**Article**

**V₂O₅ Thin Films as Nitrogen Dioxide Sensors †**

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**Abstract:** Vanadium pentoxide thin films were deposited onto insulating support 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. Thickness of the films was determined by the profilometry. It has been confirmed by GIXD that the deposited films are composed of V₂O₅ phase. The gas sensing properties of V₂O₅ thin films were investigated at temperatures from range 410–617 K upon NO₂ gas of 4–20 ppm. The investigated material exhibited good response and reversibility towards nitrogen dioxide. The effect of metal-insulator transition (MIT) on sensor performance has been observed and discussed for the first time. It was found that a considerable increase of the sensor sensitivity occurred above 545 K, which is related to postulated metal-insulator transition.

**Keywords:** vanadium pentoxide; thin film; reactive sputtering; electrical properties; nitrogen dioxide; gas sensor; metal-insulator transition (MIT)

1. **Introduction**

Increasing environmental pollution is becoming a vital global concern, particularly in relation to the imperative to reduce emissions of gases causing the greenhouse effect, acid rain, and the depletion of stratospheric ozone. Therefore, there is an urgent need to develop some devices that allow fast, portable, low-cost monitoring of the gases responsible for air pollution and/or pose danger to human health. So far, sophisticated and expensive equipment, such as gas analyzers based on IR and UV spectrophotometry, pulse fluorescence, flame photometry and gas chromatography, to determine air quality were applied. Although this equipment enables very precise gas phase analysis, it has four substantial disadvantages such as high cost, large dimensions (limited portability), slow analysis time and non-continuous monitoring of the gas composition. In this respect, chemical gas sensors may offer advantages in the form of simple construction, low cost and ability to work in situ. One large group of sensors, applied to environmental monitoring, is based on liquid (or wet) electrochemistry. However, these sensors presently suffer from the same four severe disadvantages. Moreover, these sensors cannot be applied in environments warmer than room temperature.

During the past five decades, efforts were made to develop chemical gas sensors based on solid-state technology. The potential advantages of these sensors over the wet technology sensors are (i) miniaturization, (ii) simple calibration and measurement, (iii) low cost, (iv) short response time, (v) resistance to severe conditions, such as high temperature and corrosive environment and (vi) selectivity. Their main advantage is that they can also operate at elevated temperatures, thus meeting the environmental requirements, such as for instance in car and industrial exhaust systems.
There are several types of chemical gas sensors [1]. The largest group consists of electrochemical sensors. According to Wilson et al. [2] and Janata [3] the electrochemical gas sensors have been categorized into three groups: (1) conductometric (measurement of electrical conductivity or related value such as resistivity, impedance); (2) potentiometric (measurement of electromotive force or related value such as voltage of the solid cells); (3) amperometric (measurement of current).

The most widely studied type of the gas sensors are conductometric. Their principle of operation involves a change in the resistance of the sensor sensitive phase (usually metal oxide) upon exposure to a specific component of the gas atmosphere. During adsorption of gas molecules on solid surface, the electronic charges (electrons or electron holes) are created, which change surface electrical conductivity. This process takes place within the thin layer near-surface of the solid of the thickness named the Debye length. Consequently, electrical conductivity may be used as a sensing property for detection of specific gas phase components. Various review works have referred to conductometric gas sensors [4–9]. However, there is no simple theory which can predict how the sensor’s signal depends on gas concentration.

Conductometric gas sensors are usually based on metal oxide semiconductors, such as SnO$_2$ [10–15], ZnO [16,17], WO$_3$ [18], TiO$_2$ [19–21], Fe$_2$O$_3$ [22]. Also, other materials such as graphene, metal hydroxides, metal dichalcogenides, phosphorene, boron nitride [4,5,7], and conducting polymers are investigated. However, the poor sensor recovery and stability remain the major concerns.

