THIN COMPOUND OXIDE FILMS BASED ON NiO AND TiO_2 FOR GAS DETECTION

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1. Introduction

The compound oxide materials represent logical step of advanced investigation of the single oxide materials. These compound oxides could exhibit unusual and enhanced properties with respect to the binary oxides. In this work influence of the deposition and post deposition treatment on the structural and optical properties of compound NiO/TiO_2 thin films for application in gas sensors was analyzed. Information about deposited and annealed films parameters seem to be essential in contribution to the complex knowledge of sensing films.

2. Experimental

Two main layouts of prepared metal oxides were investigated. First layout consists of the single NiO sensing film deposited on oxidized silicon or glass-corning 1737 substrate (sample code 10/26, 11/12 respectively) and second group includes compound oxides based on NiO and TiO_2 films again deposited on either oxidized silicon or glass substrate (sample code 10/3, 11/11 respectively). NiO and TiO_2 thin films were prepared at the same technological parameters for both substrates. The 10 nm thick NiO films were deposited by dc reactive magnetron sputtering from a Ni target in a mixture of Ar and O_2. The compound oxide samples were enriched with next fabrication step of 100 nm thin TiO_2 film deposition. The TiO_2 films were also prepared by dc reactive magnetron sputtering. To obtain enhancement in crystalline structure deposited thin films underwent post-annealing process in

tube furnace (Barnstead Thermolyne 21100) at 300, 400 and 500°C (max. 700°C) for 1 hour in nitrogen.

The composition of prepared samples was found out by glow discharge optical emission spectrometry (GDOES). The crystal structure was identified with a Theta-Theta X-ray diffractometer (XRD) D5000 with Goebel mirror oriented into grazing incidence focusing with Cu Kα radiation. The optical properties specifically transmittance spectra were determined by optical device Avantes equipped with a deuterium-halogen light source and fiber optic spectrometer.

3. Results and discussion

GDOES surface and depth profile analysis yield exact knowledge about the material, position and width of every layer in the investigated structure. Figure 1 depicts depth profiles of as-deposited and annealed samples 10/26 and 10/3. The depth profiles are in good agreement with fabrication process and correspond to our expectations of oxides formation. In addition the depth profiles displays dependency of moving and inter-diffusion of incorporated elements in the volume of investigated structure on the annealing temperature.

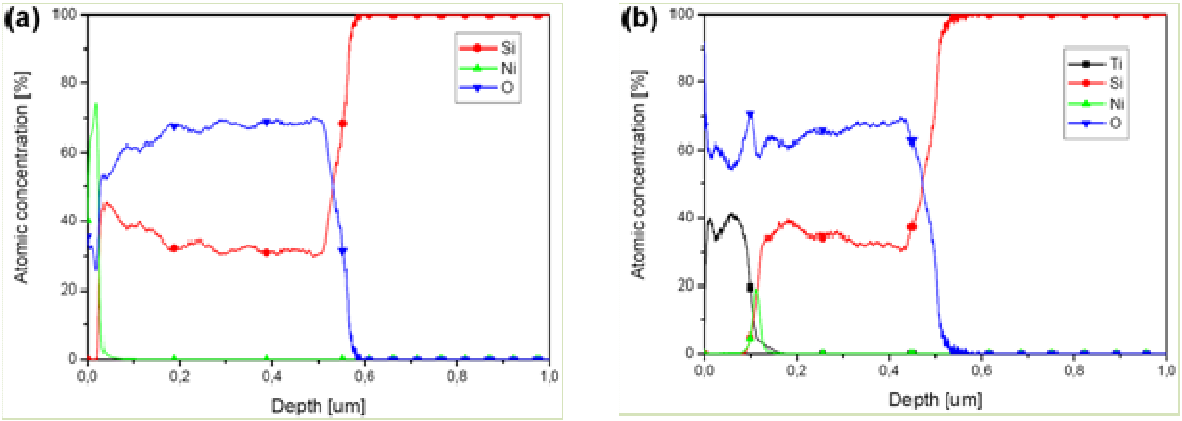

Fig. 1: *GDOES depth profiles of annealed samples 10/26 (a) and 10/3 (b) at 500°C.*

The XRD diagrams (Fig. 2) showed that as-deposited samples were amorphous, whereas annealed samples at 400, 500, 600 and 700°C were found to be polycrystalline. Diffraction patterns from annealed samples 10/26 delineate presence of major diffraction peaks that appertain to NiO lattice, as referred in JC-PDS 44-1159 (Fig. 2a). In the samples 10/3 the major diffraction peaks belongs to anatase TiO_2 lattice (as referred in JC-PDS 21-1272) and also to NiO (Fig. 2b). This fact also indicates presence of metal oxides and their crystallization.

