Nanocrystalline TiO$_2$/SnO$_2$ heterostructures for gas sensing

Barbara Lyson-Sypien$^{*1}$, Anna Kusior$^{2}$, Mieczylaw Rekas$^{2}$, Jan Zukrowski$^3$, Marta Gajewska$^3$, Katarzyna Michalow-Mauke$^{4,5}$, Thomas Graule$^4$, Marta Radecka$^2$ and Katarzyna Zakrzewska$^1$

Abstract

The aim of this research is to study the role of nanocrystalline TiO$_2$/SnO$_2$ n–n heterojunctions for hydrogen sensing. Nanopowders of pure SnO$_2$, 90 mol % SnO$_2$/10 mol % TiO$_2$, 10 mol % SnO$_2$/90 mol % TiO$_2$ and pure TiO$_2$ have been obtained using flame spray synthesis (FSS). The samples have been characterized by BET, XRD, HR-TEM, Mössbauer effect and impedance spectroscopy. Gas-sensing experiments have been performed for H$_2$ concentrations of 1–3000 ppm at 200–400 °C. The nanomaterials are well-crystallized, anatase TiO$_2$, rutile TiO$_2$ and cassiterite SnO$_2$ polymorphic forms are present depending on the chemical composition of the powders. The crystallite sizes from XRD peak analysis are within the range of 3–27 nm. Tin exhibits only the oxidation state 4+. The H$_2$ detection threshold for the studied TiO$_2$/SnO$_2$ heterostructures is lower than 1 ppm especially in the case of SnO$_2$-rich samples. The recovery time of SnO$_2$-based heterostructures, despite their large responses over the whole measuring range, is much longer than that of TiO$_2$-rich samples at higher H$_2$ flows. TiO$_2$/SnO$_2$ heterostructures can be intentionally modified for the improved H$_2$ detection within both the small (1–50 ppm) and the large (50–3000 ppm) concentration range. The temperature $T_{\text{max}}$ at which the semiconducting behavior begins to prevail upon water desorption/oxygen adsorption depends on the TiO$_2$/SnO$_2$ composition. The electrical resistance of sensing materials exhibits a power-law dependence on the H$_2$ partial pressure. This allows us to draw a conclusion about the first step in the gas sensing mechanism related to the adsorption of oxygen ions at the surface of nanomaterials.
Introduction

The TiO₂–SnO₂ system is extremely important for gas sensing as already proved by many works already published [1-12]. Particularly interesting is the generally accepted possibility of two scenarios: the formation of solid solutions within a certain compositional and temperature range [1,3] or composites of TiO₂ and SnO₂ [4-7]. The fundamental and up till now unresolved question is which form is better for gas sensing.

In fact, we have found in our research that more than two cases are possible. Our previous experience with this system [1,4,6,7,13] indicates that four classes of materials can be obtained:

A. a simple mixture of the constituents denoted as TiO₂–SnO₂

B. perfect solid solutions TiₓSn₁₋ₓO₂ where 0 ≤ x ≤ 1

C. partially decomposed TiₓSn₁₋ₓO₂–SnᵧTi₁₋ᵧO₂ where 0 ≤ x ≤ 1 and 0 ≤ y ≤ 1

D. decorated nano-heterostructures denoted as TiO₂@SnO₂, e.g., TiO₂ nanoflowers overcoated with SnO₂ nanoparticles

Synergetic effects and catalytic reactions can be expected in the case of A) and C) while changes of the morphological and the electronic structure dominate in the case of B) and D). Surface phenomena determine the gas-sensor response in the case of decorated nano-heterostructures, D). As shown in [6], electron transfer over n–n-type heterojunctions can account for sensor sensitization in the cases of A) and D). The formation of n–n-type heterojunctions at the contact between SnO₂ and TiO₂ grains and its effect on the enhancement of the sensor response has been reviewed recently [14].

Figure 1 explains why the formation of n–n heterojunctions between TiO₂ and SnO₂ grains enhances the response of the gas sensor. In fact, the sensitization comes to an effect in the first step of reducing gas detection, namely the preadsorption of oxygen at the grain surface (in our case it is assumed to be in the form of O⁻ as shown in Figure 1b). The efficiency of the O⁻ adsorption process is greatly enhanced when a sufficient concentration of electrons is provided. It is usually assumed that SnO₂ grains are more suitable for oxygen adsorption, thus electron transfer from TiO₂ grains is necessary to increase the number of adsorption sites. Electron transfer from TiO₂ to SnO₂ is provided by an appropriate electronic configuration because both conduction (CB) and valence (VB) band edges of TiO₂ are above those of SnO₂ as shown in Figure 1a. The potential difference that is formed when TiO₂ and SnO₂ grains come to contact facilitates electron transport from TiO₂ to SnO₂ thus promoting oxygen preadsorption at the surface of SnO₂ grains.

In the publications about the TiO₂–SnO₂ system [1-12,15-17] for improved gas sensing, one can find different types of materials: thick and thin films, nanostructures such as nanofibers, nanorods, nanobelts, nanopowders as well as core–shell particles. Table 1 presents some of the examples of the latest papers dealing with TiO₂–SnO₂ materials for the detection of different gases.

The performance of a resistive-type gas sensor is inherently related to the form and number of oxygen species adsorbed at the surface of the sensing material in the first step [18]. The equation describing the oxygen chemisorption can be written as [19]:

\[
\frac{\beta}{2} O_2^{\text{gas}} + \alpha e^- + S \leftrightarrow O_{\beta S}^{\alpha},
\]

(1)
where $O_2^{gas}$ is an oxygen molecule in the ambient atmosphere, $e^-$ is an electron that can reach the surface, S is an unoccupied chemisorption site, and $O_2^{chem}$ represents chemisorbed oxygen species with $\alpha = 1$ for singly ionized forms, $\alpha = 2$ for doubly ionized forms, $\beta = 1$ for atomic forms and $\beta = 2$ for molecular oxygen.

