Synthesis and Characterization of VO$_2$-based Thermochromic Thin films for Energy Efficient Windows

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Abstract

Thermochromic doped and undoped VO$_2$ thin films have successfully been grown on SiO$_2$-coated float glass by reactive DC and pulsed-DC magnetron sputtering. The influence of substitutional doping of V by higher valence cations such as W, Mo and Nb and respective contents on the crystal structure of VO$_2$ is evaluated. Moreover, the effectiveness of each dopant element on the reduction of the intrinsic transition temperature and infrared modulation efficiency of VO$_2$ is discussed. In summary, all dopant elements regardless the concentration, within the studied range, formed a solid solution with VO$_2$, which was the only compound observed by X-ray diffractometry. Nb showed a clear detrimental effect on the crystal structure of VO$_2$. The undoped films presented a marked thermochromic behavior, specially the one prepared by pulsed-DC sputtering. The dopants effectively decreased the transition of VO$_2$ to the proximity of room temperature. However, the IR modulation efficiency is markedly affected as a consequence of the increased metallic character of the semiconducting phase. Tungsten showed to be the most effective element on the reduction of the semiconducting-metal transition temperature, while Mo and Nb showing similar results the latter is detrimental to the thermochromism.

Keywords: Vanadium dioxide; Thermochromic films; Magnetron sputtering; Solar control coatings; Energy efficient windows;

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1. Introduction

Solar control coatings are a technology with growing interest due to the necessity of improving the energy efficiency of buildings avoiding excessive energy consumption with cooling systems on summer. The latest approach is based on the use of thermochromic coatings on so-called "smart" windows. These coatings possess the ability of actively changing their optical properties as a consequence of a reversible structural transformation when going through a critical temperature.

Vanadium dioxide is an example of a thermochromic material which is a promising candidate for this kind of application as proposed by Granqvist [1]. The change on its optical and also electrical properties takes place at approximately 68ºC as a result of a first-order structural transition, going from a monoclinic to a tetragonal phase upon heating [2, 3]. The atomic displacements driven by the structural transition are accompanied by a redistribution of the electronic charge in the crystal lattice, which in turn changes the nature of the interatomic bonding [4]. The low temperature semiconducting phase which is transparent to radiation in the visible and infrared spectral ranges maximizes the heating due to blackbody radiation, while the metallic high temperature phase filters the infrared radiation and maintains at the same time the transparency required, in the visible range, to keep an environment of natural light. In order to achieve a reasonable transparency (Transmittance~40-60%) in the visible range and at the same time an acceptable IR modulation efficiency the VO_2 films must not exceed thicknesses in the order of 100-150nm [5], and combined with anti-reflection coatings the transparency can be further improved [6, 7]. To obtain window coatings with controlled thicknesses in the nanometer range atomistic processes such as magnetron sputtering are well suited to fulfill the condition. A semiconductor-metal transition temperature of 68ºC is too high for this application and must therefore be reduced. At present, there are two approaches to reduce the transition temperature, the substitution of part of the vanadium cations by other metals such as tungsten [8-14], molybdenum [15-18] or niobium [16, 19, 20], or the substitution of part of the oxygen anions by other elements, e.g. fluorine [21].

In this study, we compare magnetron sputtered VO_2 thin films prepared with different doping elements such as W, Mo and Nb and different doping concentrations. We report on the influence of each element and respective concentrations on the crystal structure of the films, optical/thermochromic performance and effectiveness on the reduction of the semiconductor-metal transition from 68°C to room temperature, envisaging the application on energy efficient windows.

2. Experimental details

The vanadium dioxide films were reactively deposited onto SiO_2-coated float glass substrates by DC and Pulsed DC magnetron sputtering from a high purity (99.95%) metallic vanadium target in a given oxygen/argon atmosphere. Prior to the deposition, the vacuum chamber was evacuated down to a pressure of about $3x10^{-5}$ mbar. A pre-sputtering of the metal target was carried out before each deposition during 10 minutes, in the same conditions as for film preparation, but in an oxygen-free atmosphere. This procedure ensures an oxide-free metallic surface for each deposition. For the deposition of the films, both oxygen and argon were introduced into the chamber separately through two gas mass flow controllers. The deposition parameters chosen to deposit the three sets of films are summarized in Table 1. The doping of the films was done by placing a number of high purity dopant metal pieces in a concentric positioning over the round vanadium target so both elements could be co-sputtered allowing a homogeneous dispersion of the dopant elements in the film. In order to obtain films with different dopant concentration the number of dopant pieces has been either varied or moved along the target surface.

