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V_2O_5 Thin Films as Nitrogen Dioxide Sensors †

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Abstract: V_2O_5 thin films were deposited onto insulating support (either fused silica or alumina) 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. X-ray diffraction at glancing incidence (GIXD) and Scanning Electronic Microscopy (SEM) were used for structural and phase characterization. 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 GIXD that the deposited films are composed of V_2O_5 phase. The estimated optical band gap was ca. 2.5 eV. The gas sensing properties of V_2O_5 thin films were investigated at RT-690 K towards NO_2 gas of 0–20 ppm. The results indicated that material exhibited good response and reversibility towards nitrogen dioxide.

Keywords: vanadium pentoxide; thin film; rf reactive sputtering; electrical properties; nitrogen dioxide; gas sensor

1. Introduction

Nitrogen dioxide, NO_2 is an extremely toxic gas. It is produced by all combustion in air and by industrial processes. NO_2 can cause various problems such as smog and acid rain. Therefore there is an urgent need to develop some devices that allow fast, portable, low-cost monitoring of the NO_2 responsible for air pollution and danger to human health. Successful development of NO_2 gas sensors for commercialization requires achieving three "S": sensitivity, selectivity and stability. Several metal oxides such as SnO_2, ZnO, In_2O_3 and WO_3 were studied extensively for construction semiconductor gas sensors [1–4]. Recently, vanadium oxides have attracted considerable interest due to their multi-valence, good chemical stability and excellent catalytic properties [5]. V_2O_5, the most stable compound among above 15 known vanadium oxides, is one of good promising NO_2 sensor material [6]. It demonstrated high sensitivity and selectivity for ethanol [7], ammonia [8], hydrogen and hydrocarbons [9].

In this paper the effect of gas concentration and operating temperature of V_2O_5 thin films as NO_2 gas sensor was determined.

2. Materials and Methods

2.1. Thin Film Preparation

VO_x thin films were deposited onto insulating support (either fused silica or alumina) for sample characterization or conductometric sensor substrate type CC1.W, for electrical measurements, by means of rf sputtering in a reactive atmosphere 4.75 Pa (24% O_2–76% Ar) from a metallic V target. Conductometric supports presented in Figure 1 were provided by BVT Technologies. Details of the film deposition are given elsewhere [9].

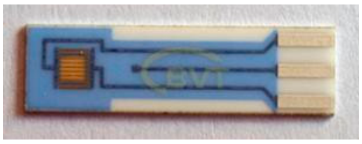


Figure 1. Conductometric support BVT.

2.2. Morphology and Structural Characterization

Scanning electron microscopy (SEM) studies were carried out for as-sputtered thin films using NOVA NANOSEM 200 (FEI Company, Hillsboro, OR, USA) microscope. Phase composition of as-sputtered thin films were studied by X-ray diffraction at glancing incidence, GIXD.

2.3. Sensing Characterization

The responses of films to the target gases, defined as changes in electrical resistance, were measured at different concentrations of flowing gases. The atmosphere of the sample chamber was a mixture of synthetic air and argon containing target gas. The flow rates of gases were independently controlled by MKS Type 1179A mass-flow controller. The total flow rate was maintained at the same level of 190 sccm. The film response to reactions on the hydrogen was measured. The concentration of target gases was up to 3000 ppm in a measurement chamber atmosphere. The sensor measurements were performed within the temperature range extending from RT to 523 K. An equipment applied for measurements of the sensor characteristics was described in detail elsewhere [10]. Sensor response (sensitivity) *S* was defined as: $S = \frac{R_{NO_2}}{R_{air}}$.

3. Results and Discussion

Structural and Microstructural Characteristics

Figure 2 presents the typical XRD patterns of the sample annealed at several temperatures in argon atmosphere. X-ray diffraction analysis of the samples revealed the presence of the V_2O_5 orthorhombic phase. The determined lattice parameters (a = 1.149 ± 0.002 nm; b = 0.436 ± 0.003 nm; c = 0.436 ± 0.003 nm) well agree with that literature reports [11]. Presented XRD patterns were used for determination of the crystallite size. Crystallite size, d_{XRD}, was calculated according to Scherrer's method: d_{XRD} = (20 ± 1.8) nm. No effect of sintered temperature on obtained XRD results is observed.

