



Low-temperature method for thermochromic high ordered VO₂ phase formation

V. Melnik, I. Khatsevych, V. Kladko, A. Kuchuk, V. Nikirin*, B. Romanyuk

V. Lashkaryov Institute of Semiconductor Physics of National Academy of Sciences of Ukraine, 41, pr. Nauki, 03028 Kyiv, Ukraine

ARTICLE INFO

Article history:

Received 9 September 2011

Accepted 21 October 2011

Available online 29 October 2011

Keywords:

Vanadium dioxide

Thermochromic coating

Semiconductor-to-metal transition

High resolution X-ray diffraction

ABSTRACT

Thermochromic VO₂ films were synthesized on glass substrates by reactive magnetron deposition ($T_{\text{dep}} = 200$ °C) and following annealing ($T_{\text{ann}} = 300$ °C). The proposed method of synthesis results in formation of the highly ordered monoclinical vanadium dioxide structure. The transition from the monoclinic to the tetragonal phase is accompanied by 50 times reduction of transmittance in the infrared region.

Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.

1. Introduction

Vanadium dioxide has attracted the interest because of its thermochromic semiconductor-to-metal transition (SMT) that exhibits large changes in infrared optical properties and in the electrical resistivity. The nature of this transition was related to the crystal structure transformation from monoclinic (below critical temperature of transition – $T_{\text{c}} \sim 68$ °C) to tetragonal [1]. VO₂ thin films are excellent materials for technological applications such as thermochromic coating [2], ultrafast switching devices [3], sensors and micromechanical systems [4–5], etc.

A great number of methods are used for VO₂ deposition [4,6–9], but most if not all of them have the problem of co-deposition of other vanadium oxides (VO, V₂O₃, V₂O₅) [9–11], which causes degradation of thermochromic films properties. Mainly, vanadium dioxide film deposition is made at 450–500 °C for VO₂ phase crystallization [2,8–9]. To improve crystallinity and thermochromic parameters, additional annealings are also used [7,10–11]. Unfortunately, high temperature in the process of film formation increases probability of other vanadium oxides nucleation (enthalpy of formation $\Delta H_{\text{V}_2\text{O}_5} = -1557$ cal/mole, $\Delta H_{\text{V}_2\text{O}_3} = -1219$ cal/mole, $\Delta H_{\text{VO}_2} = -713$ cal/mole) and enhances mechanical stresses due to different values of thermal expansion coefficients α for film and substrate ($\alpha_{\text{VO}_2} = 2.1 \times 10^{-5}$ /°C, $\alpha_{\text{glass}} = 3.3 - 8.5 \times 10^{-6}$ /°C).

In this work, we propose the low-temperature method for formation of thermochromic nanocrystalline VO₂ films.

2. Experimental

We have deposited VO₂ thin films onto glass substrates by reactive DC magnetron sputtering of pure metallic vanadium target (99.96%)

in O₂–Ar gas mixture. The deposition chamber was pumped down to about 3×10^{-6} Torr before the gas mixture inflow. The amount of “reactive” oxygen in the sputtering chamber depends on 1) power applied on vanadium target 2) oxygen flow and 3) pumping speed. If the sputtering rate is high (high applied power) as well as pumping speed is high then the oxygen flow is also high; otherwise the target will drop into “metallic” mode. In order to keep the target in transition mode, the working point was stabilized by monitoring the target voltage.

It was found that the optimum deposition parameters were 5% of O₂ in Ar at a total gas pressure of 3 mTorr, magnetron power 70 W, and the substrate temperature close to 200 °C. The target-substrate distance was 6.5 cm. The thickness of films was measured with the help of profilometer Alpha-step 100. For samples described in article the film thicknesses were typically about 100 ± 10 nm and deposition rate was 0.175 nm/s.

After deposition, the films were cooled down to the room temperature in the vacuum chamber. The deposited films were further annealed at 300 °C in air for their crystallization. Composition of the deposited VO_x films determined using Auger electron spectroscopy: the x value was 1.9 ± 0.05 before and 2.05 ± 0.05 after annealing.

The crystalline structure and phase transitions of the films were examined at 20 and 90 °C by X-ray diffraction. Glancing incidence angle (1°) of X-ray diffraction (GIXRD) was carried out using X'Pert Pro MPD diffractometer with the CuK_α wavelength ($\lambda = 0.15418$ nm).

3. Results and discussion

In the GIXRD spectra of as-deposited films (before annealing), there are no diffraction peaks, which is indicative of their amorphous nature (Fig. 1, bottom line). However, as it is shown in Fig. 1, as a result of crystallization after annealing the films exhibit a polycrystalline structure that matches to monoclinic VO₂ phase with the following cell parameters: $a = 0.573$ nm, $b = 0.452$ nm, $c = 0.539$ nm, $\beta = 122.7^\circ$

* Corresponding author.

E-mail address: nikirin_viktor@mail.ru (V. Nikirin).