Table 2 presents possible oxygen species that can be chemisorbed at the surface of the gas sensing material.
Hydrogen is considered to react in a second step, at the surface of the oxides, with preadsorbed or lattice oxygen, which, in consequence, increases the electronic conduction. The surface reaction between hydrogen and oxygen can be described in general by the following equation:

\[
\text{O}_\beta^\alpha + \beta\text{H}_2(\text{g}) = \beta\text{H}_2\text{O}(\text{g}) + \alpha e^-.
\]

It has been observed that as the result of the two step interaction described above, the electrical resistance, \( R \), of the sensor for any reducing gas can be expressed as \([1,20]\):

\[
R \propto p_{\text{gas}}^{-n},
\]

where \( p_{\text{gas}} \) is the partial pressure of the reducing gas while the power coefficient \( n \) is specific to the kind of the target gas and particular reaction with oxygen species preadsorbed at the surface of the semiconductor.

In our previous work \([1]\) one can find an analysis of TiO\(_2\)–SnO\(_2\) in the form of polycrystalline ceramics and rf-sputtered thin films upon interaction with H\(_2\) but not much is known in the case of nanomaterials. Since that time we have focused on commercial TiO\(_2\) and SnO\(_2\) starting nanomaterials for the sensing of H\(_2\) and NH\(_3\) \([4,6,7]\). One of the main conclusion from our latest research on commercial materials is that a small addition of TiO\(_2\) to SnO\(_2\) affects gas sensing characteristics to a large extent \([4,6]\). In this work, for the first time, we intend to demonstrate nano-heterostructures of the TiO\(_2\)–SnO\(_2\) system prepared by flame spray synthesis with application to gas sensing.

Flame spray synthesis is a well-known and efficient method for the synthesis of crystallized metal oxide nanoparticles with particular morphology, e.g., spherical, monodispersed nanoparticles of TiO\(_2\) with good photocatalytic properties \([21-23]\). However, its application to nano-heterostructures for gas sensing is not known.

The aim of the current work is to study the role of nanocrystalline TiO\(_2\)/SnO\(_2\) n–n heterojunctions for hydrogen sensing. Within this work the detailed study on crystallographic structure, morphology, electrical properties, H\(_2\) sensing behavior and the power-law nature of the electrical resistance of TiO\(_2\)/SnO\(_2\) heterostructures is presented. The influence of water adsorption and desorption on the electrical properties of TiO\(_2\)/SnO\(_2\) is also taken into account. The detection threshold is studied for the first time as a function of the chemical composition of TiO\(_2\)/SnO\(_2\) heterostructures.

Experimental

Nanopowders of the TiO\(_2\)–SnO\(_2\) system were obtained by flame spray synthesis, FSS, technique using an oxygen–acetylene flame. Not only end compositions, 100 mol % SnO\(_2\) and 100 mol % TiO\(_2\) were prepared. Potential heterostructures of 90 mol % SnO\(_2\)/10 mol % TiO\(_2\) and 10 mol % SnO\(_2\)/90 mol % TiO\(_2\) were synthesized as well.

Titanium diisopropoxide bis(acetylacetonate) (TiC\(_{16}\)H\(_{28}\)O\(_5\), 75 wt % in isopropanol, ABCR, CAS: 17927-72-9) and tetramethyltin (CAS: 594-27-4), dissolved in absolute ethanol (C\(_2\)H\(_5\)OH, 99%, Sigma Aldrich) were used as precursors of titanium and tin, respectively. Details of the FSS setup have been reported elsewhere \([24,25]\).

The required composition and specific surface area (SSA) were obtained by adjusting the ratio of the precursors in the precursor mixture, the total flow rate of which was kept constant at 12.64 cm\(^3\) min\(^{-1}\). The total precursor concentration in the flame was kept constant at 1.5 mol·kg\(^{-1}\). The precursor solution was fed by a syringe pump and was atomized with oxygen (583 cm\(^3\) s\(^{-1}\)) in a gas-assisted external mixing nozzle. The combustible aerosol was ignited by six oxygen-acetylene flamelets (C\(_2\)H\(_2\), 217 cm\(^3\) s\(^{-1}\); O\(_2\), 283 cm\(^3\) s\(^{-1}\)) and the produced particles were collected on glass-fiber filters (GFA/150, Whatman) using vacuum pumps. The nanopowders of TiO\(_2\)–SnO\(_2\) did not require any post-synthesis heat treatment since the technique provides well crystallized nanostructures.

The specific surface area (SSA) was determined using Brunauer–Emmett–Teller (BET) nitrogen-adsorption isotherms obtained with a Beckman–Coulter SA3100 apparatus.

The crystallographic structure was analyzed on the basis of XRD patterns recorded in Bragg–Brentano configuration with the help of a Philips X’Pert Pro diffractometer. Based on Rietveld refinement it was possible to determine the weight fractions of cassiterite SnO\(_2\), rutile TiO\(_2\) and anatase TiO\(_2\), the lattice constants and the crystallite sizes, \(d_{\text{XRD}}\).

