optical transmittance in thermochromic mode

The transmittance of the VO_2 thin film substrates in the NIR (1 to 2μm) and LWIR (8 to 12μm) was measured using an ARC SpectraPro-300i spectrometer and a sample heater coupled to a temperature controller UP150 equipped with ramp up capability. A heating rate of 1°C /min was used. A pyroelectric detector and a Mercury Cadmium Telluride (MCT) detector were used respectively for NIR and LWIR range, while a Xenophot lamp and a glow bar were used as light sources for optical measurements in NIR and LWIR. Doped thin films were measured only at LWIR.

4. Results of the VO_2 films in thermochromic mode and discussion

The specific properties investigated in this study are the T_t, the electrical resistivity and the optical transmittance. The following sections show the results obtained of the films under investigation herein, respectively VO_2, $W_xV_{1-x}O_2$ and $W_xTi_yV_{1-y-x}O_2$ films.

4.1 Electrical resisitivity

When subjected to a rise in temperature, the undoped VO_2 polycrystalline films show a significant and reversible drop in electrical resistance (about three orders of magnitude). This abrupt change corresponds to semiconducting-to-metallic phase transition occurring typically near 65°C in our samples (Figure 1). The transition temperature corresponds to the temperature where the largest slope change is observed on the heating curve. When the slope profile is less sharp, taking the midpoint of the transition region as T_t is also acceptable. Between ~55 to ~75°C, the cooling and heating curves diverge, indicating a temperature hysteresis.

The temperature coefficient of resistance (TCR) is a critical parameter examined when one must choose the heat sensing material for IR detection in bolometeric focal plane arrays.The larger the TCR, the higher the IR sensitivity. However, the use of VO_2 as a heat sensing material within the hysteretic region of large TCR must be avoided since it is less predictable where "sub-loops" may emerge [5]. TCR is defined as the slope of the log resistivity.

$$TCR = (1/R_{RT}) \times (dR/dT) \quad (1)$$

R_{RT} is the resistance at RT. The TCR value for our VO_2 films is estimated using Eq.(1) to be –2% / °C at room temperature. This value is in agreement with those reported in the open literature.

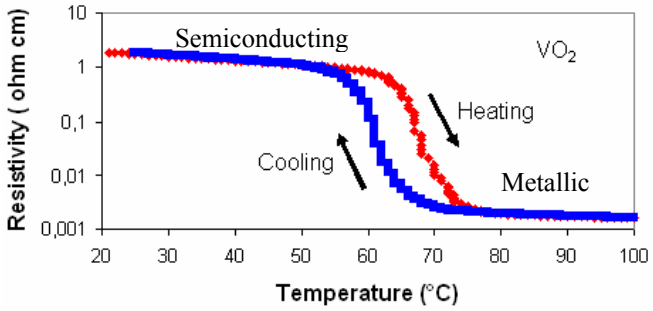

Figure 1 : Change of electrical resistivity of undoped VO_2 film due to thermally induced semiconducting to metallic phase transition.

The addition of dopants modifies significantly the characteristics of the temperature-dependent electrical resistivity. Doping our sputtered VO_2 film with W atoms shifted the transition temperature from ~65°C to RT while the electrical hysteresis width remains less than 10°C, as shown in Figure 2a. Since the transition temperature seemed to be at room

temperature, an attempt to confirm this was done by cooling the film and recording resistivity change from 0°C. Liquid nitrogen (LN) was poured in a LN dewar to which the sample was attached. Heating from RT was provided by an internal built-in heater in the dewar. One can observe in Figure 2b that T_t is between 15 and 18°C with a drop of resistivity of two orders of magnitude. The TCR value near 0°C is -3%/°C and it rapidly increases up to -8%/°C at 15°C.

It is reported that the addition of one W atom in the VO_2 lattice structure breaks up the V^{4+}-V^{4+} pair and form 2 V^{3+} ions which in turn reduce T_t in a proportion of 12 ± 1° C per V^{3+} percent; in other words, about 23°C per 1 at.% of W atom. Consequently, the temperature shift observed in our film (from ~65°C to ~15°C) leads to an estimated W concentration of 2.2 at.%.

