

Variation of the metal-insulator phase transition temperature in VO₂: An overview of some possible implementation methods

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Abstract. The great interest in VO₂, which has stimulated a large number of studies and publications in recent decades, is caused by the reversible metal-insulator phase transition (MIT) that occurs at $T = 68\text{ }^{\circ}\text{C}$ and is accompanied by the transformation of a low-temperature dielectric (semiconductor) monoclinic phase into a high-temperature metallic phase with a rutile structure. Despite the ongoing discussion about the physical mechanism of this transition, the concomitant rapid change in the electrical and optical characteristics of the material by several orders of magnitude already finds numerous applications in optics, optoelectronics and sensors. At the same time, it became obvious that both the number and performance of the applications of VO₂ would greatly increase, if it were possible to decrease the temperature of the phase transition without deterioration of other properties. This issue has become the subject of numerous studies. Mechanical stress and oxygen vacancies in the VO₂ lattice, the concentration of free charge carriers, tuned by impurity doping or implantation, have been investigated and discussed as the main factors affecting the transition temperature. In this review, we intend to summarize and analyze the literature data on these ways, primarily those which are most efficient in influencing the transition temperature while maintaining a significant change in the modulation characteristics.

Keywords: vanadium oxide, metal-insulator phase transition (MIT), temperature of MIT, stress, oxygen vacancies, doping.

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1. Introduction

The metal-insulator structural transition in VO₂ crystals was first reported in 1959 by Morin *et al.* [1]. The transition occurs at a temperature (T_{MIT}) of about 68 °C due to the transformation of the low-temperature insulator/semiconductor monoclinic phase (M_1) into the high-temperature metallic phase with the structure of rutile (R) (the so-called metal-insulator phase transition – MIT) [2–4]. The transition is reversible in both directions but exhibit a hysteresis effect [5]. Along with the transformation of structure, electrical resistivity and optical transparency in the infrared range drop by several orders of magnitude [6–8]. The high switching speed opens prospects for its use in sensors and optical modulators

[9, 10]. One of the first promising practical applications of induced high reflectivity of infrared radiation is smart window coating that reduces solar heating of the interior of a building. The possible economic impact of such an application is obvious. This immediately made reducing the phase transition temperature to room temperature one of the top priorities. At the same time, it would simplify implementation of numerous applications of VO₂ in sensor systems and microbolometer instruments for detecting infrared radiation. Later, it became obvious that the task of increasing the transition temperature by several tens of degrees is also relevant when trying to use VO₂ coatings in thermal solar collectors for heating water, overheat limiters for large-area solar panels, or to maintain the functionality of certain types of electronic devices, such as field-effect transistors [11].

However, the task of optimizing the MIT temperature in VO₂ for various applications was not the only challenge. In addition to changing the transition temperature, it is important to learn how to optimize the optical characteristics and their modulation during MIT [12]. It is also desirable to reduce hysteresis during heating and cooling cycles. All these characteristics turned out to depend on the technology of deposition of VO₂ films, types of substrates, the resulting morphology of the layers and their thermal treatment [13, 14]. Numerous physical studies of VO₂ layers, growing every year, have shown that there are several determinant factors for regulation of T_{MIT} in VO₂, in particular:

1. Mechanical strain in VO₂ film is very important. The sign of the temperature shift of the transition (decrease or increase in T_{MIT}) depends on the sign of deformation (compressive or tensile), and the magnitude of ΔT_{MIT} is proportional to the amount of deformation [5, 10].

2. The concentration of vacancies of oxygen atoms in the VO₂ lattice is of essential importance for the regulation of T_{MIT} . An increase in the number of vacancies by a few percent stimulates a significant decrease in the transition temperature [15, 16].

3. The concentration of free charge carriers in the low-temperature (insulator) phase of VO₂ is important [17]. An increase in concentration naturally favors the transition to the metallic phase and, accordingly, reduces T_{MIT} towards room temperature. Thus, VO₂ doping with impurities depending on the valence of the impurity atom and its size (lattice strain effect) is currently one of the real methods of controlling the MIT temperature.

The influence of mechanical stress and oxygen vacancies in VO₂ films on MIT is described below. A more detailed review of literature data is made regarding the effect of doping with impurities on T_{MIT} .

Table 1. Crystal lattice parameters of VO₂ and TiO₂.

Crystal lattice parameters	a (nm)	c (nm)
VO ₂	0.45540	0.28557
TiO ₂	0.45933	0.29592
Difference %	0.863	3.62

2. The influence of mechanical stress on T_{MIT}

The influence of mechanical stresses on the electrical and optical properties of VO₂ layers, especially in the temperature range near the phase transition, was already evident in the first studies. It was indicated by the influence of the type of substrate (most often it is silicon, Al₂O₃ or TiO₂), namely in the case of thin epitaxial VO₂ layer. In addition, there were significant changes associated with the size of monocrystalline VO₂ grains, especially at their small sizes. There is a lot of literature on these issues (see, for example, [2, 3, 13, 18], and a PhD thesis done at Stanford University [19]). But one of the first most convincing experimental works was reported in [20]. In that work, the effect of compression or stretching along the C -axis of VO₂ was investigated for a film grown on (001) or (110) surfaces of TiO₂ substrates. T_{MIT} decreased from its standard value of 341 K (68 °C) to 300 K in case of compression, while increased to 360 K due to tensile strain (Fig. 1). Corresponding data of VO₂ and TiO₂ lattice parameters are given in Table 1. It is important that the range of possible resistance modulation increased significantly as the temperature decreased (Fig. 1). In work [21], the discussed problem was investigated much more thoroughly both theoretically and experimentally by using synchrotron radiation.

3. The influence of oxygen vacancies on the electrical and optical properties of VO₂ in relation with the MIT mechanism

Along with the intensively studied problems of influencing the characteristics of the metal-insulator phase transition in VO₂ by such factors as the initial type of the crystal structure, sizes of the crystal grains, the mechanical stress of the lattice, the type and concentration of doping impurities, an important characteristic is the oxygen non-stoichiometry of the material. The latter is related with a possibility of three oxidation

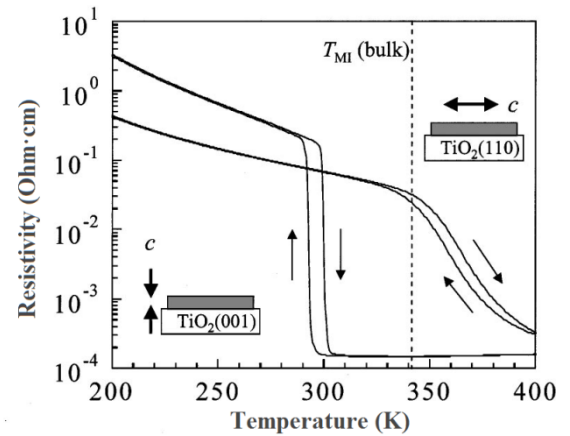


Fig. 1. The temperature dependence of the resistivity of VO₂ films on TiO₂ (001) and TiO₂ (110) substrates. Dotted line represents T_{MIT} in VO₂ single crystal ($T_{MIT} = 341$ K) [20]. Reprinted from Ref. [20], with the permission of AIP Publishing.

