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Thermochromic properties of VO_2 films made by RF-sputtering

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Abstract. Vanadium dioxide films with nano-structured grains have been prepared by RF-sputtering followed by thermal annealing in low oxygen pressure. The submicro-structured crystalline grains with the size of 200 to 250 nm were revealed by FE-SEM micrographs. XRD analysis proves the monoclinic lattice of the VO_2 crystalline structure and the size of the grains determined from XRD also consists of about 200 nm. The temperature of the semicoductor-to-metal phase transition (SMPT) of the films was found at $\tau_c = 64\ ^oC$. At temperatures higher than τ_c the resistance of the films decreased three orders in magnitude, and the transmittance at $\lambda = 1550$ nm lowered from 55% to a value as low as 30%. From these thermochromic properties of VO_2 films one can suggest a practical application in production of thermo-optical sensors that can be used for monitoring temperature change in petrol and/or toxic chemical storages.

Keywords: VO_2 thin films, thermochromic properties, semiconductor-to-metal phase transition

1. Introduction

Thermochromic coatings are the materials that can change the optical properties (transmission, reflection and absorption) under the action of temperature. One of the most prospective thermochromic materials is vanadium dioxide (VO_2), because VO_2 films can be used for many applications, such as sensors [1], smart thermochromic windows [2] and thermal glazing [3]. Many previous works have focused onto subject of V-based compounds of different structures like V_2O_5, VO_2, LiV_3O_8 aiming at searching for applications. To prepare the vanadium oxides thin films one can use different techniques, for instance, vacuum evaporation using boat resistance [4], RF-sputtering [5], CVD [6], etc. We have also used the electron beam technique for depositing VO_2 films [7]. Recently, in [8] thermochromic VO_2 films on stainless steel substrate were deposited by DC- reactive magnetron sputtering. The authors [9] showed that the semiconductor-to-metal phase transition (SMPT) temperature can be reduced simply by selecting the annealing temperature that induces local nonstoichiometry; a SMPT temperature as low as 42.7 °C was obtained by annealing the film at about 440 °C.

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With the aim to improve the efficiency of t0he thermochromic performance we prepare nanostructured VO_2 films by RF-sputtering followed by post thermal annealing. The electrical and optical properties vs. temperature of the films are also presented.

2. Experimental

Vanadium oxide films were prepared by RF-sputtering with using two types of ceramic targets, such as VO_2 and V_2O_3. Corning glass slides of 22 × 70 mm size were used for substrates. The substrates were ultrasonically cleaned in distilled warm water, followed by cleaning in ethanol and acetone. To get nano-structured films here we have deposited on unheated substrates and maintained the deposition rate at a value as low as 0.05 nm/s. As-deposited films were then put into a quartz-tube furnace in a oxygen pressure of 1.33 Pa. Firstly, the samples were heated at 100^{o}C for 30 min and then carefully annealed in the same furnace for a total time of 7 hours at temperature growing up to 450 ^{o}C for 3 hours, keeping at this temperature for 2 hours and lowering down to room temperature for 2 hours. The crystalline structure has been studied by using X-ray diffraction analysis (XRD) and the morphology of the samples surface – by scanning electron microscopy (FE-SEM). The temperature dependence of the conductance was characterized by using an Autolab.Potentiostat-PGS-12. Optical transmittance spectra vs. temperature was measured by using a Jasco-V570 spectrophotometer.

3. Results and discussion

3.1. Crystalline structure and morphology

Fig. 1 shows the XRD of the samples obtained by RF-sputtering and followed by post thermal treatment for two kinds of targets: one is the VO_2 and the other is V_2O_3. It is seen that although the stoichiometry of VO_2 target is matched to the vanadium dioxide, the sputtering process resulted in decomposition, consequently in the film there was observed majority of V_6O_{11} and minority of the VO_2 (this is confirmed by the much stronger intensities of the XRD peaks of V_6O_{11}, see patterns A, Fig. 1). Whereas, by using a V_2O_3 target, the annealed film exhibited a single phase of VO_2 film with seven peaks corresponding diffraction (hkl) planes: $(\bar{1}11)$, (011), $(\bar{1}02)$, $(\bar{2}11)$, (020), (220) and (022) (see the patterns B, Fig. 1). Thus, to deposit VO_2 films V_2O_3 targets are more suitable than VO_2 targets. Further, all the samples used for the study were deposited by RF-sputtering from the V_2O_3 target, followed by annealing in low pressure of gaseous oxygen.