Generally, semiconductor gas sensors suffer from low selectivity. Several attempts were made to improve their selectivity in respect to the detectable gas. The most frequent approach involves change of the sensor composition by doping, the use of composites with one or more other materials, variation of operating temperature etc. It was found that the successful method improving sensors’ selectivity is addition of some heterogeneous catalysts, such as noble metals (Pt, Pd, Au) to the sensor material. In addition, use of the vanadium pentoxide – well-known catalyst – is promising.

Recently, vanadium oxides have attracted considerable interest due to their multi-valence, good chemical stability and excellent catalytic properties [23]. Moreover, unlike the above-mentioned sensing oxides, vanadium oxides show metal-insulator transition (MIT), an interesting electrical property which may have impact on the sensor’s performance.

V$_2$O$_5$, the most stable compound among over 15 known vanadium oxides, is a promising NO$_2$ sensor material [24]. It demonstrated high sensitivity and selectivity for ethanol [25], ammonia [26], hydrogen and hydrocarbons [27].

Table 1 [27–49] includes examples of conductometric sensors of various gases, except of NO$_2$, with V$_2$O$_5$ sensing material or V$_2$O$_3$ as addition to other material such as SnO$_2$ [33,38], TiO$_2$ [40,50] and other [29,37,51–54]. On the other hand, Table 2 summarizes V$_2$O$_5$-based NO$_2$ sensors.
Therefore, there is an urgent need to develop devices that allow fast, portable, low-cost monitoring of NO2 gas sensors for commercialization requires the achieving of four “S”, i.e. sensitivity, selectivity, stability and speed (response and recovery rates).

Table 1. Vanadium oxide-based gas sensors, literature survey (published between 2010–2017).

| Gas                | Composition | Morphology          | Operation Temp (K) | Response | Gas Concentration [ppm] | Sensitive Against |
|--------------------|-------------|---------------------|--------------------|----------|-------------------------|-------------------|
| H2                 | V2O5        | Thin films          | 420–520            | 1.22     | 5–300 H2                | NA                |
| CH4, C2H6          |             |                     |                    |          | 50–3000 CH4             | C2H4              |
| Et1, NH3           | V2O5        | Hollow spheres      | NA                 |          | 100–500                 | NA                |
| NH3                | V2O5        | Thin film           | RT                 | 1.02–3.06| 100–400                 | H2                |
| Et, NH3            | V2O5        | Thin film           | NA                 | 1.06     | 100–500                 | NA                |
| Acetone, CH3OH, HCHO, HCHO, toluene | VO2 | nanorods            | RT                 | 1.027    | 5–100                  | NA                |
| SO2                | SnO2 + 5 wt%MgO + 2 wt% | Thick film | NA                 | 1.44     | 0.1–1                   | NA                |
| Et                 | V2O5        | Thin film           | NA                 | 1.4      | 800                     | NA                |
| Tert-butylamine    | V2O5        | Thin film           | 300                | 27.9     | 100                     | NA                |
| NH3                | V2O5        | Composite fibers with polyvinyl acetate and pyrolydine | 530 | 1.02 | 0.1–0.8                  | [37] |
| BTEX4              | SnO2/V2O5   | Composite SnO2/V2O5 | 540              | 5.5–6    | 0.5–50                  | Et, CH3OH, HCHO   |
| CH4                | VO2         | Thin films          | 298–473            | 1.008–1.032| 50–500                 | NO2, H2           |
| NH3                | V2O5–WO3–TiO2 | Potentio- metric: Au V2O5–WO3–TiO2 | 820           | 0–150    | 10–300                  | NA                |
| H2O                | VO2 (3fl) complex | Thick film 20-30µm | RT                 | NA       | RH: 35–70%              | NA                |
| NH3                | V2O5–V2O4–TiO2 | Thin film | 620              | 1.4      | 0.16–0.32               | NO2, CO           |
| Et                 | V2O5        | Thin films          | 573–773            | 1.27–1.80| 500–3000                | NA                |
| H2O                | V2O5        | Nanowiremicroyarns  | 600               | 9.90     | 50–1000                 | Higher alcohols   |
| Tert-butylmercaptan | VO2 | Thick layer (0.2 mm) from nanopowder | 600          | Cataluminescence | 3600–62,000 | Alcohols, alde-hydes, NH3 |
| NO2, H2            | V2O5 + VO2 | Thin film composed from nanotubes | 448           | 2.85     | 20–80 NO               | CO                |
| CH4                | Au–VO2      | Porous thin film    | 563               | 1.073    | 500–2000 H2            | [46,47]          |
| CH4                | C/VO2       | C nanotubes filled with VO2 | RT            | 1.015    | NA                      | NA                |