states of vanadium, V^{3+} , V^{4+} , V^{5+} , which are often all simultaneously present in the structure at a deliberate ratio. Therefore, establishing the exact ratio of O to V is one of the major tasks at analysis of VO_2 samples. Besides X-ray photoelectron spectroscopy and other common methods of elemental analysis, μ -Raman spectroscopy proved to be an efficient tool at the micro-scale, due to high sensitivity and spectral resolution [22, 23]. Recently the atomic force microscopy has shown its capability in differentiating vanadium oxides at the nanoscale, based on the elastic properties of the film [24]. The significance of the non-stoichiometry could be assumed even from general considerations based on the fact that T_{MIT} in different vanadium oxides decreases with a decreased relative content of oxygen. In particular, $T_{MIT} = 341$ K in VO_2 (O/V = 2), for V_2O_3 (O/V = 1.5) T_{MIT} is much lower (~ 155 K), while for V_2O_5 (O/V = 2.5) MIT occurs at much higher temperatures than for VO_2 . Moreover, it is known that each oxygen vacancy in VO_2 supplies two free electrons to the lattice, and an increase in the concentration of free carriers in VO_2 is one of the factors that reduces T_{MIT} . These intuitive considerations were confirmed by several theoretical and experimental studies [6, 16, 25–27], including those performed quite a long time ago. Among these publications, the work carried out by a team of 16 authors from several leading US universities and Naval Research Laboratory stands out. We found this work so impressive that we decided to consider it in detail here, along with another theoretical and computational works that gave a convincing quantitative assessment of the significant role of oxygen vacancies in VO_2 .

The first of these works was published in 2017 [28]. In the introduction of this publication, the authors draw attention to the fact that the high sensitivity of metal-insulator phase transformations to the disordering of the crystal lattice is a typical manifestation of correlation effects in metal oxides. Concerning VO_2 , they note various well-known decoupling effects that stimulate a significant modification of MIT, including stabilization of the metallic phase down to very low temperatures [29–32]. The latter works indicate that the involved defects can be different, such as substitution impurities (W or Mo instead of V), hydrogen as an interstitial impurity, or oxygen vacancies generated by electrochemical reactions between VO_2 and the liquid ionic electrolyte. The latter type of defect, in the authors' opinion, should be especially interesting, since it allows not only formation of the metallic phase VO_2 at very low temperatures (down to several Kelvin), but also the return of the non-conducting phase by appropriate annealing in oxygen.

The authors of [27] consider the process of high-temperature synthesis to be the easiest way to create an oxygen deficit in VO_2 . In this case, for $VO_{2-\delta}$, where δ is an indicator of oxygen deficiency, a decrease of T_{MIT} by 15 °C was observed. However, a further decrease in the oxygen content during high-temperature synthesis led to the transformation of vanadium dioxide into the so-called Mogneli phases V_nO_{2n-1} ($3 \leq n \leq 8$) [33].

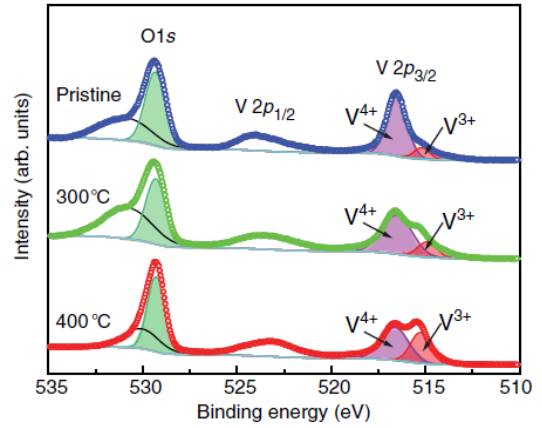


Fig. 2. XPS spectra of VO_2 and two layers of $VO_{2-\delta}$ annealed at 300 and 400 °C in oxygen-poor atmosphere. The shift of $V_{2p_{1/2}}$ to lower binding energy and the appearance of $V_{2p_{3/2}}^{3+}$ peak indicate the reduction of the oxidation state of the vanadium ion under oxygen deficiency. The estimated δ value is 0.08 for $VO_{2-\delta}$ annealed at 300 °C and 0.2 for 400 °C [28]. Copyright © 2013 the American Physical Society.

In the work [28], the authors demonstrated the possibility of realizing a reversible metallic state of VO_2 without using high-field ionic liquid gating or hydrogen or proton doping. They used low-temperature annealing (~ 450 °C) of VO_2 at an ultra-low partial pressure of oxygen ($P_{O_2} \approx 10^{-24}$ atm), which was created by a magnesium getter. It turned out that the metallic state of the rutile structure was preserved when the $VO_{2-\delta}$ film was cooled to the temperature 1.8 K, but the sample could be returned to the insulator state by annealing in oxygen atmosphere. The fundamental point was that the oxygen deficiency index reached the value $\delta \approx 0.2$, which is 50 times higher than the equilibrium value of $\delta \approx 0.004$. Such a high value of δ was ensured by the fact that the transition of VO_2 into metallic state was accompanied by the transition of the part of V^{4+} ions into the V^{3+} state when the film was heated to 400 °C (Fig. 2). The problem of the simultaneous presence of V^{4+} and V^{3+} in vanadium oxides is also discussed later in this review (Section 4), in connection with the effect of doping of VO_2 with an impurity of boron atoms, as well as the effect of Ar-implanted VO_2 -film with the reduced phase transition temperature [34].

The experimental setup used by authors of Ref. [28] for generating low partial pressures of oxygen is shown in Fig. 3.

When Ar^+ flows into the oxygen trap, the O_2 react with the hot Mg (~ 450 °C) following the reaction $2Mg + O_2 = 2MgO$. MgO is porous and does not hinder further reaction. The partial pressure of oxygen drops and can reach approximately 10^{-24} atm. It was monitored using a zirconia-based oxygen sensor. The oxygen deprivation of VO_2 in the annealing chamber is schematically shown in Fig. 3c. The combination of ultralow oxygen partial pressure and low annealing temperature enable formation of oxygen vacancies in rutile VO_2 .

The electrons generated *via* oxygen deficit reduce the vanadium ions from V^{4+} to V^{3+} in accordance with reactions: $O_o \leftrightarrow V_o^{2+} + 2e^- + 1/2 \cdot O_2$, $V^{4+} + e^- \leftrightarrow V^{3+}$.

The appearance of V^{3+} in the system weakens the strong electron correlation and enables the transformation from insulating monoclinic phase to the metallic tetragonal phase.