The \(^{119}\text{Sn}\) Mössbauer effect measurements were performed in transmission geometry using an MS-4 RENON spectrometer and CaSnO\(_3\) as source. The Mössbauer spectra were fitted using a transmission integral in order to take into account the absorber thickness effects. The spectra were refined with quadrupole doublets of Lorentzian lines assuming a non-zero value of the electric field gradient at the tin site. Hyperfine parameters, the isomer shift, \(I_S\), and quadrupole splitting, \(QS\), as well as the full width at half maximum of the Sn peaks, \(G\), were found. The values of isomer shift are given relative to the CaSnO\(_3\) source kept at room temperature.

\[\text{Brillen J. Nanotechnol. 2017, 8, 108–122.}\]
Morphology of the synthesized TiO$_2$–SnO$_2$ nanomaterials was studied by means of scanning electron microscopy (SEM) performed with a FEI Nova Nano SEM 200 apparatus. High-resolution transmission electron microscopy (HR-TEM) images were obtained using a FEI Tecnai TF 20 X-TWIN microscope. Mapping of chemical elements and diffraction patterns were provided.

The electrical properties were investigated by impedance spectroscopy (IS) in the temperature range from 20 to 550 °C in air. The impedance spectroscopy measurements were performed with a Solatron system (Fra 1260 + dielectric interface 1294). Experimental parameters and data acquisitions were controlled with the FRA software. A frequency range from 1 to 10$^6$ Hz was covered, with 10 mV amplitude. The impedance spectra were analyzed using the ZView software. An equivalent circuit containing one resistor and a constant phase element (CPE) was used for fitting.

In order to perform gas sensing measurements, the nanosensors were prepared in the form of tablets that were pressed from powders under a pressure of 25 MPa, then annealed at 400 °C and covered with planar silver electrodes. The detailed description of the experimental setup used for the H$_2$-sensing measurements can be found in [26,27]. The desired hydrogen concentration was obtained by using mass flowmeters mixing synthetic air (reference gas) with H$_2$ (0.01% H$_2$, 0.1% H$_2$, 1% H$_2$ + Ar depending on the concentration range, i.e., 1–30 ppm, 5–300 ppm and 50–3000 ppm H$_2$, respectively). The total gas (hydrogen mixture + air) flow rate was kept constant at 120 sccm. The measurements were carried out in dry atmosphere. The synthetic air contained less than 1 ppm of water vapor while that of hydrogen + argon mixture had less than 10 ppm of contaminants. The relative humidity level was verified to be of about 0–1% RH at room temperature.

Dynamic changes in the electrical resistance upon hydrogen exposure have been detected over a low-to-medium concentration range of 1–3000 ppm at a constant temperature between 200 and 400 °C. Measurements within an interval of 1–50 ppm H$_2$ were performed to determine the hydrogen detection limit. The sensor response $S$ was defined as the ratio between the electrical resistance in the reference atmosphere, $R_0$, and the electrical resistance upon interaction with hydrogen, $R$:

$$S = \frac{R_0}{R}$$

Results and Discussion

Figure 2 shows XRD patterns for SnO$_2$–rich (Figure 2a) and TiO$_2$–rich (Figure 2b) heterostructured nanopowders obtained by FSS compared with the pure end components SnO$_2$ and TiO$_2$. Table 3 recapitulates the results of XRD Rietveld refinement performed for TiO$_2$/SnO$_2$ nanopowders, and the SSA values determined from BET measurements. The FSS parameters were chosen intentionally in order to obtain approximately the same SSA, and according to the expectation the SSA were found to be within a range of 54–62 m$^2$·g$^{-1}$, independent of the chemical composition.

As it can be concluded from Table 3 and Figure 2, pure SnO$_2$ exhibits the crystallographic structure of cassiterite, whereas in the case of pure TiO$_2$ two polymorphic forms, anatase and rutile, are present with a predominance of anatase (91.1 wt %). Lattice constants $a$ and $c$ of both TiO$_2$ and SnO$_2$ determined experimentally are in good agreement with their theoretical values [28], TiO$_2$ rutile: $a = 0.45911$ nm, $c = 0.29440$ nm; TiO$_2$ anatase: $a = 0.37849$ nm, $c = 0.94997$ nm; SnO$_2$ cassiterite: $a = 0.47360$ nm, $c = 0.31857$ nm.

The main conclusion from Figure 2a is that one can observe a systematic shift of all cassiterite SnO$_2$ XRD peaks towards higher diffraction angles resulting from a decrease in the lattice constants $a$ and $c$ (Table 3) of the 90 mol % SnO$_2$/10 mol % TiO$_2$ nanopowder compared with 100% SnO$_2$. This effect is typical and is usually interpreted as Ti substitution at Sn lattice sites [1]. The absence of non-identified peaks belonging to TiO$_2$ phases supports the conclusion that under these conditions a solid solution is formed (case B). However, the presence of heterojunctions between the small amount of TiO$_2$ grains well dispersed within the primary SnO$_2$ cassiterite phase cannot be excluded.

The influence of 10 mol % SnO$_2$ in TiO$_2$ on the XRD pattern (Figure 2b) is much more pronounced. As observed previously for polycrystalline ceramics and thin films [1], even a relatively small amount of SnO$_2$ in TiO$_2$ results in a dramatic reconstruction of the crystallographic structure. The content of anatase decreases from 91.1 wt % for pure TiO$_2$ to 8.5 wt % for 10 mol % SnO$_2$/90 mol % TiO$_2$. The crystallite size of anatase remains unchanged (25 nm for 100% TiO$_2$ and 27 nm for 10 mol % SnO$_2/90$ mol % TiO$_2$). The rutile TiO$_2$ phase begins to predominate (71.1 wt %) with lattice constants slightly higher than those of 100% TiO$_2$ indicating partially decomposed solid solution (case C). Furthermore, the evidence of precipitation of 18.4 wt % SnO$_2$ cassiterite with very small crystallites of about 3 nm favors the hypothesis of a heterostructure formation.