XPS elemental analysis was done on the doped samples [15-16]. Stoichiometric ratio between V and O atomic concentration reveals that V_2O_5 (an insulator) has grown at the very surface of the W-doped sample (see Table 1). This is not unusual as the surface of polycrystalline vanadium oxide often consists of the higher order oxide. Depth profile by argon ion etching was performed in order to remove this thin V_2O_5 layer and investigate the W concentration in the film. At 9 nm below the surface, VO_2 stoichiometry is present and the W concentration is 2.1 at.%. This value slightly increases to 2.8 at.%, once etching reaches a depth of approximately 75 nm (~ half the film thickness). The presence of a gradient is a feature of interest and its influence will need to be further studied.

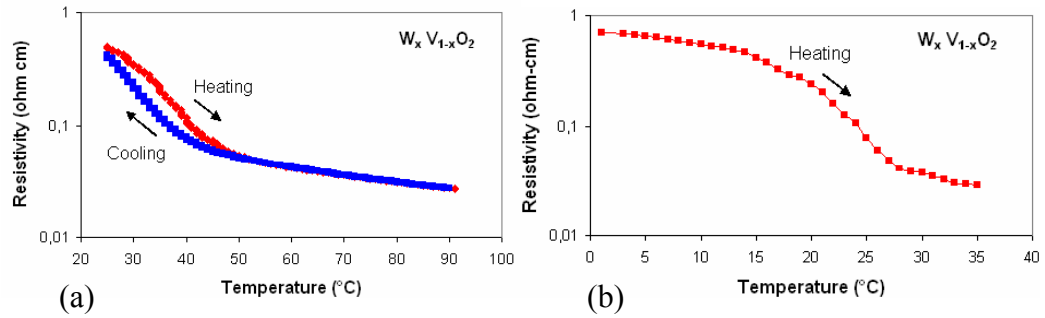

Figure 2 : Temperature dependence of electrical resistivity of W- doped VO_2 film measured from (a) RT (b) 0°C .

Table 1. XPS depth profile results of $W_xV_{1-x}O_2$ and $W_xTi_yV_{1-x-y}O_2$ samples

Impurity/depth	Elements (at.%)			
	O	V	W	Ti
W/0nm	41,4	16,0	0,7	---
W/9nm	60,8	33,3	2,1	---
W/24nm	60,8	32,4	2,1	---
W/75nm	58,1	32,8	2,8	---
W+Ti/0nm	40,2	19,7	0,4	1,3
W+Ti/9nm	60,2	30,2	0,8	4,4
W+Ti/24nm	59,3	28,3	1,0	6,0

Co-doping with W and Ti proved to change significantly the phase transition behavior. These films exhibit no abrupt phase transition but rather a smooth, linear transition over a large temperature range, as shown in Figure 3a. The T_t lies near 55°C (More evident in linear scale than in log scale). The magnitude of resistivity drop from RT to high temperature is much smaller (one order of magnitude) than that of undoped or W-doped VO_2 films. On the other hand, total suppression of electrical hysteresis is now observed in these films, which is a must if we are to use them for analog modulation purposes. The TCR ~ -2%/°C value is similar to that of the undoped films.

Thickness of the co-doped film influences its resistivity and transition characteristics. A three times thicker W-Ti doped film (350nm) showed less change of resistivity (less than one order of magnitude) and the film was initially much more conductive. Nevertheless, no electrical hysteresis was observed and T_t is still about 55°C (Figure 3b). Estimation of W and Ti concentration by XPS was conducted with the thick co-doped film. No V_2O_5 was present at the very surface of the film. Depth profile was conducted down to 25 nm below the surface. From the top surface to 25 nm below, a gradient of 0.4 to 1 at.% of W is observed and 1.3 to 6 at.% of Ti (Table 1). These numbers (particularly Ti) differ from the initial concentration of the target (1.5 at.% W and 12 at.% Ti). With these XPS numbers, knowing that 1 at.% W decreases T_t by 23°C and using the results of Soltani [15] that 1 at.% Ti should rises T_t by 2°C, the transition temperature for the films herein should fall between 54-58°C. This is consistent with the experimental observation. Again, the presence of the gradient and its influence will need to be further studied.