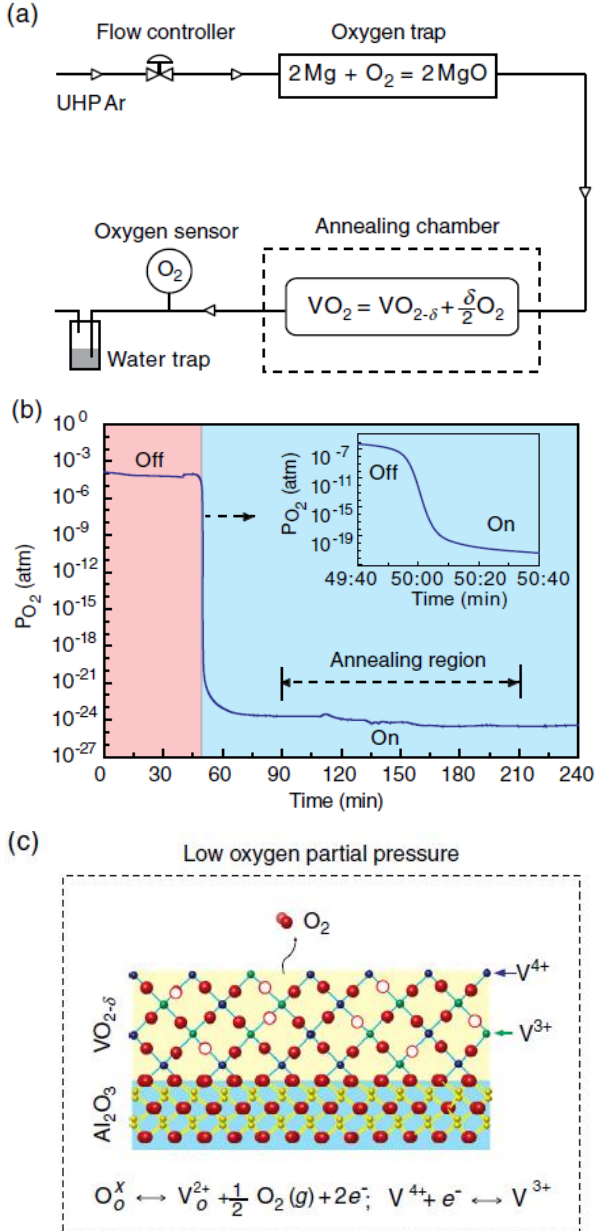


Fig. 3. Transformation of vanadium dioxide at ultra-low oxygen partial pressure in the metallic state. (a) Experimental setup for annealing VO₂ at low oxygen partial pressure. (b) Real-time oxygen partial pressure monitored by a zirconia-based oxygen sensor, where pristine VO₂ is annealed at $P_{O_2} \sim 10^{-24}$ atm. The inset shows P_{O_2} in a narrow time window. (c) At the low oxygen partial pressure, oxygen vacancies are created in VO₂, and the oxidation state of vanadium is reduced from V^{4+} to V^{3+} [28]. Copyright © 2013 the American Physical Society.

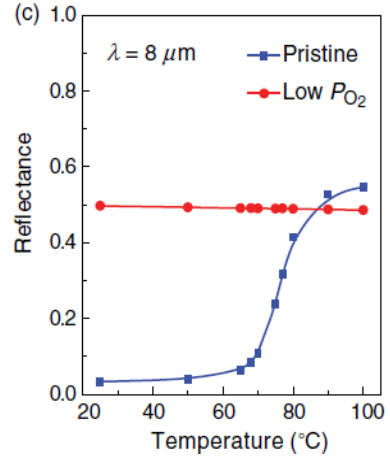


Fig. 4. Single-wavelength ($\lambda = 8 \mu\text{m}$) temperature-dependent reflectance of VO₂ after annealing at the low oxygen partial pressure and 400 °C for 2 h. The reflectance of the pristine sample increases sharply when heated above the MIT temperature. After annealing at low oxygen partial pressure, the sample shows high reflectance, similar to that of the thermally induced metallic state of the pristine sample. Moreover, the reflectance of the annealed sample decreases slightly with heating, which is indicative of metallic behavior [28]. Copyright © 2013 the American Physical Society.

The authors of Ref. [28] studied structural, electrical and optical characteristics of 40-nm VO_{2-δ} films obtained using magnetron sputtering in Ar atmosphere on C-plane sapphire substrates and then annealed at temperatures of 300 and 400 °C in an ultra-low oxygen atmosphere ($P_{O_2} \sim 10^{-24}$ atm). For the pristine sample, the temperature dependence of its IR reflectance (Fig. 4) showed the usual behavior, with T_{MIT} around 70 °C and concomitant increase in reflectance by an order of magnitude. However, after 2 h of annealing at low P_{O_2} the film shows high reflectance down to room temperature, *i.e.* the metallic phase formed at high temperature was stabilized by oxygen vacancies and did not undergo a reverse transition to the monoclinic insulating phase. The electron transport band gap (E_g) in the insulating state, estimated as based on the temperature dependence of resistivity according to the equation $\rho \sim \exp(E_g/2k_B T)$, is 0.58 eV, which is consistent with literature data. But after annealing, E_g was reduced to 0.32 eV, which nearly coincides with the hydrogenated VO₂ prior to the stabilization of the metallic state [31].

The effect of oxygen non-stoichiometry on the modification of the MIT temperature in VO₂ and corresponding changes in electrical and optical properties have been also demonstrated theoretically, being based on calculations from the first-principles [6]. The authors refer to many efforts that have been made to tune the MIT behavior in VO₂, including doping, external strain, electric field, as well as surface and interface engineering. But from their viewpoint one of the most effective routes is to control oxygen non-stoichiometry of VO₂. It can be done through controlling the oxygen

partial pressure during deposition or annealing the VO₂ samples. They pointed to publications [26, 35], where it was suggested that they are electrons released during formation of oxygen vacancies in VO₂ and corresponding donor doping, which cause a decrease in the phase transition temperature of VO₂. By the way, it must be noted that shown in the work [36] was that O-vacancies in VO₂ (M) are more stable thermodynamically than other defects, such as V-vacancy and O-interstitials.

Being based on the monoclinic and rutile VO₂ crystal structures, the basic calculations were performed in the supercells with 2×2×4 and 2×2×8 primitive unit cells containing 192 atoms for two phases labeled as VO₂(M) and VO₂(R), respectively. To reveal the effect of the O-vacancy concentration on the phase transition between VO₂(M) and VO₂(R), the cases of one and two O-vacancies were simulated by removing one and two oxygen atoms from the modelled unit of each phase, labeled as VO_{1.984} and VO_{1.969}, respectively.

The O-vacancy induced reduction in T_{MIT} for bulk VO₂ was calculated on the basis of previous publication of the same authors [37] and gave values of 226 and 142 K for VO_{1.984} and VO_{1.969}, respectively (Fig. 5), which are much lower than the phase transition temperature of pure VO₂ (340 K). It suggests that creation of the oxygen deficiency-related defects in VO₂ could enhance the electron concentration, which will modify its metal-insulator transition behavior.

Additional convincing evidence of the dramatic effect of a small number of oxygen vacancies on the change in T_{MIT} in VO₂ was obtained in other works, in particular, in [38] and [39]. In the first of these, X-ray photoemission spectroscopy results confirmed the significant influence of low O-vacancy concentrations on the sharp decrease in T_{MIT} . In the second one, the results of plasmon resonance spectroscopy confirmed the significant role of oxygen vacancies in reducing the phase transition energy and, accordingly, the transition temperature.

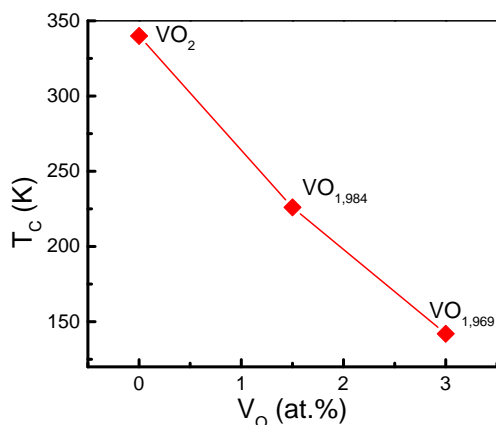


Fig. 5. The dependence of transition temperature (T_c) in VO₂ on the oxygen vacancy concentration (Plotted being based on the data from Ref. [6]).

