

INVESTIGATION OF PHASE TRANSITION MECHANISM IN VANADIUM OXIDE THIN FILMS

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Thin film materials with "smart" properties which react with temperature variations, electrical or magnetic fields, and pressure variations, attracted great attention in recent years. Vanadium dioxide thin films belong to this family of "smart materials" by having a first order phase transition metal-semiconductor. These films display a variety of conductivities under heating in the vicinity of Curie temperature. The electrical properties of vanadium dioxide films were studied in past and found to be outstanding. This paper deals with the electrical properties of specific vanadium oxide thin films, deposited on various substrates. We have been able to show that the electrical transport mechanism of the obtained vanadium oxide films differs in low and high electrical fields. In low electrical fields, conductivity is obtained by Schottky transport mechanism, whereas in high electrical fields conductivity ranges from Ohmic mechanism for low fields to Poole-Frenkel for higher fields.

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1. Introduction

During the past decade passive light sources have gained wide spread, parallel to conventional active light sources such as light emitting diodes (LEDs), incandescent lamps, gas-discharge devices, etc. Passive light sources may vary their optical properties by external parameters such as: temperature variations, electrical or magnetic fields and pressure variations. These passive light sources can generate high intensity illumination with high energy efficiency. One of the leading passive sources is the liquid crystal displays (LCD), applied in vast amounts of measuring displays and handheld computers/televisions. In spite of its evident merits, LCD has significant disadvantages such as low contrast under bright illumination and irreversible change in colors with time.

Various materials may become passive light sources under the influence of external physical parameters. Materials having a first order phase transition of metal-semiconductor with high inversion factors of their electrical and optical properties, are preferred candidates for passive light sources. All of these materials are compounds of the 3-d, 4-d, and 5-f elements [1]. One of these families of materials is the vanadium dioxide. It is well known that the first phase metal-semiconductor transition in vanadium dioxide films occurs at a temperature of 67 °C [2]. VO₂ is metal with tetragonal symmetric lattice crystal above this transition temperature. At lower temperatures of the transition point, the vanadium dioxide becomes a semiconductor with monoclinic lattice symmetry and a band-gap of approximately 0.7 eV [3].

Vanadium oxides as bulk materials have been extensively studied during the past decades due to their electrical, magnetic, catalytic and electrochemical properties. Vanadium oxide thin films were applied in various electro-optical devices such as thermoelectric sensors [4], light modulators [5] and electro - chromic electrodes [6]. However, most of the researches of semiconductor-metal phase

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transitions in vanadium oxides were focused to single crystal materials [7]. Bandgap width, temperatures of phase transitions and values of hysteresis, were obtained for single crystal VO₂ only.

Vanadium oxide thin film structures are more convenient for practical electronics and optoelectronics applications. Previous researches on the conductivity mechanism versus temperature in vanadium oxide had indicated on a change from a smooth increase with the temperature increase, which is very typical to semiconductors, up to exponential growth of 3-5 orders of magnitude in the vicinity of the temperature phase transition [8-10]. The obtained data on hysteresis values and optical properties variations were found to be distinguished as well. This was the motivation for our study to provide additional knowledge on the electro-physical properties of vanadium oxide thin films deposited on various substrates.

2. Experimental procedure

The Vanadium Oxide thin films were deposited using thermal evaporation as described in our previous paper [11]. A laboratory vacuum station, shown in Fig. 1, was utilized. Core evaporated elements in tungsten boats and baskets, were taken as: VO₂ powder, V wires, and V powder. Then the vanadium was thermally oxidized in furnace at argon-oxygen flow of (10:1) in temperatures of 350-500 °C. The obtained films were deposited on single crystal n-type (100) silicon substrates, 1 Ω¹·cm⁻¹ conductivity, on Corning glass slides. All substrates were cleaned prior to the V films deposition. Glass slides were cleaned in iso-propanol using an ultra-sound bath. The Silicon samples were cleaned in a buffer solution (HF:NH₄F = 1:7) for 1 minute in 25 °C, in order to remove the native silicon oxide from their surfaces. Then the samples were rinsed in soft water. After cleaning the samples with tri-chloro-etylan and some more rinse in deionized water, the samples were ready to a pre-treatment of washing in RCA-2 solution (H₂O:H₂O₂:HCl = 20:1:1) for 20 minutes at 50 °C and in ultra-sonic cleaning bath. The final rinse is done with iso-propanol. The thickness of the obtained vanadium films was of 80 nm.



Fig. 1. Thermal evaporation vacuum set-up lab.

Fig. 2 presents typical samples and shows the electronic measuring methods applied for electrical characterization. Samples of Al-VO_x-Si-Au were used for transversal electronic measurements. Samples of Ag-VO_x-Ag were used for lateral electrical characterization. All of these measurements were provided with various temperatures.