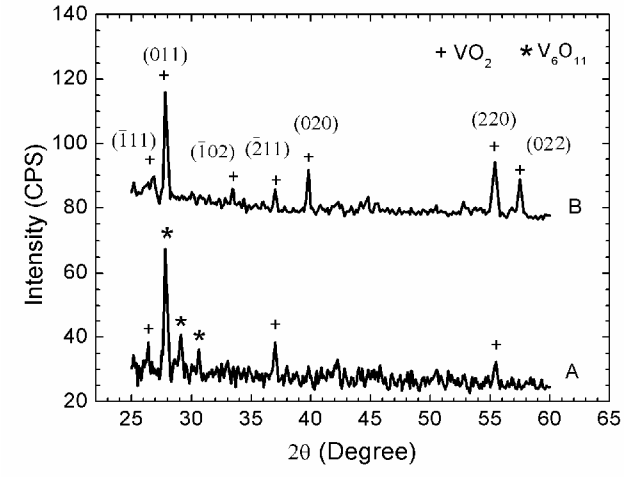


Fig. 1. XRD patterns of vanadium oxide films deposited by RF-sputtering followed by annealing. "A" patterns is of the film sputtered from VO_2 target and "B" patterns – from V_2O_3 target.

The fact that the peaks width is not very sharp shows that the VO_2 film was crystallized in rather small grains. To obtain the grain size (t) we used Scherrer's formula [10]:

$$t = \frac{0.9\,l}{b^{*} \times \cos q} \tag{1}$$

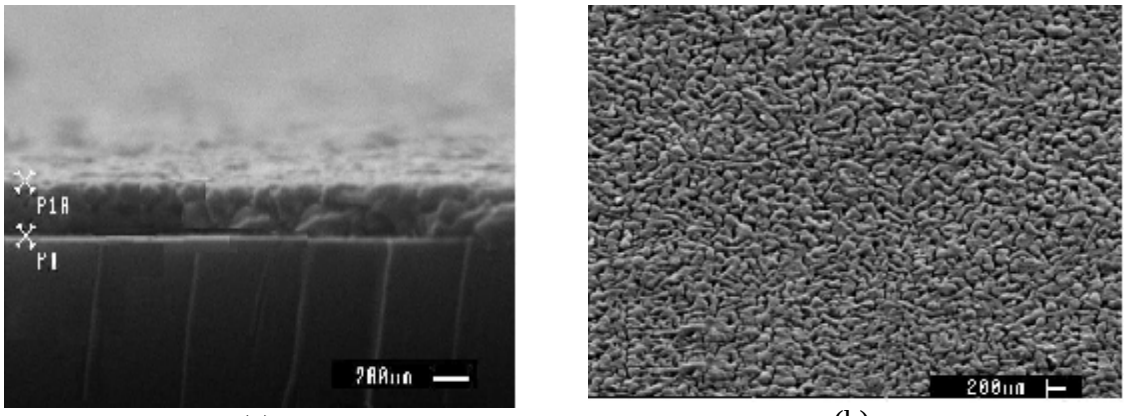
where λ is wavelength of the X-ray used (in our experiments λ_{Cu} = 0.15406 nm), β^{*} - the peak width of half height in radians and θ - the Bragg angle of the considered diffraction peak. From the XRD patterns β^{*} of the peaks were found to be from 0.00065 to 0.00075. Thus the grain size was determined from 180 to 250 nm. This is in a good agreement with the data obtained by SEM for the average size of grains. Although the films are submicro-structured, the volume of the unit cell of the crystalline lattice of VO_2 seems to be kept the same as for the VO_2 bulk crystals. Indeed, using formula for $d_{(hkl)}$ in a monoclinic lattice:

$$\frac{1}{d^2_{(hkl)}} = \frac{h^2}{a^2 \sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2\beta} - \frac{2hl\cos\beta}{ac\sin^2\beta} \tag{2}$$

and replacing five $d_{(hkl)}$ values with (hkl) of $(\bar{1}11)$, (011), $(\bar{1}02)$, (020) and (220) taken from XRD patterns (namely 0.3334 nm, 0.3209 nm, 0.2681 nm, 0.2245 nm and 0.1653 nm, respectively) one can find the constants (a, b, c and b) of the unit cell. The results of the calculation showed: a = 0.575 nm, b = 0.455 nm, c = 0.538 nm and b = 122.64°. This is quite consistent with the data from the ASTM, file No. 19-1398 for the VO_2 single crystal.

The thickness of the annealed film (d) was measured from a FE-SEM scanned at a cross section of the film by point-to-point marking technique, as shown in Fig. 2a. The average value of the thickness was evaluated as about 240 nm. As-sputtered film was fine and amorphous, during annealing the film was recrystallized with submicro-structured grains of a size about 200 - 250 nm (Fig. 2b). From the SEM picture, one can observe dark holes between the grains that reflect the glass-substrate surface. This proves the local shrinkage of the film during re-crystallization process and these holes have the

depth as large as the grains size. Thus one can suggest that the films have a single-layer submicro-structured material of vanadium dioxide.



(a). (b).

Fig. 2. SEM micrographs of a cross section of the annealed film (a) and surface morphology of the film. This clearly shows the submicro-structured grains of VO_2 which were crystallized during the annealing. The thickness d = 240 nm.

3.2. Electrical and optical properties

To measure the resistance of thin films, two aluminum bands were vacuum-evaporated onto two sides of the sample, creating a square slot on the slide of VO_2 film (see the inset in Fig. 3). That is why the resistance of this slot is called "square resistance" (R_{Sq}). Thus knowing square resistance, one can determine the resistivity (ρ) vs. the thickness as follows,

$$\rho = R_{Sq} \times d. \tag{3}$$

The temperature dependence of the resistivity of both the as-deposited and annealed films is plotted in Fig. 3. From XRD analysis it has been known that as-deposited films exhibited vanadium-rich and amorphous films. Typical resistivity of such a thin film consists of 7÷15 Ω×cm. Since the temperature dependence of resistivities obeys a law of electrical property of metal oxides, the resistivity decreases with increasing of temperature, one can expect that the lack of oxygen atoms in the vanadium oxide compounds is not so much, that the films can be recrystallized in low vacuum maintaining by gaseous oxygen flow. Indeed, during annealing at 450°C in an oxygen pressure of 1.33 Pa the amorphous film has transformed into a crystalline film. For the annealed film, the temperature dependence of resistivity in a range from room temperature to 100°C is shown interestingly. There was observed an critical temperature, where occurred an abrupt change of the resistivity. This temperature is called "temperature of SMPT" (τ_c). Bellow τ_c the ρ-T curve exhibits the property of a semiconducting phase (SP) with an activation energy as large as 0.023 eV. SP is also called "low-T phase". Above τ_c this curve seems to be similar to that of a metallic phase (MP) which is called "high-T phase". The ratio of resistivities (ρ_{sp}/ρ_{mp}) of the high-T and low-T phases is about 3 order in magnitude that can be comparative to ρ_{sp}/ρ_{mp} of a bulk VO_2 crystal. Besides, τ_c of the submicro-structured film is observed at 64 °C (Fig. 3) which is about 3 °C lower than that of a standard bulk VO_2 which possesses $\tau_c \sim 67$ °C [11]. This can be attributed to lowering of the free energy of the submicro-structured films in comparison with that of the bulk sample.