The MIT temperature control is not the only problem for expanding the possibilities of practical use of VO₂ in electronics and optoelectronics, bearing in mind the implementation of a very significant range of changes in the electrical and optoelectronic characteristics of VO₂ films during the transition. For example, the authors of [40] confirmed the effectiveness of a slight decrease in the oxygen flow during the growth of VO₂ films for increasing the concentration of oxygen vacancies and, accordingly, a noticeable decrease in T_{MIT} . But they noted that this can often be accompanied by a noticeable reduction of the magnitude of electrical resistance and optical absorption change. The main goal of their research was to demonstrate that successful control of all important MIT parameters is possible through the simultaneous use of at least two factors of influencing the phase transition. In particular, the publication [40] showed the simultaneous influence of the oxygen vacancy concentration and interfacial strain in VO₂. The effect of strain was tuned by varying the thicknesses of the VO₂ epitaxial film grown on a MgF₂ substrate.

4. The effect of doping impurities on the phase transition in VO₂

The very fact of the possible critical influence of doping impurities on the properties of VO₂ is quite expected, given that the most common low-temperature phase M1 is a typical semiconductor compound; accordingly, doping with impurity atoms of different types, even in small concentrations – thousands of percents or less, is the main way to change properties of the material.

Since during MIT in VO₂ a very fast change of the crystal structure takes place, from monoclinic to the rutile (or at least the qualitative structure of the chains of vanadium atoms changes), it could be assumed that stronger doping would be relevant, at the level of several percent. As will be shown below, these simple considerations about the actual range of dopant impurities turn out to be correct for different types of dopants. Moreover, at such a high concentration of impurity doping, the sizes of atoms of substitutional impurities, even with the same valences, turn out to play a significant role, because they cause not local point stress, but spatially extended ones, which can be important to change the phase transition temperature. It is the latter problem that motivated most of the experimental and theoretical studies of the effect of impurity doping on T_{MIT} in VO₂.

In the majority of these studies, due to the obvious perspective of large-scale practical applications of VO₂ as a material for smart windows, in various terahertz devices, or microbolometers, the authors usually emphasized the relevance of reducing the MIT temperature from 68 °C to room temperature. At the same time, it is important to keep or even increase the range of changes in optical transmittance at the maximum possible switching speed, and reduce the MIT hysteresis.

For the entire class of compounds of metal oxides, an essential factor is which of the elements (metal or oxygen) is replaced by the impurity atom. Usually, the orbitals of the metal cation form the conduction band of the oxide, while the energy terms of oxygen are responsible for the valence band. Therefore, the resulting location of the Fermi level of charge carriers is determined by the type of substitution. Moreover, this fact is relevant not only in the case of doping with impurities, but also for establishing the role of vacancies in oxides. In this regard, we think that the above-mentioned significant effect of oxygen vacancies in VO₂ on the reduction of T_{MIT} could be predicted already from the fact of a significant difference in the transition temperatures for VO₂ (O/V = 2, T_{MIT} = ~340 K) and V₂O₃ (O/V = 1.5, T_{MIT} = ~170 K). Taking into account this circumstance, it could be expected that with a V_O concentration of only a few percent, a tendency to a noticeable decrease in the transition temperature to the metallic state may appear. It was confirmed by many theoretical and experimental studies, some of which are discussed below.

An important factor in controlling T_{MIT} by impurity doping is preserving sufficient level of optical transmittance of the low-temperature (insulator) phase, because otherwise the depth of modulations of this characteristic will be insufficient for effective applications. Practically important is also the switching speed due to the maximum possible gradient $\frac{\partial \tau}{\partial T}$, where τ is the value of the optical transmittance, T is the temperature in the transition region. As will be seen from the collected experimental data for various impurities,

these two characteristics do not always correlate well with the effectiveness of a specific impurity to decrease the transition temperature. In this case, the synergistic effect of simultaneous doping of VO₂ with two different impurities can be effective, one of which ensures a significant range of change in transition temperature, and the second has a greater influence on the dynamics of changes in the optical characteristics of the VO₂ layer. At the same time, such a combined effect of various impurities turns out to be relevant not only for reducing the transition temperature, but also for the relatively rare, but no less important in practice of the need to increase the transition temperature by 20...30 °C. An example of the importance of this task is the prospect of using VO₂ coatings to regulate the temperature of water heating systems that use solar energy, but do not allow operating water heating temperatures above 100 °C.

The number of works on doped VO₂ published so far very large. Despite the fact that this problem has been particularly intensively studied in recent years, the most thorough recent review on this topic [41] with a large bibliography indicates a number of important results that were obtained 20–25 years ago but have not lost their significance. The detailed Tables contained in this review characterize the changes in T_{MIT} due to the influence of more than 50 different dopants, allowing us to highlight a limited number of impurities that cause the most significant effect. Let's return to the above-mentioned physical factors that determine the qualitative change in the transition temperature (decrease or increase) and its quantitative characteristic ($\Delta T/\text{at.}\%$ impurity content). This can be seen more clearly by using the table borrowed from the work [42], which we significantly extended.

Table 2. Effect of dopants on the thermochromic properties of VO₂ thin films.

Dopant	Optical transmission in visible range	Magnitude of transmission modulation	T _c , °C/at.%	Mechanism	Ref.
W ⁶⁺	↓	↓	↓ ~20–26	e ⁻ ↑	[43–46]
Mo ⁶⁺	↑	↓	↓ ~3	e ⁻ ↑	[35]
Nb ⁵⁺	↓	↓	↓ ~2	e ⁻ ↑	[47]
Zr ⁴⁺	↑	↑	↓ ~0.4	Large radius	[48]
Ti ⁴⁺	↑	↑	↑ 9	Smaller radius	[12, 49]
Sn ⁴⁺	–	–	↑ ~1	Smaller radius	[50]
Ge ⁴⁺	↓	–	↑ ~1–2		[51]
Al ³⁺	–	–	↓ ~2.7	h ⁺ ↑	[52]
Fe ³⁺	–	–	↑ ~6		[53, 54]
Eu ³⁺	↑	↑	↓ ~6	Large radius	[55]
Ce ³⁺	–	–	↓ ~4.5	Large radius	[56]
Ga ³⁺	–	–	↑ ~3.1		[57]
In ³⁺	–	–	↑ ~3.1		[57]
B ³⁺	↑	↓	↓ ~10; 31.5	Interstitial position	[55, 58, 59]
Mg ²⁺	↑	↑	↓ ~3	h ⁺ ↑	[60, 61]