Symbols: Et1—ethanol (C2H5OH); NA2—not reported; RT3—room temperature (298 K); BTEX4—benzene, toluene, ethylbenzene and xylene.

For some practical applications, the high operating temperature creates problems with the long-term stability and high costs of the sensor manufacture and maintenance. As can be seen in the Table 1, some authors reported that their sensors based on nanostructured vanadium pentoxide or its composite show sensitivity at room temperature [29,31,36,41,48,49]. Moreover, as per published results [40], the sensor selectivity may be substantially improved for sensors composed of oriented nanoparticles.
2. Materials and Methods

2.1. Thin Film Preparation

VO₂ thin films were deposited onto insulating support (either fused silica or alumina) for sample characterization or conductometric sensor substrate type CC1.W (BVT Technologies, Czech Rep.), for electrical measurements, by means of rf sputtering in a reactive atmosphere at working pressure 4.75 Pa (24% O₂ – 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 [27].

![Conductometric sensor support from BVT Technologies company.](image)

2.2. Morphology and Structural Characterization

Scanning electron microscopy (SEM) studies were carried out for as-sputtered thin films using NOVA NANOSEM 200 (FEI Europe Company) microscope. Phase composition of as-sputtered thin films was studied by X-ray diffraction at glancing incidence, GIXD. Thickness of the V₂O₅ thin film was (210 ± 25) nm.

2.3. Sensing Characterization

The responses S of films to the target gas (NO₂), defined as changes in electrical resistance (S = R_NO₂/R_air), were measured by custom-made setup at different NO₂ concentrations (0–20 ppm). The sample was placed in a gas chamber on a workholder, where the temperature and gas atmosphere (gas composition and humidity) were stabilized. The relative humidity was set to 50 ± 0.1%. The requested NO₂ concentration was obtained by controlling the ratio of gas to air flow rate, and total flow rate was set to 500 cm³/min. The total flow rate was maintained at the same level of 500 cm³/min. The film resistance changes upon NO₂ were measured with Keithley 6517 electrometer working in constant voltage mode (U = 0.1 V). At the beginning, the sensor response has been stabilized in pre-set conditions (at the lowest temperature, constant gas flow, pure air of 50% humidity). Then two types of measurement procedures were performed. During the first stage, the measurement of sensor response under varying temperature (range 483–623 K), and at constant NO₂ concentration (20 ppm) fed alternately with air for purging purposes, was realized. After that, the second stage was performed: The measurement at constant temperature under increasing gas concentrations (0–20 ppm with 4 ppm step), also while purging the chamber with air. The sensor resistance was sampled every 2 s. The sensor measurements were performed within the temperature range extending from RT to 700 K. Equipment applied for measurements of the sensor characteristics was described in detail elsewhere [55].

3. Results and Discussion

3.1. Structural and Microstructural Characteristics

Figure 2 presents the typical XRD patterns of the sample annealed at 673 K in argon atmosphere. X-ray diffraction analysis of the samples revealed the presence of the V₂O₅ orthorhombic phase.
Figure 2. X-ray diffraction patterns for as-sputtered V$_2$O$_5$ thin film.

The determined lattice parameters ($a = 1.145 \pm 0.003$ nm; $b = 0.436 \pm 0.004$ nm; $c = 0.355 \pm 0.003$ nm) well agree with those from literature reports [56]. Presented XRD patterns were used for determination of the crystallite size. Crystallite size, $d_{\text{XRD}}$, was calculated according to Scherrer’s method: $d_{\text{XRD}} = 20.0 \pm 1.8$ nm. No effect of sintering temperature on obtained XRD results was observed.