In order to study the possible tin oxidation states, Mössbauer spectroscopy was applied. Figure 3 demonstrates transmission spectra of: a) SnO$_2$; b) 90 mol % SnO$_2/10$ mol % TiO$_2$ and c) 90 mol % TiO$_2/10$ mol % SnO$_2$ nanopowders.
Figure 2: Comparison between XRD patterns of a) SnO$_2$ and 90 mol % SnO$_2$/10 mol % TiO$_2$; b) TiO$_2$ and 90 mol % TiO$_2$/10 mol % SnO$_2$ nanopowders.

Table 3: The results of BET and XRD Rietveld refinement of TiO$_2$–SnO$_2$ nanomaterials; “A” denotes anatase, “R” rutile and “C” cassiterite; SSA: specific surface area.

| Sample          | XRD          | C SnO$_2$ | A TiO$_2$ | R TiO$_2$ | SSA (m$^2$/g) |
|-----------------|--------------|-----------|-----------|-----------|---------------|
| SnO$_2$         |              |           |           |           | 54            |
| wt %            | 100          |           |           |           |               |
| $a$ (nm)        | 0.47360      |           |           |           |               |
| $c$ (nm)        | 0.31857      |           |           |           |               |
| crystallite size (nm) | 12      |           |           |           |               |
| 10 mol % TiO$_2$/100 mol % SnO$_2$ | wt % | 100 |           |           | 62             |
| $a$ (nm)        | 0.47929      |           |           |           |               |
| $c$ (nm)        | 0.31780      |           |           |           |               |
| crystallite size (nm) | 10     |           |           |           |               |
| 90 mol % TiO$_2$/10 mol % SnO$_2$ | wt % | 18.4 | 8.5 | 73.1 | 60             |
| $a$ (nm)        | 0.45956      | 0.37840   | 0.46007   |           |               |
| $c$ (nm)        | 0.30447      | 0.95489   | 0.29964   |           |               |
| crystallite size (nm) | 3        | 27       | 14        |           |               |
| TiO$_2$         |              |           |           |           | 57            |
| wt %            | 91.1         | 8.9       | 14        |           |               |
| $a$ (nm)        | 0.37849      | 0.45911   | 0.29964   |           |               |
| $c$ (nm)        | 0.94997      |           |           |           |               |
| crystallite size (nm) | 25     | 15       |           |           |               |
The observed peaks are characteristic for Sn$^{4+}$ (SnO$_2$) for all presented powder samples. No contribution from Sn$^{2+}$ (SnO) has been detected. The measured hyperfine parameters of SnO$_2$, i.e., the isomer shift, $\text{IS}$, and quadrupole splitting, $\text{QS}$, at room temperature exhibit similar values for all the studied samples and are in agreement with those reported for SnO$_2$ [29-31].

Figure 4 shows the dynamic responses of the electrical resistance of 90 mol % SnO$_2$/10 mol % TiO$_2$ and 10 mol % SnO$_2$/90 mol % TiO$_2$ heterostructures upon interaction with hydrogen at a constant temperature of 400 °C. As one can see in Figure 4a and Figure 4c, the electrical resistance decreases upon admission of reducing gas (hydrogen). Thus we can conclude that globally both heterostructures (SnO$_2$-rich and TiO$_2$-rich) exhibit n-type conductivity. This is not surprising because usually SnO$_2$ and TiO$_2$ are treated as n-type semiconductors [32,33]. Moreover, from the comparison of the gas sensing responses given in Figure 4a and Figure 4c it is easily seen that the heterostructure of 90 mol % SnO$_2$/10 mol % TiO$_2$ is very sensitive even to small H$_2$ concentrations (5–300 ppm H$_2$, Figure 4a) while the TiO$_2$-rich composition, i.e., 10 mol % SnO$_2$/90 mol % TiO$_2$ requires higher hydrogen concentrations (50–3000 ppm H$_2$, Figure 4c).

SEM and HR-TEM images, as well as the results of selected area electron diffraction (SAED) and mapping of elements are given in Figure 4b and Figure 4d for the gas sensing materials given in Figure 4a and Figure 4c, respectively. There are some differences between the microstructure of 90 mol % SnO$_2$/10 mol % TiO$_2$ and 10 mol % SnO$_2$/90 mol % TiO$_2$. In the case of TiO$_2$-rich heterostructures the grains are larger and spherical (Figure 4d), while for SnO$_2$-rich compositions grains are smaller, more irregular in shape and elongated (Figure 4b). The spherical nanograins of TiO$_2$ are probably composed of smaller crystallites while separate SnO$_2$ grains were not identified by SAED for 10 mol % SnO$_2$/90 mol % TiO$_2$. Element mapping suggests that a small amount of Sn (Figure 4d) is finely dispersed within the TiO$_2$ matrix. In the 90 mol % SnO$_2$/10 mol % TiO$_2$ heterostructures Ti is well incorporated into SnO$_2$ building blocks (Figure 4b).
Figure 4: Dynamic changes in the electrical resistance, $R$, of: a) 90 mol % SnO$_2$/10 mol % TiO$_2$ (H$_2$ concentration: 5–300 ppm) and c) 10 mol % SnO$_2$/90 mol % TiO$_2$ (H$_2$ concentration: 50–3000 ppm) nanomaterials upon interaction with hydrogen at a constant temperature of 400 °C along with the corresponding SEM and TEM images (b, d). Step changes in hydrogen concentrations are given on the right hand scale (a, c).
Driven by the promising sensor signal for the step changes in H₂ concentration (Figure 4), we decided to perform additional measurements in order to determine the hydrogen detection threshold for the studied TiO₂/SnO₂ heterostructures. Figure 5a and Figure 5b present dynamic changes in the electrical resistance of 90 mol % SnO₂/10 mol % TiO₂ and 10 mol % SnO₂/90 mol % TiO₂, respectively, upon interaction with 1 and 2 ppm H₂. The H₂ detection threshold for the studied TiO₂/SnO₂ heterostructures is lower than 1 ppm, especially in the case of SnO₂-rich composition (Figure 5a). As one discusses 10 mol % SnO₂/90 mol % TiO₂ it appears that at 1 ppm H₂ the signal-to-noise ratio becomes much worse. However, the sensor signal is still discernible.