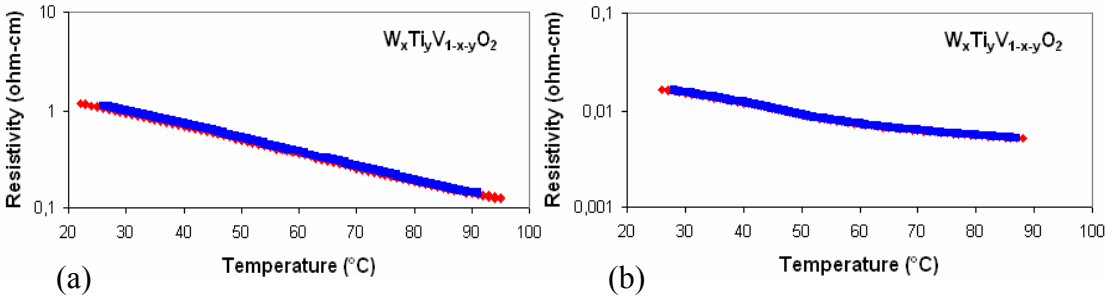

Figure 3 : Temperature dependence of electrical resistivity of W-Ti co-doped films with a thickness of (a) 150 nm and (b) 350 nm.

4.1.1 IR Transmittance

When it comes to optical transmittance, note first that the n-doped Si wafers used here as substrates are ~40% transmissive in the LWIR region at room temperature. An additional attenuation of 5% is seen when SiO_2 is thermally grown on the surface (Figure 4a). At high temperature, the transmittance of Si/SiO_2 remains constant at ~31% across the LWIR spectrum, as shown in Figure 4b. The slight decrease in transmission is attributed to the increased IR absorption by an increased free carriers in the silicon generated at elevated temperatures, as seen in Figure 4c.

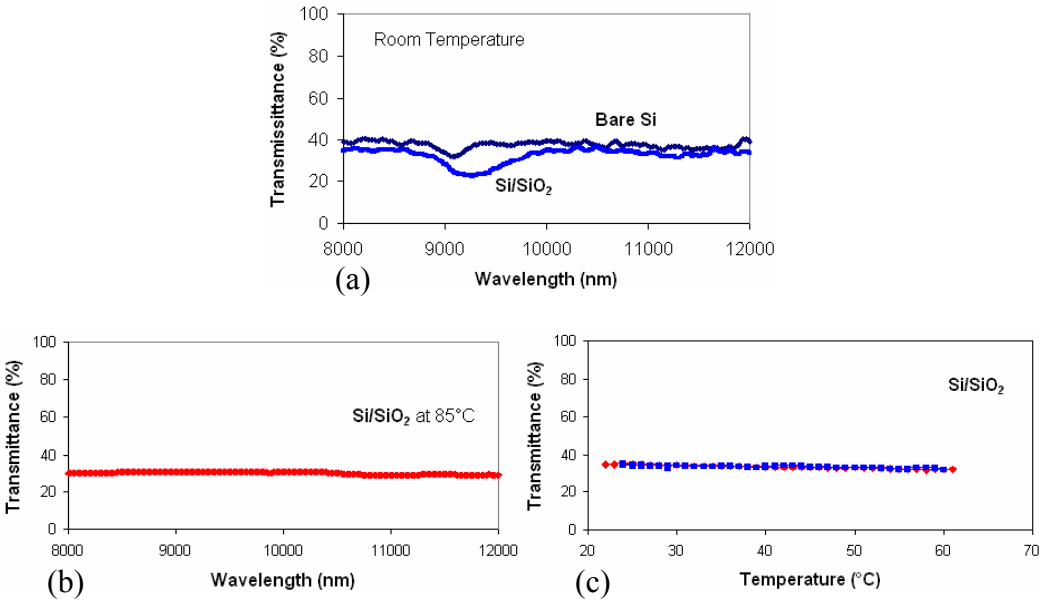

Figure 4: (a)Transmittance of bare Si and Si/SiO_2 at LWIR is about 40% and 35 %, respectively, at room temperature. (b) Transmittance of Si/SiO_2 at high temperature remains constant to about 31% in the LWIR range. (c) Upon heating and cooling Si/SiO_2, transmittance at λ= 8.0μm slightly decreases to no more than ~ 5% of its initial value at RT.