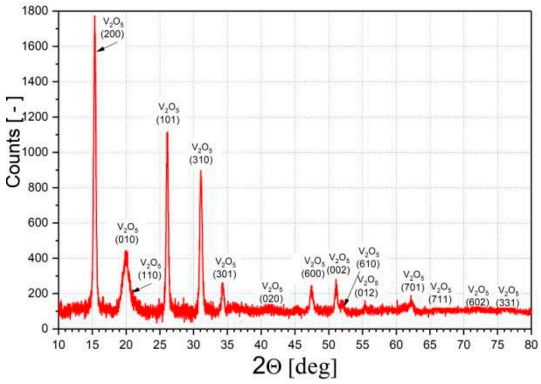
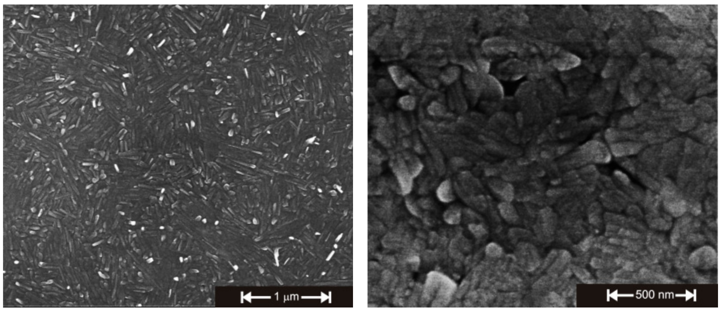


Figure 2. X-ray diffraction patterns for V_2O_5 thin film.

As can be seen, the as sputtered thin films (Figure 3a) are poly-dispersed, and the grains are mostly columnar in shape (565 ± 100 nm) of the length and (220 ± 40 nm) of the diameter. On the other hand, after sintering (Figure 3b) they are rather spherical (mean diameter = 500 ± 75 nm). Chemical analysis performed by EDS technique revealed presence of high picks coming from the silicon support and much smaller picks corresponding to oxygen and vanadium elements.



(**a**) (**b**)

Figure 3. Scanning electron micrographs of: (**a**) as sputtered thin film; (**b**) after annealing at 673 K.

V_2O_5 sensor responses to 20 ppm NO_2 are shown in Figure 4a,b. As it results from Figure 4, the electrical conductivity of the V_2O_5 thin films increases upon exposure of NO_2.

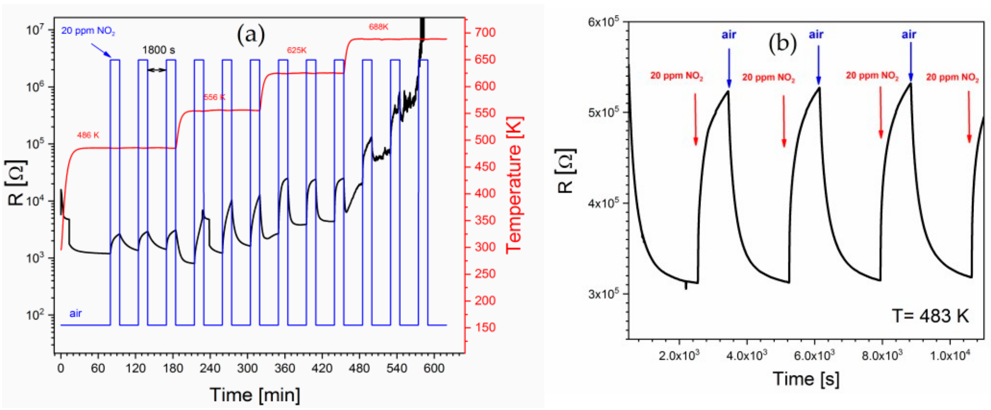


Figure 4. Dynamic changes in the electrical resistance of V_2O_5 thin film upon interaction with 20 ppm NO_2, (**a**) at several temperatures; (**b**) at 486 K.

It can be explained by the direct adsorption of NO_2 molecules according to the reaction:

$$NO_{2(gas)} + e^- \rightarrow NO_{2(ads)}^-$$

Response and recovery times at 483 K, determined from the Figure 4b are: (698 ± 2) s and (1233 ± 185) s, respectively.

Figure 5a illustrates sensor response, S, versus temperature. The abrupt increase of the sensor response is observed at 545–547 K. This behaviour may be explained by occurrence of the metal-insulator transition, MIT. According to Kang et al. [12] at temperature ca. 530 K the MIT takes place in the thin films of V_2O_5.