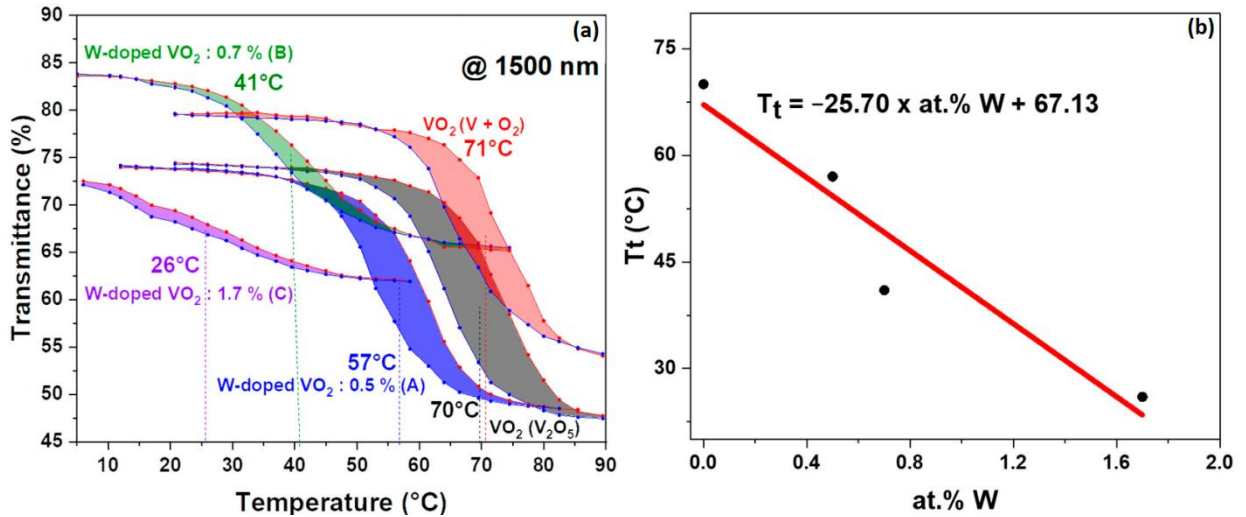


Fig. 6. (a) Hysteresis loops derived from the temperature-dependent transmittance of the undoped and W-doped (A, B, and C) thin films at a wavelength of 1500 nm. (b) The correlation between the phase transition temperature T_t and W concentration. Reproduced from [46].

A comparative analysis of the data in Table 2 for various impurities that replace V in its dioxide allows one to draw a number of qualitative conclusions. First of all, for the impurities W^{6+} , Mo^{6+} and Nb^{5+} , the valence of which is higher as compared to the valence of substituted vanadium, in all cases the concentration of free charge carriers in the low-temperature phase increases, as should be expected [17]. It facilitates the transition to the high-temperature metal phase of rutile and decreases transition temperature. The effect is maximal for the tungsten, for which at the concentration 2...2.5%, the MIT temperature decreases almost to the room one. Such a significant effect in comparison with Mo^{6+} and Nb^{5+} is associated, apparently, with the large size of the W^{6+} ion and the possible factor of additional influence of compressive deformation [20, 62, 63].

In the case of the substitution of vanadium with atoms of the same valence +4 (Zr, Ti, Sn), the situation with the influence of elastic stresses due to difference of ionic radii is no longer so obvious. Although the effect on T_{MIT} is the largest in the case of Zr^{4+} , the largest ion among these three, may also indicate an increase in the strain effect, as in the case of W-doping, however, for the latter the influence of increasing the free carrier concentration is most likely dominant.

In the case of trivalent substituting ions, the situation is more complicated. For Al^{3+} , Eu^{3+} , Ce^{3+} the transition temperature decreases by $\sim 3^\circ \dots 6^\circ$, either due to an increase in the concentration of free holes for Al and Fe or due to a larger ion radius inherent to Eu and Ce. In the case of a very small radius of boron, a very significant temperature decrease is explained by its interstitial position in the VO_2 lattice. The non-standard nature of this situation will be discussed below, along with the effect of increasing the transition temperature by trivalent impurities Ga, In and Fe.

Some of the noted factors associated with doping will be discussed in more detail below.

4.1. Doping with W, Mo, Nb and Mg

As was noted above, W is the most effective dopant for lowering T_{MIT} in VO_2 down to the room temperature. In accordance with Table 2, the substitution of V^{4+} by W^{6+} results in decreasing T_{MIT} by 20...28 °C per 1 at.%. Therefore, the greatest number of publications deals with this type of doping. There were used different doping techniques, but in accordance with one of the most recent works [46], Pulsed Laser Deposition (PLD) may be a versatile method to control doping in thin VO_2 films. This method was used for $VO_2:W$ also by others [44, 45], in particular developing all-optical switching at the telecommunication wavelength 1.55 μm [64].

In the work [46], the structure of obtained $VO_2:W$ films was analyzed using Raman spectroscopy, and the thermochromic properties were measured by collecting the transmittance in the temperature range between 15 and 10 °C in the visible (400...800 nm) and IR (900...2500 nm) ranges. Fig. 6 shows the hysteresis loop produced by plotting the temperature dependence of transmittance of undoped and W-doped VO_2 thin films at a fixed wavelength of 1500 nm. The switching temperature during heating (τ_{heat}) and cooling (τ_{cool}) were determined from the halfwidth of each curve and the average value was defined as $T_{MIT} = (\tau_{heat} + \tau_{cool})/2$.

The undoped films had a phase transition temperature ≈ 70 °C. The dependence of T_{MIT} on the tungsten content was linear (Fig. 6b), with the slope of 20 to 28 °C per 1 at.% [43–47]. As mentioned above during discussion of Table 2, the reduction mechanism of the W-doped VO_2 may be prescribed to free electron generation and strain resulting from the replacement of V^{4+} by much larger W^{6+} .

Hysteresis behavior is another important parameter of VO_2 -based thin films. Fig. 6a shows that hysteresis loop gradually narrowed from more than 10 °C in undoped sample to only ~ 4 °C for the film doped with 1.7 at.% W.

This fact means that activation energy of the phase transition is reduced, what is very important for applications, in particular, VO₂:W layers may be used in more faster switching devices, especially in optoelectronics.

In addition to the discussed data of the recent work [46], where the characteristics of VO₂:W samples obtained by the PLD method were presented, in many earlier publications on this issue, where films were grown using other methods, it was repeatedly noted that the achievement of a significant effect of reducing the phase transition temperature was accompanied by simultaneous noticeable deterioration in optical characteristics compared to undoped VO₂. The same situation is found in the case of doping with Mo⁶⁺ and Nb⁵⁺, when the mechanism of decreasing the transition temperature is related to the increase in the concentration of free electrons when replacing vanadium in the lattice [47]. However, this decrease is much weaker than that for tungsten, which may be related to a smaller contribution of elastic stresses, because of a smaller ion radius, as compared to W. Nevertheless, the authors of [47] noted that Mo provides significant narrowing of the temperature hysteresis, while for niobium a noticeable increase in optical transparency in the IR range is achieved.

In this regard, an interesting opportunity to “fix” the situation appears when using a synergistic effect of co-doping of VO₂ with two impurities, and partial neutralization of the effects of free e^- and h^+ type carriers [42]. In the latter work, samples of VO₂ doped simultaneously with tungsten and magnesium were studied. The latter is an element of group II; accordingly, replacing vanadium with it helps to increase hole conductivity. This provides a slight decrease in the transition temperature, by ~ 3 °C/at.% of the impurity, but very effectively increases the optical transmission in the entire range of 250 to 2500 nm, due to an increase in the optical band gap. With a fixed concentration of the W impurity of 2%, the authors experimentally investigated the effect of variation in the concentration of the impurity Mg in the range of 0 to 5% on the transition temperature τ_c and the optical transparency. It turned out that for the V_{0.94}W_{0.02}Mg_{0.04}O₂ samples, the transition temperature is about 30 °C, but the transparency increases by more than 10%, reaching the value close to 81%.