In the subsequent paragraphs, transmission results are presented using the relative transmittance (that is transmission of samples relative to that of uncoated Si/SiO_2). The optical digital switch (on/off) capability of the film resides in the optical contrast it can offer in transmittance. For undoped VO_2 films, temperature dependence of transmittance is reported in Figure 5 at a fixed λ (8 μm). At room temperature, VO_2 film is fairly transparent. Near 61°C, an abrupt decrease of transmission is observed, the film becomes nearly opaque with a transmission value less than 5%. A small optical hysteresis of less than 5°C, can be observed upon cooling the film.

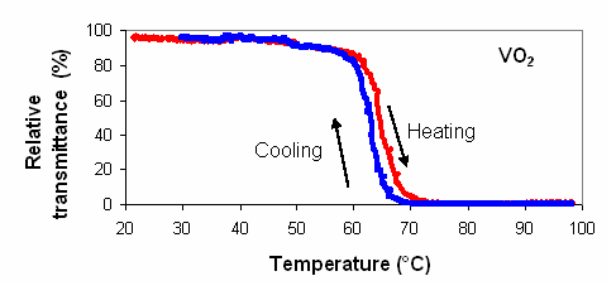

Figure 5: Temperature dependence of relative transmittance for undoped VO_2 at λ = 8 μm.

If we examine transmission as a function of wavelengths, Figure 6a illustrates that transmission at room temperature gradually rises from 40 to 80% for the SWIR range. From 8 to 12 μm (the LWIR range), the transmission remains quite constant with a value above 75% at room temperature (Figure 7b). For both SWIR and LWIR ranges, the films become nearly opaque when the temperature is brought above 60°C.

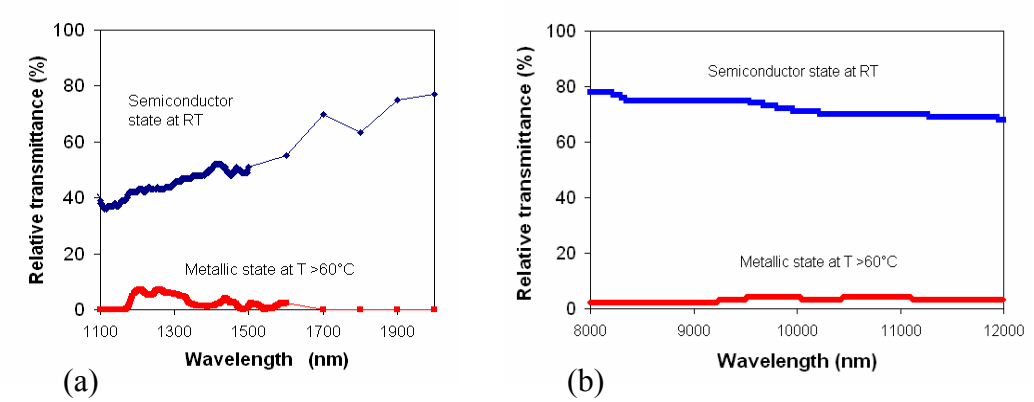

Figure 6: Relative transmittance of undoped VO_2 in the semiconducting and metallic state in (a) SWIR and (b) LWIR.