Within the studied temperature range SnO₂-rich nanomaterials exhibit better gas-sensing performance (Figure 5c,d). The larger sensor response, $R_0/R$ (by about 20 times) for SnO₂-rich heterostructures compared to TiO₂-rich ones is typical as titanium dioxide requires higher temperatures for improved sensing characteristics.

In Figure 5c and Figure 5d one can also analyze the influence of the formation of heterostructures on the sensor response, $R_0/R$. In both cases the sensor response increases compared to the pure oxides. The improvement in gas-sensing by a small addition of TiO₂ to SnO₂ was reported previously [5]. The explanation of this phenomenon is based on the charge transfer be-
between TiO$_2$ and SnO$_2$ due to the differences in the positions of the conduction and valence band edges of both oxides (Figure 1). A similar effect was reported in our previous work for 2 mol % TiO$_2$/98 mol % SnO$_2$ nanocomposites working as H$_2$ sensors [4].

In this work, for the first time, based on Figure 5e, we can conclude that the addition of SnO$_2$ to TiO$_2$ (10 mol % SnO$_2$/90 mol % TiO$_2$) has a much more pronounced effect than the addition of TiO$_2$ to SnO$_2$ (90 mol % SnO$_2$/10 mol % TiO$_2$). Moreover, one should also take into account the kinetics of interaction described by response and recovery times.

Despite the fact that SnO$_2$-rich heterostructures exhibit larger responses to gases over the whole measuring range, it appears that their recovery time, $\tau$, for the sensor to reach 90% of the initial electrical resistance, $R_0$, is much longer than that of TiO$_2$-rich heterostructures at higher H$_2$ concentrations (Figure 6). In the case of 90 mol % SnO$_2$/10 mol % TiO$_2$ (1100 ppm H$_2$), $\tau$ is about 2500 s, whereas for 10 mol % SnO$_2$/90 mol % TiO$_2$ (1100 ppm H$_2$), $\tau$ is less than 30 s. The longer recovery time of SnO$_2$-rich sensors can be attributed to a constricted gas desorption that probably results from the differences in the microstructure evidenced by SEM (Figure 4).

A fast desorption process is a prerequisite for the reproducible response and from this point of view TiO$_2$-rich heterostructures exhibit better performance at higher H$_2$ concentrations (1000–3000 ppm). From the analysis presented in Figure 5 and Figure 6 one can make the conclusion that TiO$_2$/SnO$_2$ nanoheterostructures can be intentionally modified by changing the chemical composition in order to meet requirements for successful detection of both small (SnO$_2$-rich content) and large H$_2$ concentrations (TiO$_2$-rich compositions).

Figure 7 demonstrates the temperature variation of the electrical resistance in the reference gas (air), $R_0$, and its value upon interaction with 100 ppm H$_2$, $R$, as well as the sensor response defined as a ratio of $R_0/R$ for the two compositions of 90 mol % SnO$_2$/10 mol % TiO$_2$ (Figure 7a,b) as well as 10 mol % SnO$_2$/90 mol % TiO$_2$ (Figure 7c,d).

It can be seen that $R_0$ decreases with increasing operating temperature. As for $R$, it seems that this effect is more pronounced for the TiO$_2$-rich sample. In the case of the SnO$_2$-rich composite the electrical resistance $R$ upon interaction with 100 ppm H$_2$ seems to be independent of the temperature. For 90 mol % SnO$_2$/10 mol % TiO$_2$, the temperature dependence of $R_0/R$ follows $R_0$ vs temperature, because $R$ is almost constant. On the other hand, in the case of the TiO$_2$-rich sample both $R_0$ and $R$ exhibit a similar temperature dependence, which leads to a gas response $R_0/R$ almost independent of the temperature.

In order to study the electrical properties of TiO$_2$/SnO$_2$, impedance spectroscopy was applied. Figure 8 presents: a) the impedance spectra obtained at 400 °C as well as the electrical resistance as a function of the temperature for: b) 90 mol % SnO$_2$/10 mol % TiO$_2$ and c) 10 mol % SnO$_2$/90 mol % TiO$_2$.

The impedance spectra (IS) in Nyquist representation (Figure 8a) consist of a well-developed semicircle, followed by a deformed semicircle at lower frequencies. The equivalent circuit fitted to all spectra is a loop composed of one resistor $R$ in parallel with a constant phase element CPE. Resistor $R$ and CPE represent the bulk/surface process and their values have been determined by fitting (Figure 8a). The CPE in the majority of cases resembles a Debye capacitor $C$. The resulting electrical resistance $R$ as a function of temperature exhibits a maximum, the position of which $T_{\text{max}}$ depends on the competing processes.
Figure 7: Temperature dependence of the electrical resistance in air, \( R_0 \), compared with that upon interaction with 100 ppm H\(_2\), \( R \), together with the sensor response, \( R_0/R \), for the samples of 90 mol % SnO\(_2\)/10 mol % TiO\(_2\) (a, b) and 90 mol % TiO\(_2\)/10 mol % SnO\(_2\) (c, d).