The actual doping concentration in the films has been determined by X-ray photoelectron spectroscopy (XPS) which permitted to assess the elemental composition of the films. The structural characterization has been done by X-ray diffractometry (XRD) using a X-ray diffractometer operating with a continuous scan of Cu $K_{\alpha1}$ radiation with λ=1.54056Å. The optical/thermochromic behavior has been evaluated in an optical spectrophotometer (Shimadzu UV-3101PC) with an embedded sample heating-cooling cell. It has been done by measuring the spectral

normal transmittance at the UV-VIS-NIR range, from 250 to 2500 nm, under and above the transition temperature. The determination of the transition temperature was carried out by evaluating the optical transmittance change with temperature at a given near-infrared (NIR) wavelength, in this case at $\lambda=2500$nm. The transition temperatures were then estimated by determining the first derivative of both curves of the hysteresis loops (heating and cooling) and considering the mean value.

3. Results and discussion

3.1. Structural characterization

The crystal structure of the three sets films has been assessed by XRD and the obtained diffraction spectra are shown in Fig. 1. The XRD patterns show the range where the most significant reflection peaks of VO_2 appear. The poor signal intensities of the crystallite reflected plane directions are due to the nanocrystallinity and small thicknesses of the films which are estimated to be around 125nm, for the chosen processing conditions [5]. Despite the broad shoulder found within 15-40º which is due to the contribution of the amorphous volume of glass substrate, all patterns can be indexed to single-phase $VO_2(M)$ which holds a monoclinic structure [22]. No reflections were observed attributable to other vanadium oxides or to compounds deriving from the dopant elements, which suggests that a solid solution of vanadium dioxide with dopant homogeneously dispersed is formed. It can be seen in Fig. 1(a) that for the given processing parameters, pure vanadium dioxide reveals a structure preferably oriented in the (002) plane direction, as observed by the peak at $2\theta=39.6º$, although some traces of (011) reflection are detectable at $2\theta=27.8º$. With addition of tungsten to a certain extent, as seen in pattern (2) for film $V_{0.97}W_{0.03}O_2$, the same preferential crystal orientation is maintained. The film with the highest W content, $V_{0.95}W_{0.05}O_2$, reveals an evident polycrystalline structure in which the (011) plane direction becomes the dominating crystal orientation. This indicates the existence of a critical level of W

contents in the VO_2 solid solution above which the structure becomes more stable oriented along the (011) direction. All Mo-doped films reveal preferential crystal orientation along the (002) direction for all films regardless the Mo-doping level, although some traces of crystallites oriented along the (011) and (21-1) directions are barely noticeable at $2\theta = 27.8º$ and $37.0º$, respectively. In summary, no significant differences on the crystal structure can be observed in the films with different Mo contents. This is in agreement with results reported for Mo-doped VO_2 on single crystal sapphire substrates prepared by pulsed laser deposition [23] and RF sputtered Mo-doped VO_2 [17] although the latter present strong (011) preferred orientation. Concerning to the VO_2 films prepared by pulsed-DC sputtering, shown in Fig. 1(c), the main crystal orientation is again along the (002) direction although the (011) is also noticeable in some of the films. Comparing the patterns for different Nb contents in the region of the (002) diffraction peak, as seen in the inset, a shifting of the peak to lower angles accompanied by a broadening is observed as the Nb at.% in the film is increased. X-ray diffraction peaks broaden either when crystallites become smaller or if lattice defects such as microstresses, stress gradients and/or chemical heterogeneities are present in large enough abundance [24]. Peak shift is related to different types of internal stresses and planar faults in the crystal lattice, especially stacking faults or twin boundaries. In this particular case, the peak shifts towards lower diffraction angles which implies an increase of interplanar spacing after Nb doping. These changes on the (002) diffraction peak parameters have not been observed in our previous studies for tungsten [14], molybdenum [25, 26] and Indium [26] as dopants in VO_2.