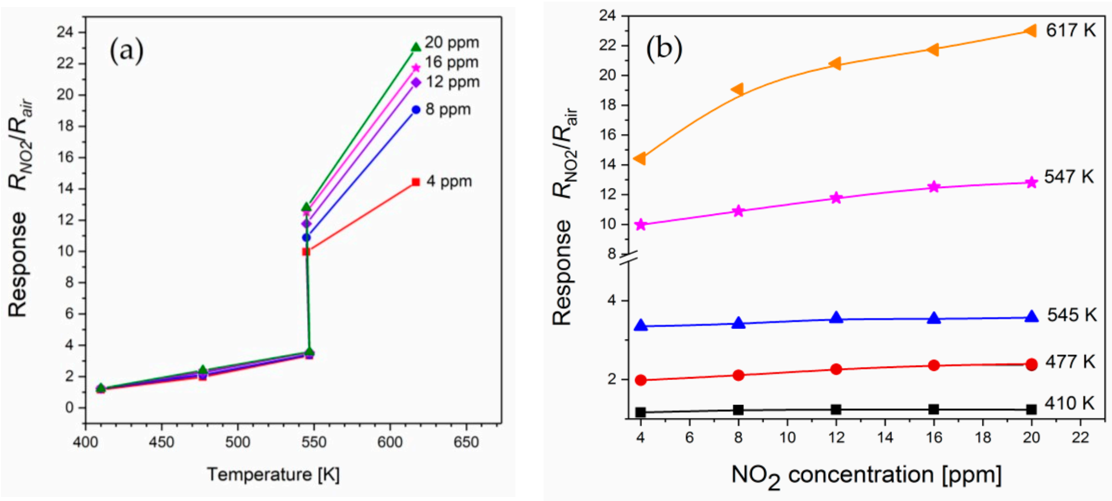


Figure 5. Temperature dependence of: (**a**) NO_2 sensor response, *S* and (**b**) response vs. NO_2 concentration.

4. Conclusions

In the present work, we fabricated V_2O_5 thin films by rf reactive sputtering. The film structure and morphology were studied by X-ray diffraction at glancing incidence (GIXD) and Scanning Electronic Microscopy (SEM). Gas sensing studies showed that the V_2O_5 thin films were sensitive to NO_2 at a relatively low operating temperatures. The considerable increase of the sensor sensitivity was observed above 545 K, which is related with postulated metal-insulator transition.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Comini, E.; Faglia, G.; Sberveglien, G.; Pan, Z.; Wang, Z.L. Stable and highly sensitive gas sensors based on semiconducting oxide nanobelts. *Appl. Phys. Lett.* **2002**, *81*, 1869–1871.
2. Kim, B.-M.; Kim, J.-S. Sensor array based on metal oxide semiconductors for detecting gas mixtures and its sensing properties. In Proceedings of the 5th International Conference on Sensors Networks, SENSORNETS 2016, Gdansk, Poland, 11–14 September 2016; pp. 169–174.
3. GFine, F.; Cavanagh, L.M.; Afonja, A.; Binions, R. Metal oxide semi-conductor gas sensors in environmental monitoring. *Sensors* **2010**, *10*, 5469–5502, doi:10.3390/s100605469.
4. Peterson, P.J.D.; Aulja, A.; Grant, K.H.; Brundle, A.G.; Thomson, M.R.; Hey, J.V.; Leigh, R.J. Practical Use of Metal Oxide Semiconductor Gas Sensors for Measuring Nitrogen Dioxide and Ozone in Urban Environments. *Sensors* **2017**, *17*, 1653, doi:10.3390/s17071653.
5. Beke, S. A review of the growth of V_2O_5 films from 1885 to 2010. *Thin Solid Films* **2011**, *519*, 1761–1771, doi:10.1016/j.tsf.2010.11.001.
6. Han, S.D.; Moon, H.G.; Noh, M.S.; Pyeon, J.J.; Shim, Y.S.; Nahm, S.; Kim, J.-S.; Yoo, K.S.; Kang, C.-Y. Self-doped nanocolumnar vanadium oxides thin films for highly selective NO_2 gas sensing at low temperatures. *Sens. Actuators B* **2017**, *241*, 40–47.
7. Liu, J.; Wang, X.; Peng, Q.; Li, Y. Vanadium pentoxide nanobelts: Highly selective and stable ethanol sensor material. *Adv. Mater.* **2005**, *17*, 764–767.
8. Huotari, J.; Björklund, R.; Lappalainen, J.; Lloyd Spetz, A. Nanostructured mixed phase vanadium oxide thin films as highly sensitive ammonia sensormaterial. *Procedia Eng.* **2014**, *87*, 1035–1038.
9. Schneider, M. Lubecka, A. Czapla, V_2O_5 thin films for gas sensor applications. *Sens. Actuators B* **2016**, *236*, 970–977.
10. Radecka, M.; Łyson, B.; Lubecka, M.; Czapla, A.; Zakrzewska, K. Photocatalytical decomposition of contaminants on thin film gas sensors. *Acta Phys. Pol.* **2010**, *117*, 415–419.

11. Chakrabarti, A.; Hermann, K.; Druzinic, R.; Witko, M.; Wagner, F.; Petersen, M. Geometric and electronic structure of vanadium pentoxide: A density functional bulk and surface study. *Phys. Rev. B* **1999**, *59*, 10583–10590.
12. Kang, P.; Kim, I.; Kim, S.; Park, H.Y. Metal-insulator transition without structural phase transition in V_2O_5 film. *Appl. Phys. Lett.* **2011**, *98*, 131907–131916.