From the thermodynamics of chemical reactions it is well known that oxygen adsorption (described, e.g., by the coverage degree \( \Gamma \)) is an exothermic process and decreases with temperature [34]. Under the experimental conditions this situation is given when the adsorption processes remain in thermodynamic equilibrium, i.e., at temperatures larger than a characteristic value \( T_{\text{eq}} \). In the case of oxygen adsorption at the surface of oxides, \( T_{\text{eq}} \) is of the order of 400 °C [35]. At temperatures smaller than \( T_{\text{eq}} \) the coverage degree \( \Gamma \) increases with temperature as described by the laws of chemical kinetics.

The interpretation of the results given in Figure 8, assuming that the resistance changes are related only to the gas adsorption, is based on the fact that the experimental \( T_{\text{max}} \) is much smaller than the theoretically predicted \( T_{\text{eq}} \). At these relatively low temperatures water desorption is believed to predominate over oxygen adsorption. However, both processes are possible. In the literature one can find three types of mechanisms explaining the increase in the surface conductivity in the presence of water vapor as in all these cases the electron concentration is increased [36]. Water adsorption becomes important at temperatures below \( T_{\text{max}} \) and certainly at room temperature.

The subsequent increase in the temperature above 100–200 °C (see Figure 8b,c) leads to a decrease in the electrical resistance, which is a typical effect for semiconductors and is related to the creation of additional charge carriers.

The temperature \( T_{\text{max}} \) at which the semiconducting behavior begins to prevail over water desorption/oxygen adsorption depends on the TiO\(_2\)–SnO\(_2\) composition. The higher \( T_{\text{max}} \) for TiO\(_2\)-rich heterostructures can be explained on the basis of the higher ionic defect concentration (mainly oxygen vacancies) at the surface of TiO\(_2\). It is well known that oxygen vacancies act as water adsorption centers. Moreover, in the case of SnO\(_2\) water adsorption takes place because of the formation of weak van der Waals bonds between water dipoles and lattice ions (Sn\(^{4+}\) and O\(^{2-}\)) [19]. This facilitates water desorption from the surface of SnO\(_2\)-rich heterostructures at lower temperatures.

As one discusses the interaction between the gas phase and the semiconducting sensor, the two-step mechanism described in
Figure 8: a) Impedance spectra of 90 mol % SnO$_2$/10 mol % TiO$_2$ and 90 mol % TiO$_2$/10 mol % SnO$_2$ at 400 °C along with the electrical resistance as a function of the temperature (b, c) obtained on the basis of impedance measurements.

the Introduction section has to be taken into account. The second step given in a general form by Equation 2 is the surface reduction, which appears upon interaction with hydrogen and can be described in detail as follows [1,37]:

\[ \text{O}^2^- + \text{H}_2(g) = \text{H}_2\text{O}_2(g) + 2\text{e}^- , \]  
\( \text{O}^2^- + \text{H}_2(g) = \text{H}_2\text{O}(g) + 2\text{e}^- . \]

Applying the law of mass action to Equations 5–7 yields:

\[ n_e = \frac{K_1}{(p_{H_2}O)^2} (p_{H_2})^2 , \]  
\[ n_e = \frac{K_2}{P_{H_2}} p_{H_2} , \]  
\[ n_e = \frac{K_3}{(p_{H_2}O)^{1/2}} (p_{H_2})^{1/2} , \]

where \( n_e \) denotes the concentration of electrons, and \( K_1, K_2, K_3 \) are the equilibrium constants of the reactions described by Equations 5–7. The concentration of adsorbed oxygen is assumed to remain constant during its interaction with hydrogen. This is justified by \( p_{O_2} >> p_{H_2} \) and a high rate of oxygen chemisorption under the experimental conditions [1].

As the electron mobility \( \mu_e \) is practically independent of the gas partial pressure, and the relationship for the electrical resistivity reduces to \( \rho = 1/(e\mu_e n_e) \) for n-type semiconductors, the \( 1/R(p_{H_2}) \) dependence assumes the same form as \( n_e(p_{H_2}) \) does (Equations 8–10). Thus, \( n = 1/2, 1 \) or 2 are theoretically predicted for different oxygen species preadsorbed on the surface of the semiconductor.

In the case of formation of oxygen vacancies \( V_{O_2} \), the following reaction could be proposed:

\[ \text{O}_2 + \text{H}_2(g) = V_{O_2}^{k} + k\text{e}^- + \text{H}_2\text{O}_2(g) . \]

The condition of lattice electroneutrality requires that:

\[ n_e = [\text{e}^-] = k \left[ V_{O_2}^{k} \right] , \]

where \( k = 1 \) or 2 corresponds to singly or doubly ionized defects, respectively.

Applying the law of mass action to Equation 11 (with \( k = 1 \) or 2) gives power-law coefficients of \( n = 1/2 \) or \( 1/3 \) according to the relation:
\[ n_e = \frac{K_k}{P_{H_2O}} \left( P_{H_2} \right)^{\frac{1}{k+1}}. \]  

(13)  