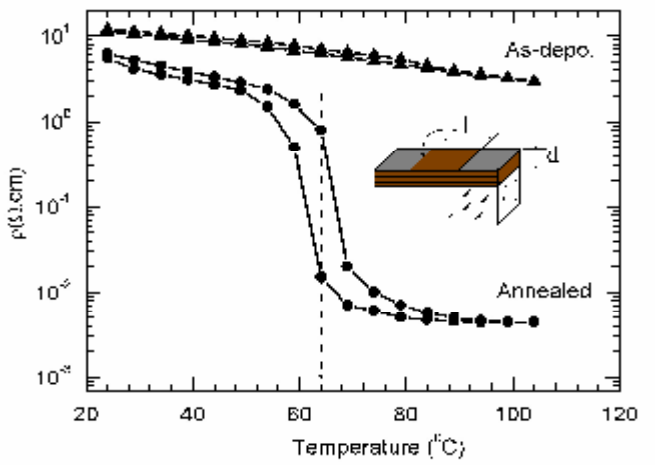


Fig. 3. The temperature dependence of the resistivity of as-deposited film (top loop) and annealed film (bottom loop).

Overcoming the τ_c, nano-structured VO_2 films also possess an abrupt change in the transmittance spectra (Fig. 4). The largest difference between transmittances of the high-T phase and the low-T phase was observed at an IR-wavelength of 2500 nm. However, at λ = 1550 nm – the wavelength of popular fiber-optic lasers – the difference reaches a value as high as 25% (namely T_{SP} - T_{MP} = 55% - 30%, see Fig. 4). This difference is explained as follows. At temperature higher than τ_c when the VO_2 film completely transformed into the metallic phase with a tetragonal crystalline lattice (whereas semiconducting phase of VO_2 has a monoclinic lattice). In the high-T phase the electronic structure of VO_2 is strongly changed: Vd and Op orbitals are overlapped resulting in disappearance of the band gap which is existent in the low-T phase of VO_2. Thus the density of quasi-free electrons in metallic phase increases, consequently the resistivity of the film is lowering and IR-reflectance – increasing, that is why the transmittance decreased. This behavior of VO_2 when overcoming τ_c suggests a potential application in production of thermo-optical sensors used for monitoring accidental change of temperature in environment, especially for toxic chemicals and petrol storages where the remote optical control of temperature should be utilized.

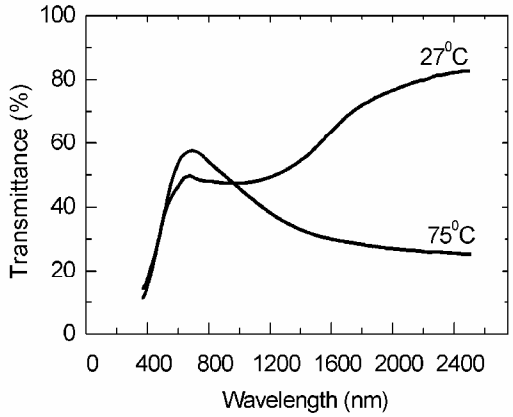


Fig. 4. Transmittance spectra of VO_2 film recorded at temperature lower τ_c (top curve) and at temperature higher τ_c (bottom curve).

4. Conclusion

Nano-structured vanadium dioxide films have been prepared by RF-sputtering with use of a V_2O_3 ceramic target and followed by thermal annealing in an oxygen pressure of 1.33 Pa . SEM and XRD structural analysis showed that the VO_2 film were crystallized in a single layer with submicro-structured grains of 200 to 250 nm in size. The films have temperature of the semicoductor-to-metal phase transition τ_c = 64^{o}C which is slightly smaller than that of the bulk crystals of VO_2. At temperatures higher τ_c the resistivity of the films decreased three orders in magnitude and the transmittance (at λ = 1550 nm) lowered from 55% to a value as low as 30%. This suggests a practical application in production of a thermo-optical sensor that can be used in monitoring temperature change of liquid and/or toxic chemicals in storages.

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