STRUCTURAL AND OPTICAL PROPERTIES OF VO$_x$ THIN FILMS

WŁASNOŚCI STRUKTURALNE I OPTYCZNE CIENKICH WARSTW VO$_x$

VO$_x$ thin films were deposited on Corning glass, fused silica and Ti foils by means of rf reactive sputtering from a metallic vanadium target. Argon-oxygen gas mixtures of different compositions controlled by the flow rates were used for sputtering. Influence of the oxygen partial pressure in the sputtering chamber on the structural and optical properties of thin films has been investigated.

Structural properties of as-sputtered thin films were studied by X-ray diffraction at glancing incidence, GIXD. Optical transmittance and reflectance spectra were recorded with a Lambda 19 Perkin-Elmer double spectrophotometer. Thickness of the films was determined from the profilometry. It has been confirmed by XRD that the deposited films are composed mainly of V$_2$O$_5$ phase. The estimated optical band gap of 2.5 eV corresponds to V$_2$O$_5$.

Keywords: VO$_x$ thin films, reactive sputtering, microstructure, optical properties, energy band gap

1. Introduction

Vanadium has various valence states and exists in a number of oxide forms of vanadium oxide. There are at least 15 different vanadium oxides reported till now, such as VO, V$_2$O$_3$, VO$_2$, V$_2$O$_5$, V$_6$O$_{13}$ and so on. Vanadium oxide thin films have been widely studied for optical, electrical, electrochemical, thermo-chronic and thermal switching materials [1-11]. The interest in these materials has increased in the last few years due to their potential scientific and technological applications, for example as a catalyst [12], a window for solar cells [13], electrochromic devices [14], electronic information displays [15] and color memory devices [16, 17].

The structural changes of vanadium thin films are of vital importance for their practical applications. The aim of this paper was to determine the structural and optical properties of vanadium oxide thin films deposited by rf reactive sputtering. The influence of gas atmosphere during deposition on the microscopic structure, morphology and the band gap of the films has been studied.

Numerous techniques have been used for preparing vanadium oxide thin films such as:

- sol-gel [18],
- electrochemical [19],
- vacuum deposition techniques including plasma-enhanced chemical vapour deposition (PECVD) [20],
- pulsed laser deposition [21],
- thermal evaporation technique [22],
- atomic layer deposition [23],
- reactive magnetron sputtering [24-26],
- rf sputtering deposition [27-30].

From thin film deposition methods listed above, the reactive process, i.e. the sputtering rf the metallic target under oxidizing controlled atmosphere permits greater control over deposition parameters and provides an important fabrication approach for optimization. Moreover, reactive sputtering provides thin films that are dense and uniform in thickness and which is very important, in case of VO$_x$, is available to control the film stoichiometry, x.

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2. Experimental details

2.1. Thin film deposition

Vanadium oxide thin films have been deposited by rf reactive sputtering from metallic V target in Ar+O2 flow controlled gas atmosphere. Corning glass and fused silica served as substrates. Deposition process was carried out under predefined conditions of the total gas pressure, varied oxygen (within range: 0.3-2.1 sccm) and constant argon (6.7 sccm) flows rates, constant input power (280-290 W) and voltage (1150 V) as well as the controlled substrate temperature (560 K). Prior to the sample deposition, the target pre-sputtering in Ar+O2 atmosphere was performed in order to stabilize the sputtering conditions (voltage, pressure, gas composition) and to equilibrate the oxidized target surface. Deposition conditions of the thin films are collected in Table 1.

| Comparative data of thin films: deposition conditions, thickness, bandgap |
|---------------------------------|-----------------|-----------------|-----------------|
| flow(Ar) during deposition      | 6.7             | 6.7             | 6.3             |
| flow(O2) during deposition      | 2.1             | 0.7             | 0.3             |
| input power [W]                 | 290             | 280             | 290             |
| rf voltage (U_rf) during deposition [V] | 1150           | 1150            | 1150            |
| Ar+O2 pressure [mbar]           | 4.7·10^{-2}     | 4.3·10^{-2}     | 4.1·10^{-2}     |
| time of deposition [min]        | 240             | 240             | 240             |
| film thickness [nm]             | 431±28          | 421±43          | 420±49          |
| band gap [eV] from optical transitions m = 2 | 2.21±0.05     | 2.47±0.05       | 2.42±0.05       |

2.2. XRD analysis

The crystallographic studies were carried out by means of X-ray diffraction at grazing incidence (GID) with X'Pert Philips diffractometer within the range of diffraction angles 2θ from 20 deg to 80 deg with the CuKα filtered radiation.

2.3. SEM and EDS

The images of microstructure of the films were studied using the scanning electron spectroscopy (SEM) technique (Nova 200 NANOsem, Fei Company). An energy dispersive X-ray spectrometer (Oxford Instruments) coupled with scanning electron microscope was used to determine the chemical composition of the samples. The analysis was focused on vanadium distribution.