3.2.   Optical analyses

The optical properties of the films have been studied by optical spectrophotometry in the UV-VIS-NIR range and the obtained results are shown in Fig. 2. On the left is shown the optical transmittance as a function of wavelength and on the right is shown the optical transmittance at $\lambda=2500nm$ as a function of temperature. It can be seen in Fig. 2(a1) that maximum luminous

transmittances of about 30-40% coupled with a sharp thermochromic switch behavior at the near-IR

spectral range that is reduced by increasing W doping concentrations. The differences regarding the

maximum luminous transmittances are mainly due to slight variations in thickness from film to film

and not due to a significant influence of tungsten, which is in accordance to what was observed by

Burkhardt *et al.* [8]. With increasing W doping concentrations up to 5% the IR modulation

efficiency (Ts-Tm) reduced from 35%, for the undoped film, down to 23%. Moreover, it can be

observed a slight loss in the luminous transparency when switching from semiconducting to metal

state, which is common in all films regardless the dopant element and concentration. The Mo-doped

films showed maximum optical transmittances in the visible range from 35 to 45% and decreased

IR modulation efficiency from 36 to 25% with increasing substitutional Mo content from 3 to 11%.

The infrared modulation efficiency of the pure VO_2 film prepared by pulsed-DC sputtering, shown

in Fig. 2(a3) was found to be higher than that of VO_2 prepared by conventional DC sputtering, as

seen in Fig. 2(a1). The use of an asymmetric-bipolar pulsed DC power supply allows higher

sputtering yields by periodically reversing electrode voltage and thus neutralizing charge build-up

on the target surface during poisoning in the reactive process. In addition, it was also reduced the

working gas pressure and increased the ion current density. All these factors contribute to a higher

ion bombardment during film growth which contribute to and improved film density/crystallinity

and enhance its properties. The infrared modulation efficiency is again affected by the Nb contents

in the film and a marked drop is obvious for Nb over 4 at.%. Above this Nb content, the material

starts revealing a very pronounced metal-like character, as demonstrated by the decrease of

transparency to infrared light of the low temperature phase. Moreover, the maximum luminous

transmittance is around 40%, for pure VO_2, and progressively decreases down to 22% with the

increase of substitutional Nb up to 11 at.% in the VO_2 solid solution. The decrease in the IR

modulation efficiency resulting from doping is mainly due to decrease in the transmittance in the

semiconducting state. This decrease is explained by the enhancement of the carrier concentration

due to the presence of dopant ion donors [21, 27] which also lowers the resistivity of the films [27].

The doping of VO_2 increased the electron density in the film, which caused the Fermi energy level shift towards the conduction band. Since intrinsic VO_2 thin film is *n* type, introduction of ion donors cause an inevitable degradation of the transmittance (and resistivity) of the semiconducting low temperature phase. Likewise, it is expected that the enhancement of the carrier concentration would also lower the transmittance at the infrared in the metallic state, which does indeed in the case of the Nb doped films, as seen in Fig. 2(a3). However, W and Mo doped films do not show the same trend. Although we were not able to effectively determine crystallite sizes due to poor peak statistics of XRD patterns for the different doped films, it has been shown that doping reduces the crystallite size [28, 29]. Therefore, the number of crystallites as well as boundaries volume will increase and contribute to trap charge carriers which will result in loss of the metallic behavior. We speculate that in case of W and Mo doped films this effect could be more marked than that of increase in carrier concentration due to W and Mo donors. Substitution of V^{4+} by higher valence cations such as Nb^{5+}, W^{6+} and Mo^{6+} give rise to the same $V_{1-x}M_xO_2$ system [2]. According to studies conducted by Tang *et al.* [30] , each added W ion breaks up a V^{4+}-V^{4+} homopolar bond and causes the transfer of two 3d electrons to the nearest V ions for charge compensation, forming two new bonds, V^{3+}-W^{6+} and V^{3+}-V^{4+}. The loss of homopolar V^{4+}-V^{4+} bonding destabilizes the semiconducting phase and lowers the metal-semiconductor transition temperature. As for W doping, Mo acts in the same way on the reduction of phase transition temperature, i.e. introducing extra electrons in the d bands of vanadium which induce a charge transfer from Mo to V [2]. In the case Nb, according to Magariño and co-workers [20], the Nb^{4+} ion substitutes the V^{4+} ion in the V^{4+}-V^{4+} bonding and due to charge transfer a V^{3+}-Nb^{5+} bond is formed.