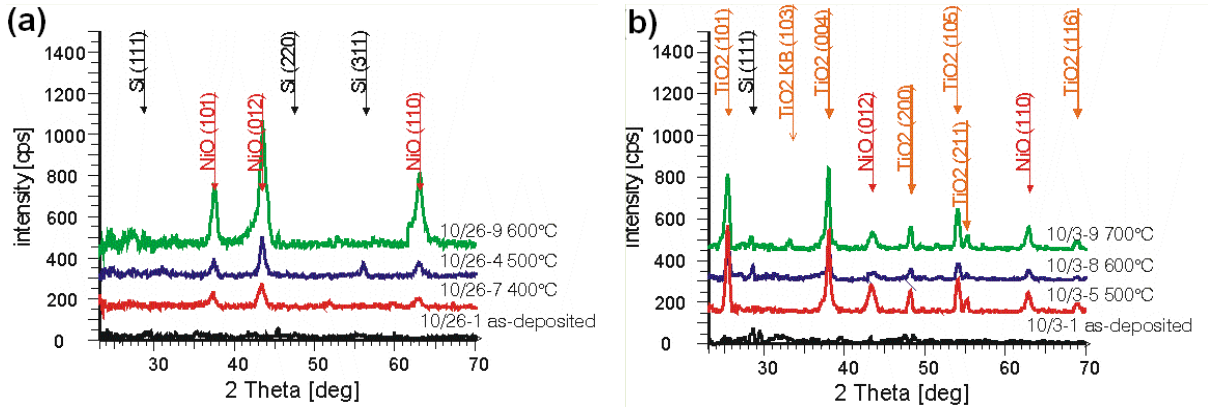

Fig. 2: *XRD patterns of as-deposited and annealed samples 10/26 (a) and 10/3 (b).*

The optical measurement apparatus was before testing of the samples calibrated to the light and dark reference with or without the glass substrate. In the case of the absence of the glass substrate during the reference settings, the glass substrate was treated by the following equation

$$T_{FILM} = \frac{T_{COMPLEX}}{T_{GLASS}} \cdot 100[\%] \qquad (1)$$

where T_{FILM}, $T_{COMPLEX}$ and T_{GLASS} are transmittance of the film, complex of the film plus glass substrate and glass substrate respectively.

The optical energy gap of the investigated as-deposited and annealed films was determined by optical transmittance measurements (Fig. 3a). For direct transitions between the edges of the parabolic bands the variation in the absorption coefficient α with photon energy hv is given by

$$\alpha = A(h\nu - E_g)^{1/2} \qquad (2)$$

where A is a constant and E_g is the optical energy gap between the valence and conduction bands. The above relationship, plotted as $\alpha^2 E$ vs. hv, is shown in figure 3b for the compound oxide structure. By extrapolating the linear region of such a curve, we obtained E_g=3.70 eV. Stamate et al. [1] demonstrated for poly- crystalline TiO_2 films prepared by dc reactive magnetron sputtering that the energy gap values varies in the range of 3.0–3.4 eV, depending on the oxygen partial pressure during deposition. Sawitzky et al. [2] demonstrated energy gap value for NiO to be 4.3 eV. We have observed that the values of the optical energy gaps of our compound oxide films were essentially in the range given by the margins of the pure TiO_2 and NiO. Moreover, effect of changing the E_g with annealing temperature takes place

[3]. It can be seen that the optical band gap energy decreases (from 3.73 eV to 3.69 eV) when the annealing temperature increases (Fig. 3b).

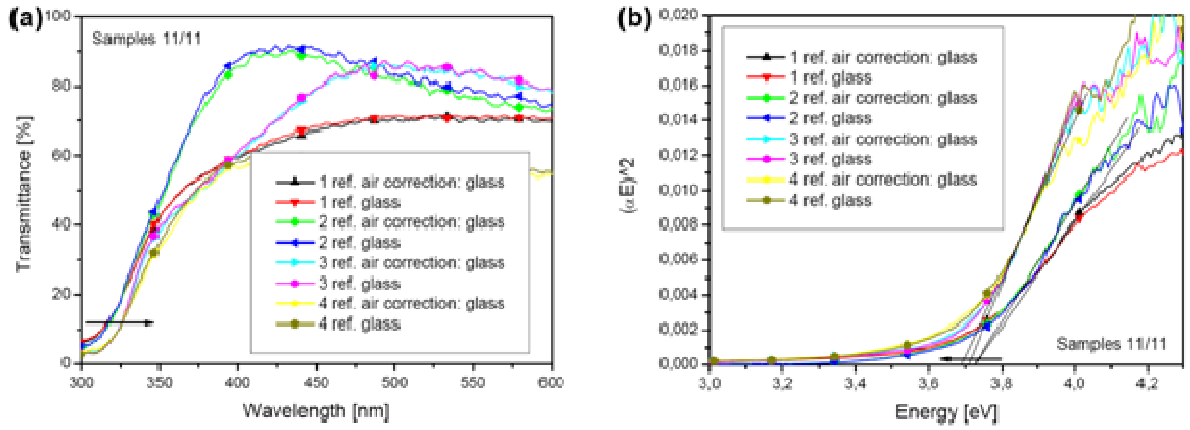

Fig. 3: *Optical transmittance spectra of samples 11/11-1 to 4 (as-dep, annealed at 300, 400 and 500°C) (a). Second part (b) depicts plot of* $\alpha^2 E$ vs. $h\nu$.

4. Conclusion

Shift of the E_g to the lower energies with raising annealing temperature represents change in the internal structure of the thin films. This findings correlate with XRD diagrams, which revealed modification of the structure from amorphous to polycrystalline caused by annealing. We expect that these compound oxides will exhibit enhanced gas sensing properties.

Acknowledgement:

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