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

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

3.2. Sensing Characteristics

An example of V$_2$O$_5$ sensor responses to 20 ppm NO$_2$ are shown in Figure 4a,b.

Figure 4. Dynamic changes in the electrical resistance of V$_2$O$_5$ thin film upon interaction with 20 ppm NO$_2$, (a) at several temperatures; (b) at 483 K.
As one can see from Figure 4, the resistance of the investigated V$_2$O$_5$ thin films increases upon exposure to NO$_2$, which is characteristic of n-type semiconductors.

NO$_2$ sensing mechanism can be explained in terms of defect structure of vanadium pentoxide [57]. V$_2$O$_5$ equilibrated in air shows deficit, x, of oxygen (V$_2$O$_{5-x}$). Doubly positive ionized oxygen vacancies are compensated by V$^{4+}$ ions. Electrical conductivity is achieved by small polaron mechanism, via electron hopping from neighbouring two ions V$^{4+}$ and V$^{5+}$ (marked as 1 and 2):

\[
V^{4+}_1 + V^{5+}_2 \rightarrow V^{5+}_1 + V^{4+}_2
\]  

Equation (1) indicates that the increase of the resistance upon exposure of NO$_2$, as observed in Figure 4a,b, results from decrease of the concentration of V$^{4+}$ ions.

When NO$_2$ is added to gas atmosphere, adsorption of NO$_2$ molecules takes place according to the reaction:

\[
\text{NO}_2^{(g)} + V^{4+} \rightarrow \text{NO}_2^{-(ad)} + V^{5+}
\]  

Equation (2) indicates that the increase of the resistance upon exposure of NO$_2$, as observed in Figure 4a,b, results from decrease of the concentration of V$^{4+}$ ions.

Electrical conductivity is proportional to concentration of V$^{4+}$ ions.

As one can see from Figure 4, the resistance of the investigated V$_2$O$_5$ thin films increases upon exposure to NO$_2$, which is characteristic of n-type semiconductors.

Figure 5a illustrates sensor response, $S = R_{\text{NO}_2}/R_{\text{air}}$, versus temperature. The abrupt increase in the sensor response is observed at 545–547 K. This behaviour may be explained by the occurrence of the metal-insulator transition, MIT.

One of the most spectacular phenomena occurring in most vanadium oxides is the abrupt change of the electrical resistivity from the values typical for semiconductor to those typical of metal phase. This phenomenon, called semiconductor–metal phase transition, SMPT [58] or more frequently metal-insulator transition, MIT, offers immense prospects for various practical applications, in particular oxide electronics, photoelectronics [59,60] and gas sensors. Strelcov et al. [61] studied gas sensor properties of nanowire VO$_2$ close to temperature of MIT ($T_{\text{MIT}} = 338$ K). They observed that varying the temperature of the nanowire close to the $T_{\text{MIT}}$, the conductance of the nanowire becomes extremely responsive to the tiny changes in the ambient gas environment. According to our knowledge, the effect of MIT on gas sensor properties of V$_2$O$_5$ have not been studied yet.

The single valence vanadium oxides V$_2$O$_3$, VO$_2$, and most of double valence vanadium oxides (i.e., Magneli or Wedsley series) show metal-insulator transition. During this transition, the polymorphic phase transition occurs from lower to higher symmetrical crystallographic structure. However, vanadium pentoxide, V$_2$O$_5$ thin film is an exception. At temperatures close to 540 K ($T_{\text{MIT}} = 530 \pm 5$ K, Blum [59]; $T_{\text{MIT}} = 533$ K, Kang et al. [60]), MIT takes place in nanostructured and thin films of V$_2$O$_5$ without any phase transition. This fact can be explained that MIT in V$_2$O$_5$ is limited to the surface layer [59]. Our recent studies revealed that MIT is observed in V$_2$O$_5$ thin films annealed in air, while in V$_2$O$_5$ thin films annealed in gas atmosphere containing NO$_2$ MIT effect was not observed. From these facts and Equation (2), we postulate that sufficient V$^{4+}$ ion concentration on the surface is a prerequisite to MIT in vanadium pentoxide. The abrupt change (Figure 5a) of sensor response $S$, which is observed close to $T_{\text{MIT}}$, results from MIT in sample in air (i.e. abrupt decrease of $R_{\text{air}}$, and much smaller increase in $R_{\text{NO}_2}$).