As observed in Fig. 2(b1-b3), the semiconductor-metal phase transition exhibits a characteristic thermal hysteresis which is due to latent heat evolved and absorbed during the first-order structural transition [17]. It is clear the shifting of the hysteresis loops to lower temperatures as a consequence of the increasing contents of substitutional W in the VO_2 solid solution. The resulting transition temperatures determined from the optical transmittance hysteresis loops were adjusted from 63ºC to

28ºC. The addition of Mo or Nb to VO_2 also affects the hysteresis loops which is also shifted to lower temperatures as the doping concentrations increase. Transition temperatures as low as 32 and 34ºC were achieved for Mo-doped and Nb-doped films, respectively. The transition temperature (Tt) obtained for the pure VO_2 film prepared by pulsed-DC sputtering was 59 ºC, which is lower than that obtained for VO_2 prepared by DC sputtering, 63ºC. It is know that the transition temperature of pure VO_2 in thin film form may present reduced values depending on properties such as stresses, thickness, stoichiometry, structure, grain size, etc. [9, 15], which are directly associated to the chosen processing conditions. Pure VO_2 shows a clear transition region with well defined semiconducting and metal domains. The doped $V_{0.96}Nb_{0.04}O_2$ film shows a similar hysteresis loop shape but with a clear shift to lower temperatures without any significant loss in the transmission in the semiconducting state. For higher Nb concentrations it is obvious a degradation of the hysteresis which makes ambiguous the boundaries of the transition. The estimated transition temperatures in these cases are not in fact a result of a real reduction in the temperature, which would be given by a shift of the hysteresis, but rather in a reduction of the slope of the transition. In all cases it is also observable a reduction of the hysteresis width which is assumed to result from reduction of crystallite size distribution with doping [17, 21].

The effectiveness of each dopant on the reduction of the semiconducting-metal transition temperature in VO_2 is compared in Fig. 3. All three elements showed a linear decrease of the transition temperature with the increase in the concentration of substitutional doping element. Tungsten is clearly the most effective dopant element showing a decrease of about 7ºC per at%. Mo and Nb showed close results, about 3ºC and 2ºC, per Mo and Nb at%, respectively.

4. Conclusions

Thermochromic VO_2 thin films were successfully synthesized by DC and pulsed-DC reactive magnetron sputtering. Different dopant elements, such as Tungsten, Molybdenum and Niobium, with different doping concentrations were introduced in the VO_2 solid solution during the film

growing by co-sputtering the respective metal dopants and Vanadium in a reactive O_2/Ar atmosphere. XRD results showed single phase $VO_2(M)$ for all films regardless dopant element and concentration. The dopants effectively decreased the transition temperature of VO_2 whereas the thermochromism of the films was markedly affected, specially the in the Nb-doped ones. Nb causes significant amount of defects in the crystal lattice which clearly degrade the optical properties while reducing the semiconductor-metal transition to room temperature.

Acknowledgements

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List of Tables

Table 1. Processing conditions used to deposit the VO_2 films.