The same positive effect of co-doping was reported in [48] for the samples doped simultaneously with W and Zr atoms. The concentration of the latter was fixed (8.5 at.%), and the concentration of W was varied within the range of 0 to 2.4 at.%. In this case, the achieved minimum transition temperature was 28.6 °C, but as the main advantage of such combined doping, the authors note a significant improvement in the optical characteristics of the VO₂ film in the visible range. Due to the increase of the optical band gap due to the Zr impurity, the film changed its brownish color to yellow, which is a positive result for the use of VO₂ as a coating material for smart windows.

4.2. Boron-doped VO₂ thin films

We will consider doping of VO₂ with boron atoms in more detail. Due to their small size, B is embedded into VO₂ interstitial sites and, due to its valency 3+, having three valence electrons in the 2s- and 2p-orbitals, it can provide their building-in to the VO₂ lattice. This is more reliable than in the case of substitutional W⁶⁺. Moreover, a theoretical estimate (by first principle calculation) [58] shows that in this case one can expect a record reduction in the T_{MIT} temperature – 83 K per 1 at.% of B interstitials, which is three times more than for the case of W substitution. This quantitative assessment by the authors of [58] is valid for any of the three possible interstitial positions of impurity boron in the lattices of both the monoclinic and rutile phases of VO₂ (Fig. 7).

Experimental studies of a VO₂:B prepared using the hydrothermal method [59], revealed a really high value of $T_{MIT} \approx 10$ °C/at.% of B (Table 1), but significantly less than the theoretical estimate in Ref. [58].

However, more recent detailed study was carried out on VO₂:B films grown by the reactive PLD [55], which is the most controlled and reproducible method of film doping. A KrF excimer laser with the wavelength $\lambda = 248$ nm, pulse duration 25 ns and pulse frequency 10 Hz was used. High-resistivity Si was used as a substrate. During the synthesis process, the substrate temperature and oxygen pressure were 500 °C and 15 mTorr, respectively.

Three types of films VO₂ (I), VO₂ (II) and VO₂ (III) prepared under different deposition modes were studied. Their composition was controlled using high-resolution XPS and the boron content for samples I, II and III was 0, 0.8 and 1.6 at.%, respectively. Of particular interest to us are the XPS data on the chemical state of vanadium in the samples (Fig. 8). A fairly large amount of V⁵⁺, which authors of Ref. [55] related with the film surface, in our opinion, cannot be the reason of reduced T_{MIT} of the whole film. Another thing is a noticeable increase in the amount of V³⁺ with an increase in B content. Above, when discussing the difference in the temperatures of the

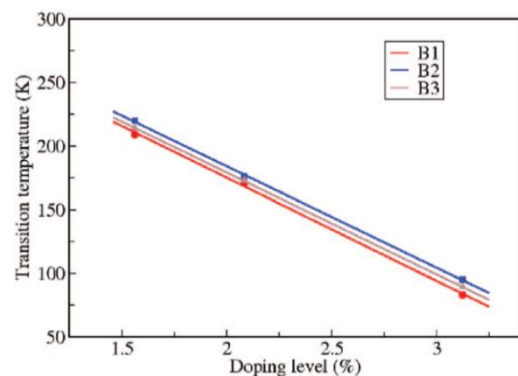


Fig. 7. The relationship between the transition temperature and the doping level of boron. The circle, square, and triangle represent sample points for dopant boron at B1, B2 and B3 sites, respectively. Reprinted from Ref. [58] with the permission of AIP Publishing.

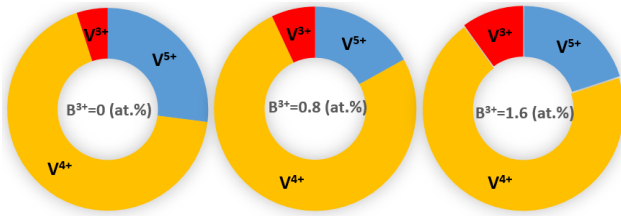


Fig. 8. Vanadium valence content of the undoped and boron-doped VO₂ films. Based on data of Ref. [55].

MIT phase transition in VO₂ (~340 K) and V₂O₃ (~170 K), we suggested that a small addition of V³⁺, as well as an increase in the number of oxygen vacancies, may be a stimulus for a decrease in T_{MIT} . As for the influence of oxygen vacancies, it has been repeatedly confirmed both theoretically and experimentally in publications. But the role of a small addition of trivalent vanadium was apparently first noted in [55].

The authors of Ref. [55] studied the dependence of T_{MIT} and hysteresis of resistance in the samples with a different content of boron. They ascertained that the transition temperature decreases at the rate 31.5 °C per 1 at.% B. This value is almost three times higher than the result obtained earlier in [58] on samples grown by the hydrothermal method and is currently a record for VO₂ films doped with impurities.

4.3. Doping of VO₂ with impurities of the third and fourth groups (Fe³⁺, Cr³⁺, Ge⁴⁺)

As can be seen from Table 2, for doping of VO₂ with elements of groups V and VI, there is a qualitative agreement between all the works that increase in the concentration of free electrons causes a decrease of T_{MIT} . The quantitative deviations in some works are associated with the simultaneous influence of elastic lattice deformation (stress) associated with the (different) size of the doping ion.

In the case of doping with elements of groups III and IV, the situation is not so clear. Only in recent years it became clear that the qualitative conclusions of individual earlier studies regarding the decrease or increase of T_{MIT} were contradictory and sometimes incorrect. There were two reasons for this. Firstly, in some cases, when the change of T_{MIT} was small, the technological factors of different methods used in various works turned out to be determinant for structural and morphological features of the samples prepared. Secondly, most of the works aimed at decreasing the transition temperature, necessary for many applications. Therefore, much less studies have been made on doping of VO₂ with elements of groups III and IV (Cr³⁺, Fe³⁺ and Ge⁴⁺) as compared to W⁶⁺-doping which initially showed the lowest T_{MIT} and thus attracted the most attention of researchers. Only in the recent