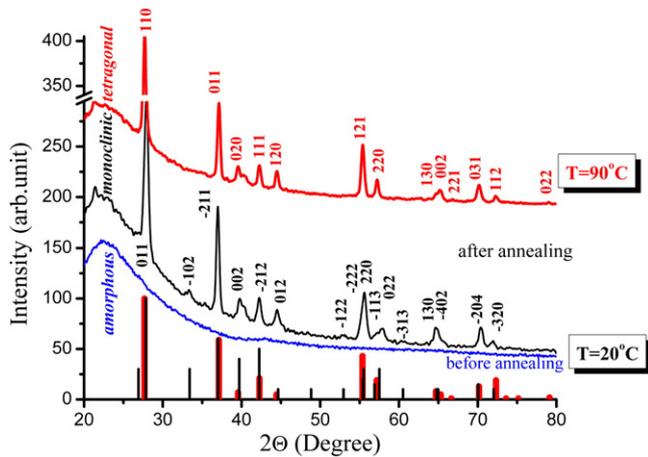


Fig. 1. Glancing angle X-ray diffraction of VO₂ thin films at 20 and 90 °C. Peaks from the reference VO₂ phase are denoted as black bar (monoclinic [12]) and red bar (tetragonal [13]). Dashed blue line (bottom line) – film after deposition, before annealing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

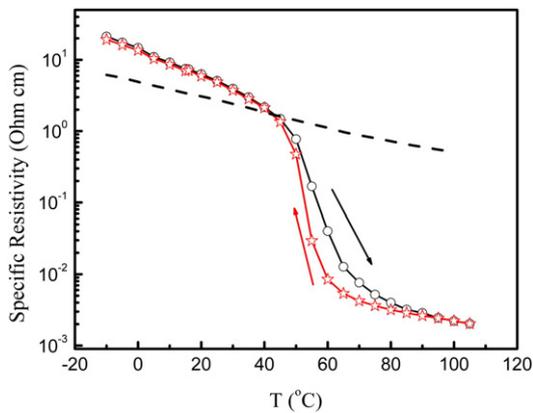


Fig. 2. Temperature dependence of the specific resistance for synthesized VO₂ films (dashed line – film before annealing) at heating and cooling.

[12]. It has to be emphasized that no other vanadium oxide phases have been observed by XRD pattern analysis and the exclusive formation of single-phase VO₂ films is realized. Moreover, the Bragg peaks from planes with different Miller indexes and their intensity ratio correlated with those measured in reference samples [12]. This fact explicitly indicates on non-textured high ordered monoclinic VO₂ phase formation. By considering that the broadening of Bragg peaks results from pure size effects, the crystal sizes were directly deduced from the full width at half maximum (β_{hkl}) of the peaks. The mean size of crystallites

(d) calculated using the classical Scherrer formula ($d_{hkl} = \frac{0.9 \cdot \lambda}{\beta_{hkl} \cdot \cos \theta}$) was about 16 ± 4 nm.

Measurements of the GIXRD spectra of the synthesized films at the temperature close to 90° indicate the transition from monoclinic phase to the higher-temperature tetragonal phase with the following cell parameters: $a = 0.455$ nm, $b = 0.455$ nm, $c = 0.285$ nm, $\alpha = \beta = \gamma = 90^\circ$ [13].

The SMT in the films was studied by the measurements of temperature dependences of electrical resistivity (using the standard four-point probe technique) and light transmittance at the wavelengths within the range 400 to 2600 nm.

Fig. 2 shows the change in electrical resistance of synthesized films as a function of temperature by using the heating and cooling cycles. The SMT is not observed for deposited films before annealing (Fig. 2, dashed line). For crystalline VO₂ films (after annealing), transition from a semiconductor to metal phase is accompanied with the change in specific resistance by four orders of magnitude. The SMT temperatures at heating and cooling were 57 and 53 °C, correspondingly. Transition parameters were defined by the method described in the paper [8].

The spectral transmittance (Fig. 3a) was measured within the range of 450 to 2600 nm at the temperatures 20 °C (below T_t) and 90 °C (above T_t). Essential transmittance changes in the infrared (IR, >760 nm) spectral region at heating were observed. Importantly, 50 times reduction of transmittance in the IR spectral region is not accompanied with appreciable changes in the visible spectral region. Fig. 3b demonstrates temperature dependence of transmittance at the wavelength 2000 nm for heating and cooling procedures. SMT temperature for heating was 58 °C, and 49 °C for cooling. In our films the optical transmittance is relatively low in comparison with the films deposited at higher temperatures [11,14]. In our opinion, it is caused by single-phase nature of our films (absence of optical-transparent inclusions, such as V₂O₅) and their nanocluster structure (nano-sizes crystals strongly scatter the optical light) but must be investigated further in details.

It is necessary to notice that these SMT temperatures are much less than those mentioned in papers devoted to undoped VO₂ films (typical values of T_t is 68 °C) [3,6,8]. This peculiarities are not related with doping the films during deposition or/and annealing [15–17]. SIMS measurements have detected some impurities (Fe, Si) in the films, but their concentrations (<0.1 at.%) are too low for influence on the SMT temperature.