Figure 9 and Table 4 demonstrate the results of the power-law analysis of the sensor response for: a) 90 mol % SnO\textsubscript{2}/10 mol % TiO\textsubscript{2} and b) 10 mol % SnO\textsubscript{2}/90 mol % TiO\textsubscript{2}. In the log–log plot the dependence \( R \propto P_{H_2}^n \) can be fitted with a linear function. The values of the power coefficient \( n \) corresponding to

| Theoretically predicted \( n \) | Equation | Form | Experimentally determined \( n \) | Figure | Interpretation |
|-------------------------------|---------|------|-------------------------------|------|---------------|
| 2                             | \( O_2^- \) | not observed | Figure 9 | | the ratio of \( O^-/O_2^- \) increases with temperature |
| 1                             | \( O^- \) | 0.88–1.26 for 90 mol % SnO\textsubscript{2}/10 mol % TiO\textsubscript{2} | Figure 9a | | |
| 1/2                           | \( O^{2-} \) | not observed for 90 mol % SnO\textsubscript{2}/10 mol % TiO\textsubscript{2} | Figure 9a | | |
| 1/2                           | \( V_O^- \) | not observed for 10 mol % SnO\textsubscript{2}/90 mol % TiO\textsubscript{2} | Figure 9b | | |
| 1/3                           | \( V_{O^{**}} \) | 0.25–0.4 for 10 mol % SnO\textsubscript{2}/90 mol % TiO\textsubscript{2} | Figure 9b | | our simplified model does not work here, the formation of point defects should be considered |

**Figure 9:** Log–log plot of the inverse of electrical resistance vs the hydrogen partial pressure for: a) 90 mol % SnO\textsubscript{2}/10 mol % TiO\textsubscript{2} and b) 10 mol % SnO\textsubscript{2}/90 mol % TiO\textsubscript{2} at temperatures of 200–400 °C.
the predominating form, along with the experimentally determined values (Table 4) can be attributed either to the specific oxygen form preadsorbed at the surface of the sensor or to the oxygen vacancies following the equations given above.

In our case the parameter $n$ is around 1 for 90 mol % SnO$_2$/10 mol % TiO$_2$ at temperatures of 200–300 °C and slightly higher than 1 at 350 and 400 °C (Figure 9, Table 4). According to the literature [19] the adsorbed oxygen forms O$_2^-$, O$^-$ and O$^{2-}$ tend to predominate at the surface of SnO$_2$ with increasing temperature. Referring to this data one can conclude that in the case of 90 mol % SnO$_2$/90 mol % TiO$_2$ nanomaterial, $n$ is in the range of 0.25–0.40. The reduction of titanium dioxide leads to the formation of oxygen vacancies.

For TiO$_2$-rich nanomaterials, the sensing properties cannot be explained within this simplified model. It appears that not only oxygen species preadsorbed on the surface of the semiconductor but also formation of point defects need to be considered.

**Conclusion**

1) TiO$_2$/SnO$_2$ heterostructures are well crystallized, anatase, rutile and cassiterite forms are present. Tin exhibits only the oxidation state $4^+$.  

2) The detection threshold is below 1 ppm H$_2$ for SnO$_2$-rich heterostructures.

3) The addition of a small amount of SnO$_2$ to TiO$_2$ has a much more pronounced effect on the sensor response than the modification of SnO$_2$ by a small amount of TiO$_2$.

4) The recovery time of SnO$_2$-based heterostructures is longer than that of TiO$_2$-rich samples at higher H$_2$ concentrations.

5) TiO$_2$/SnO$_2$ heterostructures can be intentionally modified in order to meet the requirements for the successful detection of both small (SnO$_2$-rich) and large H$_2$ concentrations (TiO$_2$-rich).

6) The temperature $T_{\text{max}}$ at which the semiconducting behavior begins to prevail upon water desorption/oxygen adsorption depends on the TiO$_2$/SnO$_2$ composition.

7) The electrical resistance of the sensor materials exhibits a power-law dependence on the partial pressure of H$_2$. In the case of 90 mol % SnO$_2$/10 mol % TiO$_2$, O$_2^-$ and O$^-$ ions are adsorbed and the ratio of O$^2-$/O$_2^-$ increases with temperature.

**Acknowledgements**

This work has been financed by the National Science Centre, Poland grant decision DEC-2011/03/B/ST7/01840. M Radecka has performed her research within National Science Centre, Poland project DEC-2012/07/B/ST8/03879. B. Lyson-Sypien acknowledges the project of Ministry of Science and Higher Education (“Dean” Grant for Young Scientists) at the Faculty of Computer Science, Electronics and Telecommunications AGH UST.