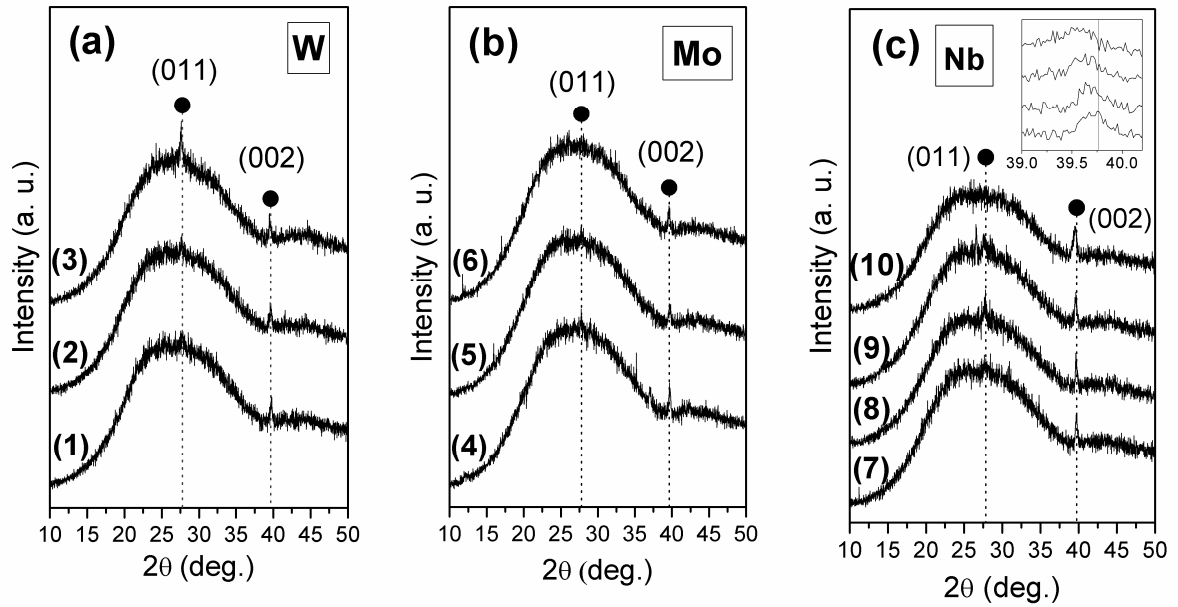|	W- and Mo-doped films	Nb-doped films
Base pressure (mbar)	3x10-5	3x10-5
Work pressure (mbar)	4x10-3	1x10-3
Oxygen/Argon ratio (%)	14.3	50
Total gas flow (sccm)	19.2	6
DC current (A)	0.5	-
Pulsed-DC current (A)	-	0.58
Frequency (kHz)	-	10
Reverse time (μs)	-	5
Substrate temperature (ºC)	450	450
Deposition time (min)	5	3