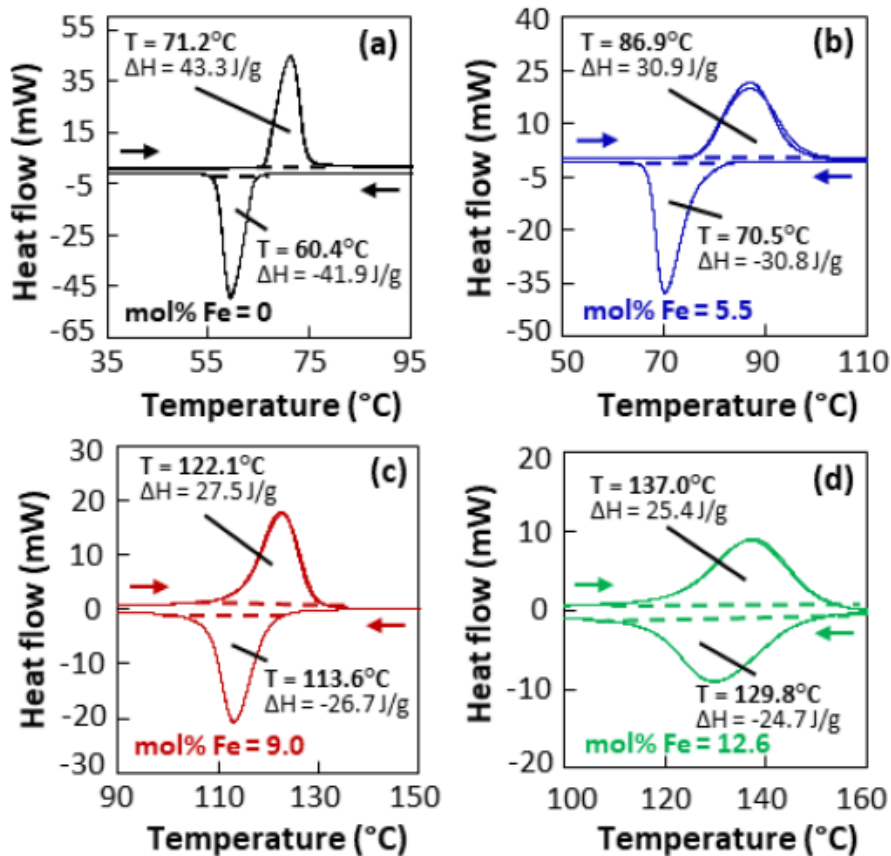


Fig. 9. DSC curves of 0 (a), 5.5 (b), 9.0 (c), and 12.6 mol.% (d) Fe-doped VO₂ samples. Reprinted (adapted) with permission from Ref. [53]. Copyright © 2021 American Chemical Society.

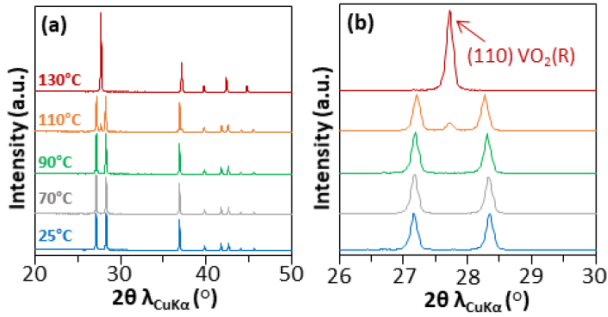


Fig. 10. XRD patterns of the 9.0 mol.% Fe-doped VO₂ sample prepared at different temperatures during heating (a) and focused on 2θ region from 26 to 30° (b). Reprinted with permission from Ref. [53]. Copyright © 2021 American Chemical Society.

5–7 years, the situation changed, and results have appeared indicating alternative use of the MIT transition in VO₂ in the temperature range around ~ 100 °C for the optimization of solar thermal collectors or solar batteries, as well as a number in microelectronic devices [53, 57].

Let's look briefly at a few of these possibilities involving doping of VO₂ with iron, chromium and germanium, where the highest transition temperatures have been reported.

A recent publication [53] entitled “Doubling of the phase transition temperature of VO₂ by Fe doping” reports the pyrolytic synthesis and characterization of crystalline VO₂ powder with Fe contents close to 5.5%, 9.0% and 12.6% (the radius of the Fe³⁺ ion, 0.645 Å is notably larger than that of V⁴⁺ ion, 0.58 Å). The features of crystal structure, morphology and phase transition during heating the samples were monitored using X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). For all the samples at room temperature, XRD data showed a monoclinic M₂ phase (but not more common M₁). For the most heavily doped sample, an additional weak signal due to the Fe₂O₃ phase, indicating that solubility limit of iron was reached at certain doping concentration. The phase transition temperature was determined by the midpoint between the positions of the endothermic and exothermic peaks in DSC curves (Fig. 9). For the undoped sample, it was 76 °C, and for the three doped – 78.5, 117.8 and 133.4 °C, respectively. The transition temperature being almost doubled for largest doping concentration is higher than in any previous reports on VO₂:Fe, for instance in [54]. The noticeable broadening of the DSC peaks for the sample with 12.6% Fe is apparently associated with the formation of Fe₂O₃ phase. However, the result of 118 °C for a sample with an impurity concentration close to 9% is very positive, especially since for this sample the DSC peak width is even smaller than in the sample with 5.5% Fe.

For the sample containing 9% Fe³⁺, the XRD data fully confirmed the DSC result. Fig. 10 shows XRD spectra with the sample DSC temperature varying within the

range 25...130 °C. At $T < 90$ °C, the peaks of the M₂ phase are clearly visible. At the temperature $T = 110$ °C, they slightly decrease, a weak reflection appears between them from the tetragonal phase VO₂(R), which becomes the only dominant one in the spectrum at $T = 130$ °C.

Among the publications dedicated to doping with elements of the third group, most are related to Cr³⁺. One of the reasons is a more complex mechanism of the phase transition, which, unlike pure VO₂ or VO₂:W⁶⁺, *e.g.*, is not realized *via* direct transformation of the monoclinic M₁ into the metallic rutile (R) structure, but involves intermediate phases: M₁ → M₂ → Orthorhombic → R (Fig. 11). All the low-temperature semiconductor phases M₁, M₂ and T are characterized by very close XRD reflections, so clearly distinguishing between them is possible only with analyzing Raman spectrum in the range of V–V vibrations, around 600 cm⁻¹, as demonstrated earlier for pure VO₂ [65]. For VO₂:Cr³⁺ crystals, such a real picture of the MIT phase transition was studied in [66] using synchrotron X-ray absorption fine structure (XAFS). For the samples with Cr concentrations of 3.5% and 10% $T_{MIT} = 80.8$ °C and 111.5 °C was recorded by DSC measurements.

As for the influence of Ge impurity on the properties of VO₂, a patent was published back in 1968 [67], which proposed the use of such doping to increase the MIT temperature of VO₂ single crystals. Experimental confirmation of this possibility for VO₂ films appeared only in 2016–2017 [51, 68], and was proposed to use Ge dopant for the absorption coating of solar thermal collectors. The layers with a Ge content of up to 8.6 at.% were prepared using reactive magnetron sputtering. Using the standard four-probe method, the temperature dependence of the resistance was measured at Ge concentrations of 0.5, 4.3 and 5.9 at.% (Fig. 12). The data obtained are summarized in Table 3. Thus, the maximum transition temperature actually achieved was 93.6 °C at the Ge concentration close to 5.9%. For the Ge concentration near 8.6%, amorphization of the sample began.

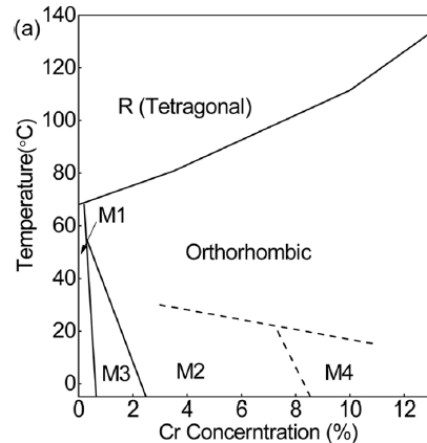


Fig. 11. T - x (Cr) phase diagram of V_{1-x}Cr_xO₂. R, M₁, M₂, M₃, and M₄ indicate the rutile and four monoclinic phases. Reprinted with permission from Ref. [66]. Copyright © 2016 American Chemical Society.