T_t decrease can be related with small sizes of crystallites. It was reported in [7] that for VO₂ films with the crystallite size 12 to 18 nm the SMT temperature is ~55 °C. For our films, the values of average grain size and T_t are very similar to values reported in [7]. Decrease in mechanical stresses in a film, due to low temperatures of formation, also promotes reduction of T_t [5,18–19].

Without any protection coating, the synthesized films demonstrate high stability when keeping them in natural conditions. After 500 heating-cooling cycles during one year, it was not observed any noticeable changes of thermochromic characteristics inherent to the films.

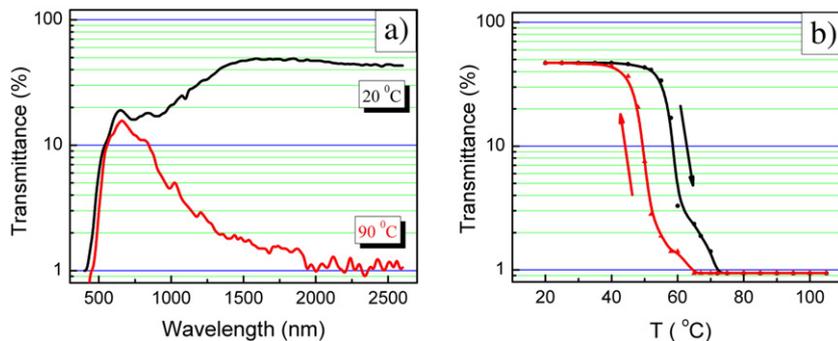


Fig. 3. Spectral transmittance of VO₂ thin films at temperatures below and above T_t (a) and temperature dependence of transmittance at the wavelength 2000 nm at heating and cooling (b).

4. Conclusions

In conclusion, for the offered low-temperature method of VO₂ synthesis the two processes were separated: deposition and phase crystallization. As a result, the synthesis process becomes more adjustable and realized at a lower temperature. This allow to suppress nucleation of other vanadium oxides and produce a nanocrystalline film containing the high ordered VO₂ phase with good thermochromic characteristics and stability.

This work was supported by the Ministry of Education and Science of Ukraine (Grant No. M/90 – 2010).

References

- [1] Morin FJ. Phys Rev Lett 1959;3:34.
- [2] Granqvist CG, Lansåker PC, Mlyuka NR, Niklasson GA, Avendaño E. Sol Energy Mater Sol Cells 2009;93:2032.
- [3] Cavalleri A, Toth Cs, Siders CW, Squier JA, Raksi F, Forget P, et al. Phys Rev Lett 2001;87:237401.
- [4] Cao J, Fan W, Zhou Q, Sheu E, Liu A, Barrett C, et al. J Appl Phys 2010;108:083538.
- [5] Fan W, Huang S, Cao J, Ertekin E, Barrett C, Khanal DR, et al. Phys Rev B 2009;80:241105(R).
- [6] Lopez R, Boatner LA, Haynes TE, Feldman LC, Haglund RF. Appl Phys Lett 2001;79:3161.
- [7] Suh JY, Lopez R, Feldman LC, Haglund RF. J Appl Phys 2004;96:1209.
- [8] Brassard D, Fourmaux S, Jean-Jacques M, Kieffer JC, El Khakani MA. Appl Phys Lett 2005;87:051910.
- [9] Gentle A, Maarooof AI, Smith GB. Nanotechnology 2007;18:025202.
- [10] Cui H-N, Teixeira V, Meng L-J, Wang R, Gao J-Yu, Fortunato E. Thin Solid Films 2008;516:1484.
- [11] Lee M-H, Kim MG. Thin Solid Films 1996;286:219.
- [12] Powder Diffraction Files, Card No. 00-019-1398, Database Edition, International Centre for Diffraction Data (ICDD), Newton Square, PA 19073-3273, USA, 2005.
- [13] Powder Diffraction Files, Card No. 01-076-0675, Database Edition, International Centre for Diffraction Data (ICDD), Newton Square, PA 19073-3273, USA, 2005.
- [14] Christmann T, Felde B, Niessner W, Schalch D, Scharmann A. Thin Solid Films 1996;286:134.
- [15] Mlyuka NR, Niklasson GA, Granqvist CG. Appl Phys Lett 2009;95:171909.
- [16] Soltani M, Chaker M, Haddad E, Kruzelecky RV, Margot J. Appl Phys Lett 2004;85(11):1958.
- [17] Romanyuk A, Steiner R, Marot L, Oelhafen P. Sol Energy Mater Sol Cells 2007;91:1831.
- [18] Jones AC, Berweger S, Wei J, Cobden D, Raschke MB. Nano Lett 2010;10:1574.
- [19] Viswanath B, Ko Ch, Yang Z, Ramanathan Sh. J Appl Phys 2011;109:063512.