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Fig. 1. XRD spectra of VO_2 films deposited by (a-b) DC and (c) pulsed-DC sputtering, doped with different dopant element and contents: (a1) pure VO_2, (a2) $V_{0.97}W_{0.03}O_2$ and (a3) $V_{0.95}W_{0.05}O_2$; (b4) $V_{0.97}Mo_{0.03}O_2$, (b5) $V_{0.94}Mo_{0.06}O_2$ and (b6) $V_{0.89}Mo_{0.11}O_2$; (c7) pure VO_2, (c8) $V_{0.96}Nb_{0.04}O_2$, (c9) $V_{0.93}Nb_{0.07}O_2$ and (c10) $V_{0.89}Nb_{0.11}O_2$.
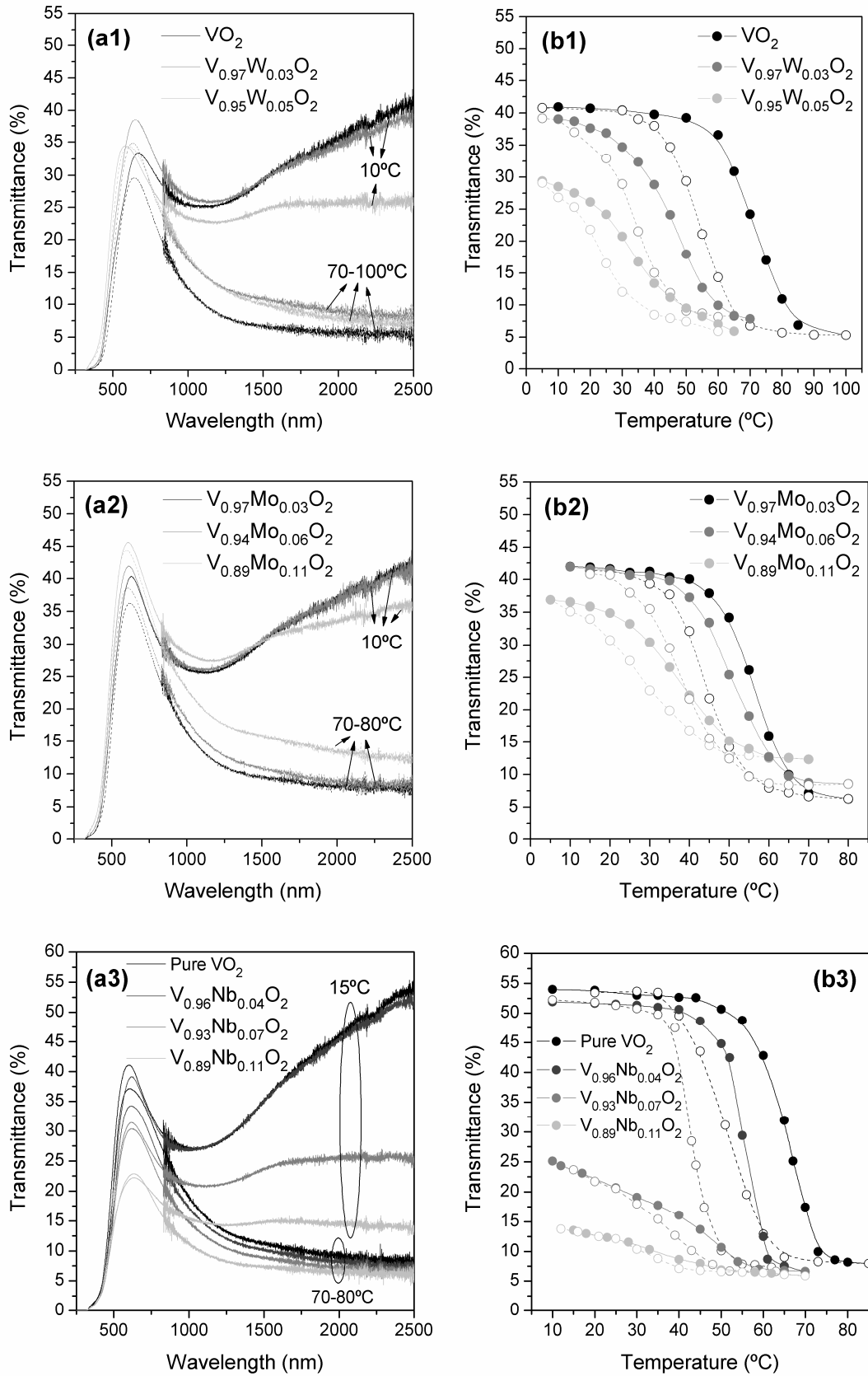
Fig. 2. Optical transmittance spectra of VO_2 films: (a1-a3) optical transmittance as a function of wavelength, in semiconducting and metallic states; (b1-b3) optical transmittance as a function of temperature obtained at $\lambda=2500nm$.
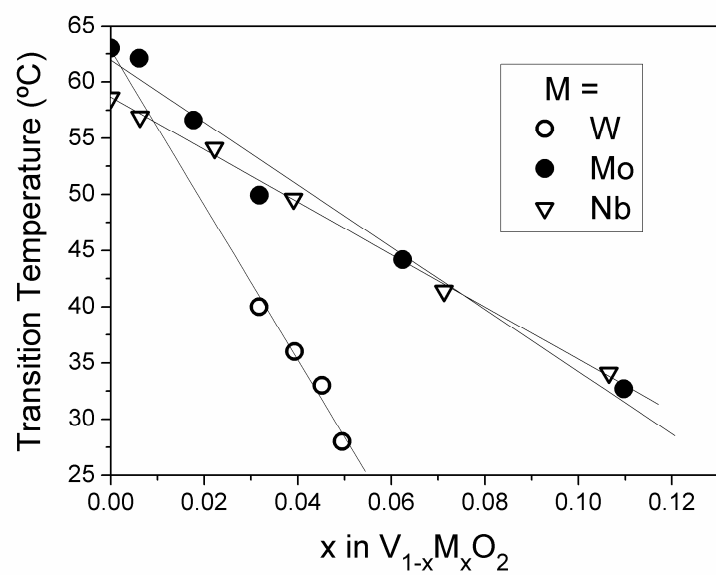
Fig. 3. Relationship between the dopant contents in the film and the resultant semiconductor-metal phase transition temperature.