The challenge of doping VO_2 films is to tailor T_t, preferentially closer to RT, without substantial degradation to its optical switching characteristics. With the W-doped film, the optical transmission curve (Figure 2a) is quite similar compared to that of resistivity (Figure 7a). Since no experimental setup was available to prevent water condensation that absorbs IR on the film surface during transmission measurements, no experiments were conducted below RT. Consequently, we can roughly estimate that T_t lies in the vicinity of RT (Figure 7a). Note here that the initial recorded points also lie directly in the hysteresis portion of the transition. The true optical contrast seen here is therefore probably slightly underestimated. Nevertheless, transmission at RT still remains at ~85% and it becomes rather opaque beyond 45°C with less than 20% transmission throughout the LWIR range (Figure 7b). Optical hysteresis width is similar to that of undoped film.

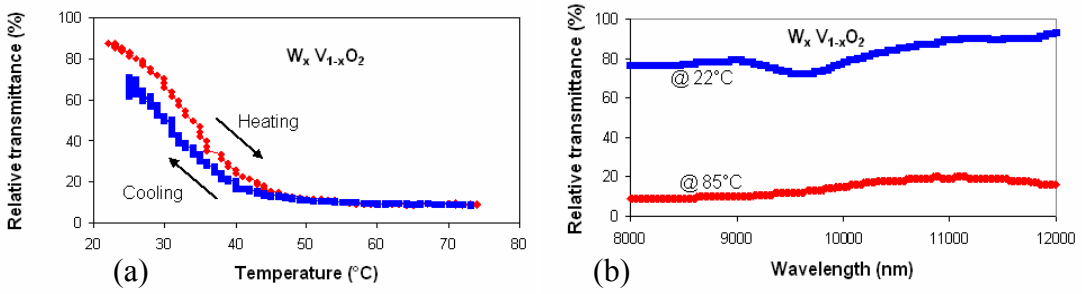

Figure 7: Optical transmittance of W-doped VO_2 film in the semiconducting and metallic state (a) temperature dependence at λ= 8.0 μm and (b) wavelength dependence for LWIR at RT and high temperature.

For Ti-W co-doped film, the transmittance curve changes significantly its allure from those of undoped and W-doped spectra. As it was the case for resistivity (Figure 3a), the curve here does not show an abrupt transition but a smooth decrease with an inflexion point somewhere near 45-48°C (Figure 8a). A very small optical hysteresis (2°C) was seen; this differs slightly from the resistivity curve (Figure 3a) where no electrical hysteresis was observed. Moreover, the cooling curve is on top instead. This can possibly be related to the cooling rate upon which we have less control than the heating rate in transmittance measurements. Better ramp

control would be beneficial here. The optical contrast between RT and high temperature remains constant to ~ 40% for the LWIR range with an initial high transmittance value which is similar to undoped films.

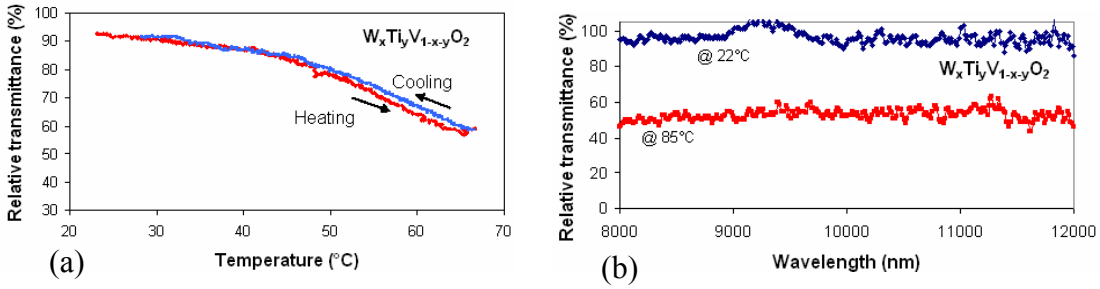

Figure 8: Optical transmittance of typical 130 nm thick W-Ti co-doped VO_2 film (a) temperature dependence at λ= 8.5 μm and (b) wavelength dependence in LWIR at RT and high temperature.

However, as seen for resistivity (Figure 3b), thickness of the film influences strongly the initial transmittance level. A thick film of 350 nm has lower transmittance at RT even though it showed similar contrast (Figures 9a & b). This last result shows the importance of optimizing the thickness of doped film according to applications.