2.4. Optical spectroscopy

Optical transmittance and reflectance spectra over a wide wavelength range from 180 to 3200 nm were measured with Lambda 19 Perkin-Elmer double beam spectrophotometer equipped with a 150 mm integrating sphere. The band gap energy $E_g$ of a semiconductor can be evaluated from the experimentally measured transmittance $T$ and reflectance $R$ within the range of the fundamental absorption.

2.5. Thin film thickness

The thickness of the films was measured using Bruker’s DektakXT™Stylus Profiler.

3. Results and discussion

Majority of films prepared by the reactive sputtering show only weak crystallization. Special care has to be taken to improve the crystallization conditions. Therefore, only GID patterns have been presented and discussed in this paper Fig. 1 demonstrates X-ray diffraction patterns of as sputtered VOx thin films. The experimental data were interpreted using XRD patterns distributed by the International Centre for Diffraction DATA –ICDD. As can be seen VOx3 film is weakly crystallized. From the other hand, films VOx1 and VOx2 are much better crystallized. X-ray phase analysis confirmed that all peaks correspond to the $\text{V}_2\text{O}_5$ orthorhombic compound.

![Fig. 1. XRD patterns of the as-sputtered thin films](image-url)
The average mean crystallite size of the materials was calculated from Scherrer’s equation [31]

\[ \lambda \beta \theta_{XRD} = \frac{K}{\cos} \]  

(1)

Where, \( \theta_{XRD} \) is the crystallite size, \( \lambda \) – is the wavelength of the X-ray radiation (CuK\( \alpha \) = 0.1540598 nm), K is constant equal to 0.89 and \( \beta \) is the line broadening at the half-maximum intensity after subtraction of equipment broadening. The average crystallite size was: 53 and 52 nm for VOx1 and VOx2, respectively. The obtained \( \theta_{XRD} \) are in relatively good agreement with SEM measurements.

Fig. 5 demonstrates reflectance spectra of studied films. The spectra of VOx1 and VOx2 show similar character. Wide
maximum and minimum is observed at λ range of 550-600 nm and ca 750 nm, respectively. The spectrum of VOx3 is much complex. The optical refractive index, n, has been determined from the experimental data presented in Fig. 5. Assuming that the excitation coefficient is negligible [32] we have:

\[ R = \frac{(n - 1)^2}{(n + 1)^2} \]  (2)

\[ \alpha = \frac{1}{d} \ln \left( \frac{(1 - R)^2}{T} \right) \]  (3)

where d is film thickness. Fig. 9 show dependence of \( \alpha \) on photon energy h\( \nu \) for VOx1 sample.

The value of \( E_g \) can be found from the plot of \( (\alpha h\nu)^{1/m} \) as a function of the photon energy h\( \nu \); \( \alpha \) is the absorption coefficient:

\[ a h\nu = a(h\nu - E_g)^m \]  (4)

where a is a constant. The power coefficient m takes a value of 1/2, 3/2, 2 or 3 depending on the type of transition: direct allowed, direct forbidden, indirect allowed or indirect forbidden, respectively.

Equation 3 as well as 4 are only valid over the high absorption region, where, in the case of thin films, transmittance and reflectance spectra do not show any interference effects. The band gap \( E_g \) is determined by extrapolating the linear part of the fit \( (\alpha h\nu)^{1/m} \) versus h\( \nu \). In case of the amorphous non-metallic materials Eq 4 gives the best fit with m=2.

The examples of this method for m=1/2 and m=2 are shown in Figure 10. Determined band gap values are collected in Table 1. The presented results \( E_g \) are close to that reported by Maki et al [34]: 2.25 eV, determined to \( V_2O_5 \) thin film, deposited by magnetron sputtering and then annealed at 500°C in oxygen atmosphere. They are also close to the results reported by Li-Jang Meng et al. [25] obtained for \( V_2O_5 \) thin film deposited by magnetron sputtering: 2.16-2.59 eV (substrate temperature: 400°C and room temperature, respectively).
In this paper the main structural and optical characteristics of vanadium oxide thin films were studied. Films were deposited by means rf reactive sputtering. The effect of oxygen concentration during deposition on structural and optical properties has been observed. At higher oxygen concentration the as-sputtered films are well crystalized. According to XRD analysis they crystalize as V$_2$O$_5$ orthorhombic phase. Determined refractive index varies values 1.6-2.3 within 500-800 nm of wavelength. The optical bandgap assumes values 2.21-2.47 eV.

**4. Conclusions**

In this paper the main structural and optical characteristics of vanadium oxide thin films were studied. Films were deposited by means of reactive sputtering. The effect of oxygen concentration during deposition on structural and optical properties has been observed. At higher oxygen concentration the as-sputtered films are well crystalized. According to XRD analysis they crystalize as V$_2$O$_5$ orthorhombic phase. Determined refractive index varies values 1.6-2.3 within 500-800 nm of wavelength. The optical bandgap assumes value 2.21-2.47 eV.

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