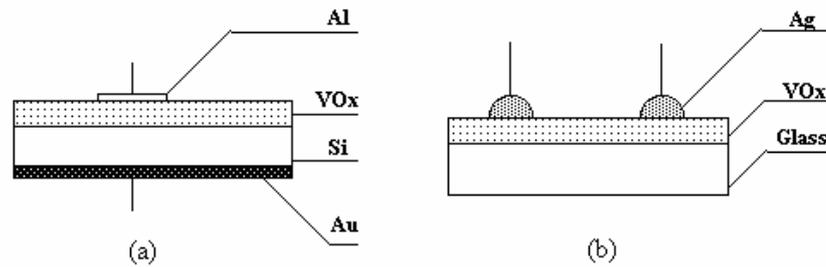


Fig. 2. Typical structures of electrical characteristics: (a) Al-VO_x-Si-Au structure, (b) Ag-VO_x-Ag structure.

3. Results and discussion

Fig. 3 presents temperature characteristics of the lateral resistance measured in the samples shown in figure 2-b. Resistance of the samples, as shown in the figure, is smoothly changed in two orders of magnitude. The hysteresis loop looks wider than in single crystal VO₂ described by N. Mott [7]. It also looks different from VO₂ epitaxial layers grown on single-crystal sapphire substrates [8]. Maximum hysteresis in our samples was found to be about 10 °C in the steepest zone. This steep reduction in resistance in comparison with single-crystal films is explained by the crystalline structure of films. P. Jin et al. [8] have compared the temperature hysteresis loops for various vanadium oxide films and observed a significant decrease in resistance variations for the case of polycrystalline films. Moreover, the temperature hysteresis loop width may vary from 0.5 up to 50 °C in various oxides of vanadium [1]. Therefore, this widening effect in the hysteresis loop is explained by two reasons: (1) the polycrystalline or amorphous structure of the deposited films (unlike the single crystal structure), (2) non-stoichiometric composition of the films. In other words, the vanadium oxide films in our experiments represent a complex structure of various oxides with various temperatures of phase transition for each one of them. Thus, this coercive temperature gets the following interpretation: it shows the energy value required for the beginning the phase transition. In addition to that, the multiplication in vanadium oxides types results in to a hysteresis loop widening.

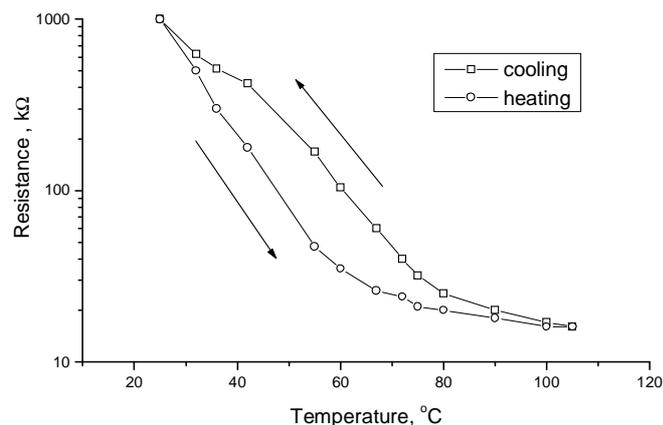


Fig. 3. Longitudinal resistance influenced by temperature variations.

The thin film structure Ag-VO_x-Ag under applied voltage sometimes appears as a two back-to-back diodes pair. For a metal-semiconductor transition (Ag-VO_x) diode, we can obtain the known formulation in first approximation [12]:

$$I = A^* S T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] \quad (1)$$

where A^* is the Richardson's constant, S is a contact area, T is the absolute temperature, q is the elementary charge, k is the Boltzmann's constant, ϕ_B is a potential barrier on the interface metal-semiconductor, and V is the applied voltage. The two diodes are in equilibrium state. Therefore, our interpretation is that the current in the system is defined by backward saturation current only. Rouge estimation of the second term influence in equation 1 is done using the tentative value of the potential barrier value of the Ag-VO_x interface. The values of the potential barriers for the systems: Ag-Si and V-Si were measured by G. Golan et al. [13]: $\phi_{B(Ag-Si)} = 0.47$ eV, $\phi_{B(V-Si)} = 0.68$ eV. Thus, it can be assumed that $\phi_{B(Ag-V)}$ will be about 0.21 eV. The voltage applied to the system of back-to-back diodes will be divided between to diodes, in forward and backward biases. Therefore, the value of the voltage drop V will be equal to the difference between the supplied voltage (1 V in our case) and $\phi_{B(Ag-V)} = 0.21$ V. In this case the second term will be equal to ≈ -1 and we'll obtain a simplified expression:

$$I = A^* S T^2 \exp\left(-\frac{q\phi_B}{kT}\right) \quad (2)$$

This expression describes a Schottky diode mechanism of free charge carriers transport in our studied samples. In order to verify the electrical behavior in these samples, a current influence on temperature in the Schottky coordinates: $\ln(I/T^2) \sim f(1/T)$, has to be made. Fig. 4 presents the saturation current influenced by temperature variations. A linear change in the current from room temperature and up to the phase transition zone, can be observed. Following completion of the phase transition, the current changes starts changing linearly again. It is observed that the phase transition occurs in the temperature range of 55 – 75 °C. A linear behavior of the current in Schottky coordinates illustrates the Schottky mechanism of the electrical conduction in the vanadium oxide films before and after the phase transition. In our case, the electrical field magnitude may be estimated from the distance between electrodes and the applied voltage. For a distance of 1 mm and applied voltage of 1 V we obtain an electrical field of 0.1 V/cm, which is a weak electrical field. Thus, in the weak electrical field, the Schottky mechanism defines an electrical transport in the vanadium oxide thin films.

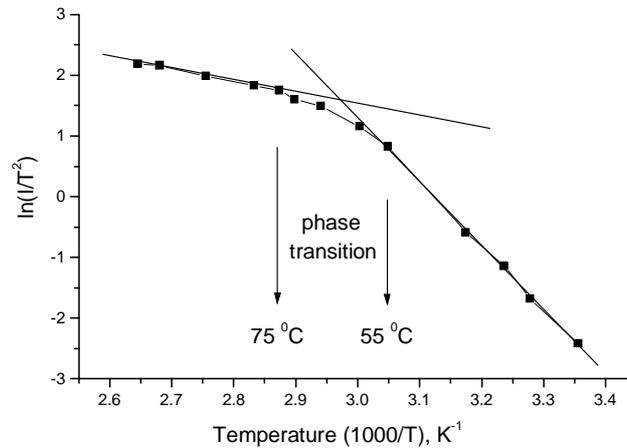


Fig. 4. Saturation current influenced by temperature variations.

Expression (2), following the correction in lowering the Schottky barrier due to the presence of an electrical field, may be transformed as follows:

$$\ln\left(\frac{I}{A^*ST^2}\right) = -\frac{q}{kT}\left(\phi_B - \sqrt{\frac{qE}{\pi\epsilon}}\right) \quad (3)$$

where E is the applied electrical field and ϵ is the permittivity of the material (vanadium oxide). The Richardson's constant may be shown as well as [14]:

$$A^* = \frac{4\pi q m^* k^2}{h^3} \quad (4)$$

where m^* is the effective mass of charged carriers and h is the Planck's constant.

The above mentioned equations expose only two parameters that are defined by the crystalline structure of the material. These parameters are the effective mass m of the charged carriers, defined by the geometrical shape of the crystal, and the permittivity, ϵ . Therefore, the slope angle of the characteristics shown in figure 4 is defined by the structure variations in the material under phase transition. A better symmetrical structure of the heated vanadium oxide structure results in lowering of the permittivity and increasing of the effective mass of the charge carriers.

Fig. 5 presents a typical I-V characteristic of the system Al-VO_x-Si-Au designated as transversal structure. These measurements were provided for temperatures lower than the phase transition temperature. The obtained characteristic is symmetrical and behaves linearly for electrical fields lower than $6 \cdot 10^4$ V/cm. This behavior may be explained by the Ohmic mechanism of conductivity in the medium electrical field. A further increase in the applied voltage results in an exponential behavior (increase) in the current mechanism. This mechanism is typical for Schottky [7] or Poole-Frenkel [12] structures. Unlike the Schottky mechanism, defined by thermo-electron emission of the free charge carriers, the Poole-Frenkel transport is defined by emission from structural defects in energetic traps. The Poole-Frenkel mechanism is described by follows expression [14]:

$$I = qn_0\mu E \exp\left[-\frac{q}{kT}\left(\phi_B - \sqrt{\frac{qE}{\pi\epsilon}}\right)\right] \quad (5)$$

where n_0 is the carrier density, μ is the mobility of carriers, and ϕ_B is the depth of the traps in the vanadium oxide films. The second component in the square brackets is equivalent to the Schottky barrier lowering due to the presence of an electric field.