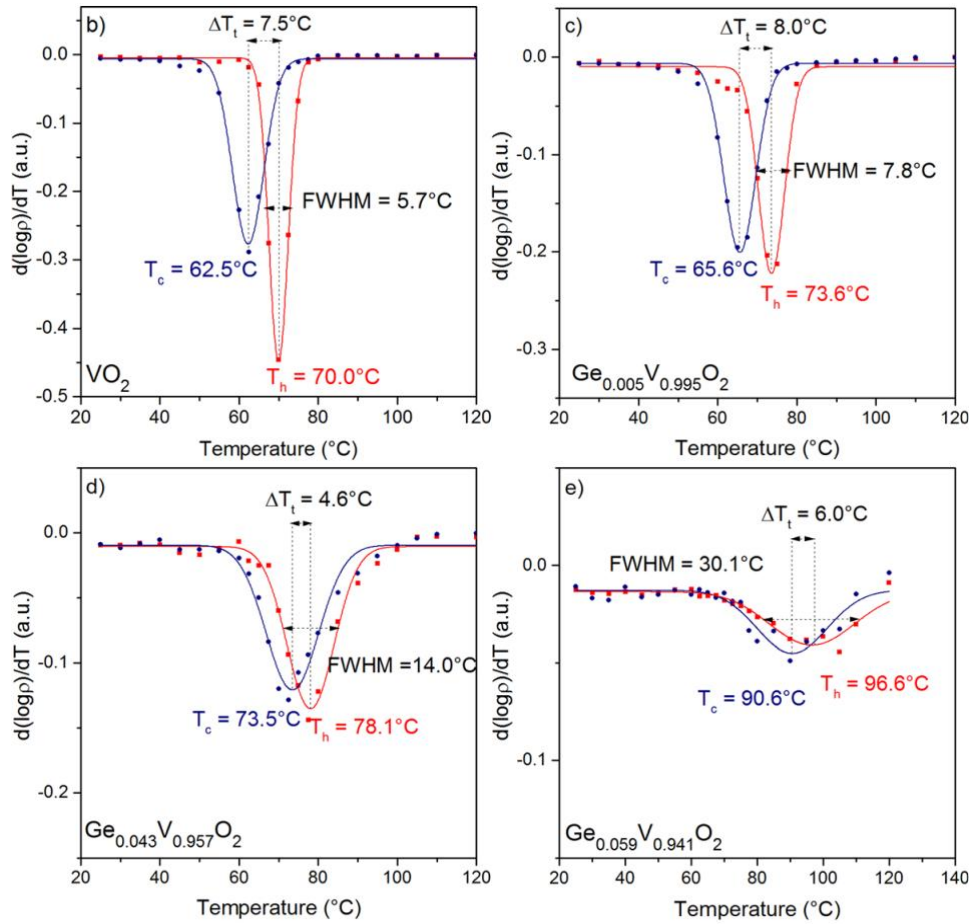


Fig. 12. (b)–(e) The $d(\log \rho)/dT$ vs T curves are plotted for all samples. Measured data points (symbols) are fitted with Gaussian functions (lines) whose minima denote the transition temperatures upon heating, T_h , and cooling, T_c . The difference between T_h and T_c gives the hysteresis width, ΔT_t , while FWHM determines the sharpness of the semiconductor-to-metal transition. Reprinted from [51], with the permission of AIP Publishing.

Table 3. Detailed switching parameters determined for doped vanadium dioxide films with various impurity contents of Ge in Ref. [51].

Ge content (at.%)	T_h (°C)	T_c (°C)	T_{MIT} (°C)	ΔT_t (°C)	FWHM (°C)
0.1	70.0	62.5	66.3	7.5	5.7
0.5	73.6	65.6	69.6	8	7.8
4.3	78.1	73.5	75.8	4.6	14.0
5.9	96.6	90.6	93.6	6	30.1

5. Conclusions

1. Varying the temperature of the metal-insulator phase transition of VO_2 films relative to the standard temperature of 68°C is a realistic way to expand the technical capabilities of controlling electrical and optical characteristics in various types of electronic, optoelectronic and optical devices in the infrared and visible ranges.

2. T_{MIT} depends on the structural and morphological properties of VO_2 films and is defined by the substrate material, mechanical stresses and dopants in

the film. Depending on the valence and size of the doping atoms, the transition temperature can vary from the room one up to $\sim 100^\circ\text{C}$. Substitutional impurities having a higher valence reduce T_{MIT} , with the maximum temperature reduction being achieved with W^{6+} . The highest transition temperature of about 100°C is achieved by doping with lower valence atoms (from the groups II and III), such as Cr^{3+} and Fe^{3+} . Doping of VO_2 films with a germanium impurity at a concentration of up to 6% can be also used to increase the phase transition temperature to almost 100°C , in particular for use in thermal water collectors heated by solar radiation.

3. Doping with boron (B^{3+}) is a special case, because due to their very small size, these atoms occupy interstitial positions in the VO_2 lattice, and provides an anomalous decrease in T_{MIT} .

4. The experimental studies of recent years, including VO_2 films doped with boron, show that the most controlled and reproducible doping of the films is achieved when growing the films using pulsed laser deposition (usually by using excimer lasers). It allows transition of a noticeable part of V^{2+} ions into V^{3+} state, which provides a record-breaking decrease in T_{MIT} , up to 31.5°C per one atom % of B.

5. For the effective control of VO₂ parameters, a positive effect can be achieved by simultaneous doping with two types of impurities (for example, W⁶⁺ and Mg²⁺), the former of which defines a significant change in the transition temperature, and the latter improves the resulting optical characteristics within the range 250...2500 nm due to increasing the optical band gap of VO₂.

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Варіювання температури фазового переходу метал-ізолятор у VO₂: огляд деяких можливих варіантів реалізації

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Анотація. В основі величезного інтересу до VO₂, який стимулював велику кількість досліджень і публікацій в останні десятиліття, є фазовий перехід метал-ізолятор, який реалізується в ньому при $T = 68\text{ }^{\circ}\text{C}$ із зміною низькотемпературної напівпровідникової моноклінної фази у високотемпературну металічну фазу зі структурою рутилу. Незважаючи на дискусію, яка триває до сьогодні, про фізичний механізм переходу, той факт, що він супроводжується радикальними швидкими змінами електричних та оптичних характеристик матеріалу на декілька порядків свідчить про реальні можливості його використання у вирішенні широкого переліку практичних проблем у оптиці, оптоелектроніці і сенсорній техніці. На сьогодні є вже немало свідчень реалізації з VO₂ таких задач. При цьому став очевидним той факт, що реалізація вирішення таких практичних задач набагато розширилася б та спростилася при можливості управління температурою фазового переходу, в першу чергу, її пониженні до кімнатної температури. Це стало предметом численних досліджень і багатьох десятків публікацій. Як основні можливі фактори впливу на температуру переходу досліджуються механічні напруження в ґратці VO₂, роль кисневих вакансій, концентрація вільних носіїв заряду, що регулюється домішковим легуванням або імплантуванням низькотемпературної напівпровідникової фази VO₂, та ще ряд інших шляхів. Співставленню деяких із цих шляхів і присвячено цей огляд. У першу чергу обговорюються варіанти декількох найбільш ефективних варіантів впливу на температуру переходу із збереженням при цьому суттєвої зміни модуляційних характеристик VO₂.

Ключові слова: оксид ванадію, фазовий перехід метал-ізолятор (МІП), температура МІП, напруження, кисневі вакансії, легування.