As Figure 5b indicates, below $T_{\text{MIT}}$ ($T < T_{\text{MIT}} = 546$ K), the sensor response $S$ increases slightly with temperature. On the other hand, for $T > T_{\text{MIT}}$ the sensor response exhibits much larger increase.
Table 2. Vanadium oxide-based semiconducting NO$_2$ sensors.

| Materials                      | Operation          | Temperature [K] | Concentration | Response | Reference |
|--------------------------------|--------------------|-----------------|---------------|----------|-----------|
| VO$_2$ thin film nanocolumnar  |                    | 423             | >100 ppm      | 5        | [24]      |
| V$_2$O$_5$ thin film nanotubes |                    | 563             | 20–80 ppm     | 6        | [47]      |
| V$_2$O$_5$ thin film nanotubes |                    | 448             | 20–80 ppm     | 2.9      | [47]      |
| Composite porous Si/          | from-nanorods V$_2$O$_5$ | 298–523       | 0.25–3        | 5–10     | [51]      |
| V$_2$O$_5$ thin film          |                    | 553–573         | 100 ppm       | 1.6      | [62]      |
| V$_2$O$_5$ thin films composed | from-nanorods      | 473             | 100 ppm       | 1.24     | [63]      |
| V$_2$O$_5$ thin films 450 nm  |                    | 323             | 2–20 ppm      | 1.8      | [64]      |
| V$_2$O$_5$ nanorods           |                    | 473             | 100 ppm       | 1.24     | [65]      |
| V$_2$O$_5$ thin films 410–545 |                    | 410–545         | 4 ppm         | 1.16     |           |
| V$_2$O$_5$ thin films          |                    | 546–617         | 20 ppm        | 3.35     | This work |
|                                |                    |                 | 4 ppm         | 14.4     | This work |
|                                |                    |                 | 20 ppm        | 23.0     | This work |

Some examples of NO$_2$ sensor with vanadium pentoxide sensing material are given in Table 2 [47,62–65]. Among gas sensing oxides presented in Table 2, two materials distinguish oneself: composite porous Si/nanorod V$_2$O$_5$ [51] and thin film V$_2$O$_5$ (this work) sensors. They enabled detection of low NO$_2$ concentrations below 5 ppm. They showed the highest response $S = 5–10$ [51] and $S = 14–23$ (this work), respectively. Proposed by Yan et al. [51] sensor can work at room temperature. However, the instability of gas sensitivity, lack thermal stability of porous silicon [66], as well as complex technology of manufacturing of the porous Si/nanorod V$_2$O$_5$ composite [51] limit the commercial applications.

![Figure 5. The sensor response S: (a) vs. temperature for various NO$_2$ concentrations and (b) vs. NO$_2$ concentration for different temperatures.](image)

4. Conclusions

In the present work, we fabricated V$_2$O$_5$ thin films by rf reactive sputtering. The film structure and morphology were studied by X-ray diffraction at glancing incidence and scanning electronic microscopy. Gas sensing studies showed that the V$_2$O$_5$ thin films were sensitive to NO$_2$ at relatively low operating temperatures. The considerable increase of the sensor sensitivity was observed above 545 K, which is related to postulated metal-insulator transition. Presented studies on vanadium pentoxide thin film NO$_2$ sensor will be continued regarding selectivity (especially in respect to water vapor).
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