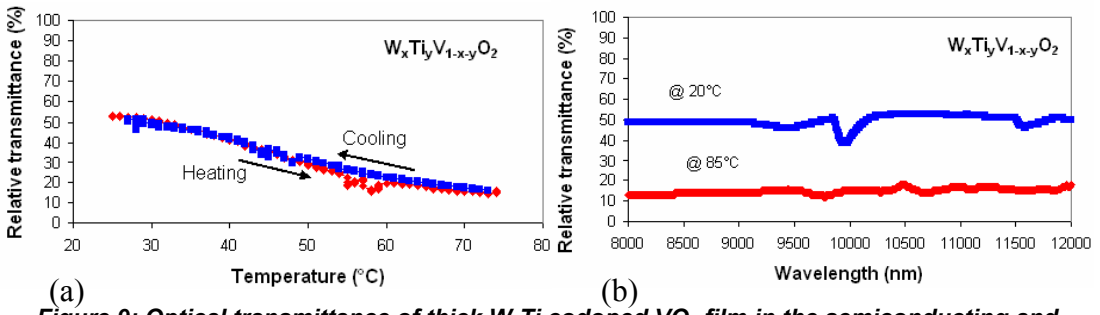

Figure 9: Optical transmittance of thick W-Ti codoped VO_2 film in the semiconducting and metallic states (a) temperature dependence at a fixed λ and (b) wavelength dependence for LWIR at RT and high temperature.

5. Conclusions

The challenge of doping VO_2 is to tailor its T_t without substantial degradation of its optical switching characteristics such as transmission and contrast. This study showed that RF magnetron sputtered W-doped and W-Ti co-doped thin films of VO_2 possess tunable electrical, optical and phase transition properties according to doping elements and level. In fact, the infrared transmittance, the electrical resistivity as well as the transition temperature were found to be consistent and influenced by the dopants used according to expectations. The transition temperature was brought down from ~65°C to 15°C with ~2.1 at.% W while maintaining high optical contrast (~75%). With further improvement, this feature could be exploited in applications where a digital action (on/off) is needed such as for a new multiband and tunable uncooled IR detector [1]. Co-doping with ~1 at.% W and 6 at.% Ti suppressed the electrical hysteresis while maintaining a rather linear optical contrast of ~ 40% in the LWIR range. Gradual and smooth change of transmission is relevant for analog modulation purposes such as IR signature management or in the case of smart radiator devices for spacecraft.

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The purpose of this memorandum is to investigate the effect of selected dopants (namely tungsten (W) and W-titanium (Ti)) on vanadium dioxide (VO2) semiconducting to metallic phase transition in the longwave infrared (LWIR) range. The specific properties investigated in this study are the transition temperature Tt, the electrical resistivity and the optical transmittance. Fabrication of films was done by magnetron radio-frequency sputtering technique. The results indicated that Tt of our undoped VO2 films is ~ 65°C and can be brought down to ~ 15°C with ~2.1 at.% of W doping. When the film is in the metallic phase (above the Tt), the electrical resistivity of undoped films drops three orders of magnitude while it drops two orders of magnitude in W-doped films with an electrical hysteresis of less than 10°C in both cases. Co-doping with W (~1 at.%) and Ti (of ~6 at.%) greatly modifies the resistivity slope, the latter showing no abrupt transition but rather a smooth, linear transition over a large temperature range with Tt near 55°C. The resistivity drop upon heating of the co-doped film is less than one order of magnitude but its electrical hysteresis is totally suppressed. Regarding optical transmittance, all films under investigation have high transmission (>75%) at room temperature (RT) in the IR region. In the metallic phase (above Tt), undoped films become nearly opaque with a transmittance in LWIR of less than 5%, less than 20% for W-doped films and less than 35% for those co-doped with W and Ti. The latter films give a barely noticeable optical hysteresis (~2°C). The results of this study show the possibility and efficiency of doping VO2 to modulate the transmission in the longwave infrared range and vary the hysteresis.

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