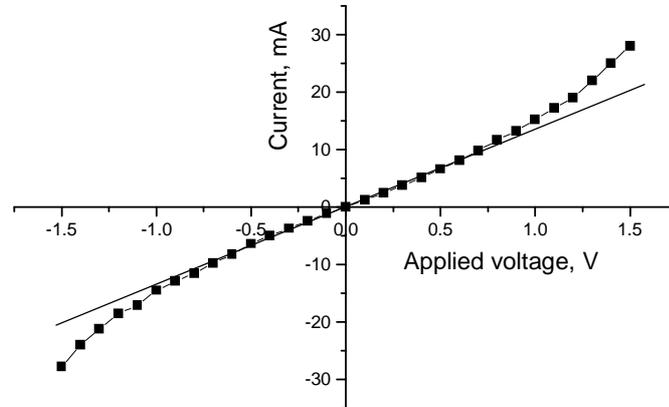


Fig. 5. I-V characteristics of Al-VO_x-Si-Au structures in the transversal plane.

Fig. 6 presents the positive part of the I-V characteristics of the transversal system, rebuild as a function of $\log(I)$. The aim of this plot is to analyze the conduction mechanism in high fields (enlarged voltages) [15]. It is seen that the conductance behavior within fields that are lower than $6 \cdot 10^4$ V/cm, may be described as a Schottky behavior and right after this value as a Poole-Frenkel behavior. Vanadium oxide thin films, deposited by metal powders or vanadium wires and oxidized in oxygen atmosphere, were found to have many bulk and surface defects. Therefore, Poole-Frenkel emission in this case is the preferable mechanism that agrees with the results described in [16].

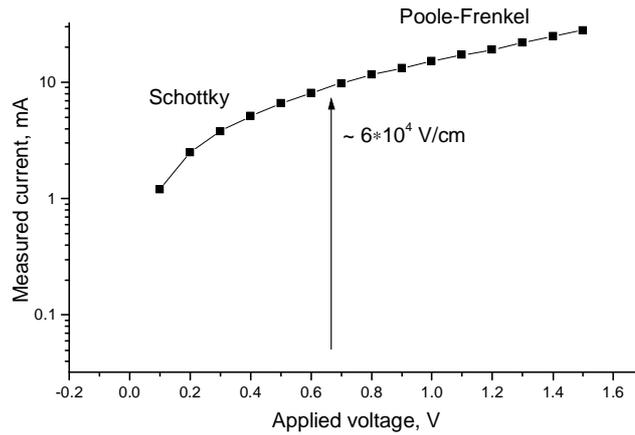


Fig. 6. First quadrant I-V characteristics.

In order to verify this thesis, the temperature influence of the measured current in the transversal system was monitored and presented in Fig. 7. Here, measurement was provided for a constant voltage supply with an electrical field of $\sim 1.2 \cdot 10^5$ V/cm. Three major different regions may be distinguished in this figure: i. from 25 °C and up to 55 °C - prior to the phase transition, ii. phase transition region at temperatures: 55-75 °C, iii. a region with temperatures of more than 75 °C. In the first region, the Poole-Frenkel mechanism is dominant on the other conduction mechanisms and conductivity increases linearly with temperature. The second region is the phase transition zone consisting of a dynamic transformation of vanadium oxide crystallites structures. The third region is typical for a metal state. Conductivity of the film decreases in this region, however this decrease is small due to the non-stoichiometric composition of vanadium oxide layers. Thus, we find in the film structure various types of vanadium oxides, resulting in a small decrease in conductivity with a temperature increase.

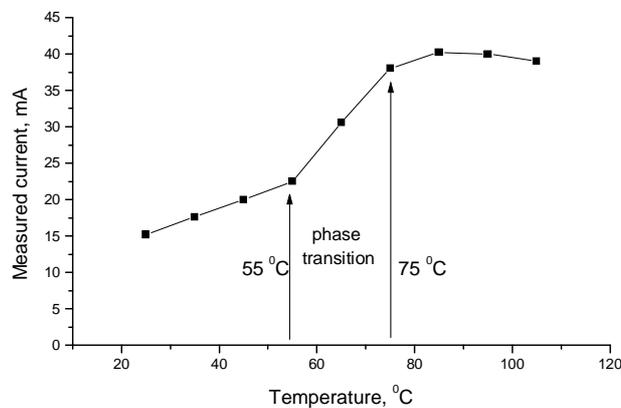


Fig. 7. Temperature influence on the measured current in the transversal planes.

4. Conclusions

Conductivity mechanisms of thin vanadium oxide films, before and after phase transition (semiconductor-metal), were studied in this work. It was found that the type of conductivity mechanism depends on the magnitude of the applied electrical field. In addition, it was shown that this mechanism varies its nature from Schottky for weak electrical field to Ohmic mechanism in medium fields and Poole-Frenkel mechanism in high fields.

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