**References**

1. Radecka, M.; Zakrzewska, K.; Rękas, M. Sens. Actuators, B 1998, 47, 194–204. doi:10.1016/S0924-4247(98)00023-9
2. Shaposhnik, D.; Pavelko, R.; Llobet, E.; Gispert-Guirado, F.; Vilanova, X. Sens. Actuators, B 2012, 174, 527–534. doi:10.1016/j.snb.2012.05.028
3. Carotta, M. C.; Cervi, A.; Gherardi, S.; Guidi, V.; Malagu, C.; Martinelli, G.; Vendemini, B.; Sacerdoti, M.; Ghidotti, G.; Morandi, S.; Lettieri, S.; Maddalena, P.; Setaro, A. Sens. Actuators, B 2009, 139, 339–339. doi:10.1016/j.snb.2009.03.025
4. Lyson-Sypien, B.; Czapla, A.; Lubecka, M.; Kusior, E.; Zakrzewska, K.; Radecka, M.; Kusior, A.; Balogh, A. G.; Lauterbach, S.; Kleee, H.-J. Sens. Actuators, B 2013, 187, 445–454. doi:10.1016/j.snb.2013.01.047
5. Zeng, W.; Liu, T.; Wang, Z. Physica E 2010, 43, 633–638. doi:10.1016/j.physe.2010.10.010
6. Kusior, A.; Radecka, M.; Zych, L.; Zakrzewska, K.; Reszka, A.; Kowalski, B. J. Sens. Actuators, B 2013, 189, 251–259. doi:10.1016/j.snb.2013.07.029
7. Radecka, M.; Kusior, A.; Lacz, A.; Trenczek-Zajac, A.; Lyson-Sypien, B.; Zakrzewska, K. J. Therm. Anal. Calorim. 2012, 48, 1079–1084. doi:10.1007/s10973-011-1966-y
8. Carney, C. M.; Yoo, S.; Akbar, S. A. Sens. Actuators, B 2005, 108, 29–33. doi:10.1016/j.snb.2004.11.058
9. Kim, D. H.; Kim, W.-S.; Lee, S. B.; Hong, S.-H. Sens. Actuators, B 2010, 147, 653–659. doi:10.1016/j.snb.2010.03.065
10. Wen, Z.; Tian-mo, L. Physica B 2010, 405, 1345–1348. doi:10.1016/j.physb.2009.11.086
11. Wang, Y.; Liu, J.; Fu, X.; Zhang, X.; Meng, F.; Yu, X.; Jin, Z.; Kong, L.; Liu, J. Talanta 2012, 99, 394–403. doi:10.1016/j.talanta.2012.05.070
12. Wang, X.; Sang, Y.; Wang, D.; Ji, S.; Liu, H. J. Alloys Compd. 2015, 639, 571–576. doi:10.1016/j.jallcom.2015.03.193
13. Kusior, A.; Koliktek, K.; Kowalski, K.; Borysiewicz, M.; Wojciechowski, T.; Adamczyk, A.; Trenczek-Zajac, M.; Radecka, M.; Zakrzewska, K. Appl. Surf. Sci. 2016, 380, 193–202. doi:10.1016/j.apsusc.2016.01.204
14. Miller, D. R.; Akbar, S. A.; Morris, P. A. Sens. Actuators, B 2014, 204, 250–272. doi:10.1016/j.snb.2014.07.074
15. Jin, C.; Park, S.; Kim, H.; Ko, T.; Lee, C.; Jeong, B.-Y. J. Korean Phys. Soc. 2012, 61, 1370–1375. doi:10.3938/jkps.61.1370
16. Vaezi, M. R.; Shendy, S. K.; Ebadzadeh, T. Indian J. Phys. 2012, 86, 9–13. doi:10.1007/s12648-012-0002-9
17. Zhou, H.; Li, Z.; Niu, X.; Xia, X.; Wei, Q. Ceram. Int. 2016, 42, 1817–1826. doi:10.1016/j.ceramint.2015.09.145
18. Bielański, A.; Haber, J. Catal. Rev.: Sci. Eng. 1979, 19, 1–41. doi:10.1080/03602459808650699
19. Barsan, N.; Weimar, U. J. Electroceram. 2001, 7, 143–167. doi:10.1023/A:1014405811371

121
20. Yamazoe, N.; Shimanoe, K. Sens. Actuators, B 2008, 128, 566–573. doi:10.1016/j.snb.2007.07.036
21. Michalow, K. A.; Ota, E. H.; Burnat, D.; Fortunato, G.; Emerich, H.; Ferri, D.; Heel, A.; Graule, T. Catal. Today 2012, 209, 47–53. doi:10.1016/j.cattod.2012.10.007
22. Radecka, M.; Rekas, M.; Kusior, E.; Zakrzewska, K.; Heel, A.; Michalow, K. A.; Graule, T. J. Nanosci. Nanotechnol. 2010, 10, 1032–1042. doi:10.1166/jnn.2010.1865
23. Strobel, R.; Baiker, A.; Pratsinis, S. E. Adv. Powder Technol. 2006, 17, 457–480. doi:10.1163/156855206778440525
24. Akuratì, K. K.; Vital, A.; Delleímann, J.-P.; Michalow, K.; Graule, T.; Ferri, D.; Baiker, A. Appl. Catal., B 2008, 79, 53–62. doi:10.1016/j.apcatb.2007.09.038
25. Michalow, K. A.; Vital, A.; Heel, A.; Graule, T.; Reffer, F. A.; Ritter, A.; Zakrzewska, K.; Rekas, M. J. Adv. Oxid. Technol. 2008, 11, 56–64. doi:10.1515/ajots-2008-0107
26. Lyson-Syplen, B.; Czapla, A.; Lubecka, M.; Gwizdó, P.; Schneider, K.; Zakrzewska, K.; Michalow, K.; Graule, T.; Reszka, A.; Rekas, M.; Lacz, A.; Radecka, M. Sens. Actuators, B 2012, 175, 163–172. doi:10.1016/j.snb.2012.02.051
27. Radecka, M.; Lyson, B.; Lubecka, M.; Czapla, A.; Zakrzewska, K. Acta Phys. Pol., A 2010, 117, 415–419. doi:10.12693/APhysPolA.117.415
28. Madelung, O., Ed. Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology; Springer: Berlin, Germany, 1983; Vol. 17, pp 133–149.
29. Herber, R. H. Phys. Rev. B 1983, 27, 4013–4017. doi:10.1103/PhysRevB.27.4013
30. Moreno, M. S.; Mercader, R. C. Phys. Rev. B 1994, 50, 9875–9881. doi:10.1103/PhysRevB.50.9875
31. Zakrzewska, K.; Radecka, M.; Przewoźnik, J.; Kowalski, K.; Czuba, P. Thin Solid Films 2005, 490, 101–107. doi:10.1016/j.tsf.2005.04.035
32. Frederikse, H. P. R. J. Appl. Phys. 1961, 32, 2211–2215. doi:10.1063/1.1777045
33. Ishiguro, K.; Sasaki, T.; Arai, T.; Imai, I. J. Phys. Soc. Jpn. 1958, 13, 296–304. doi:10.1143/JPSJ.13.296
34. Brunauer, S.; Emmett, P. H.; Teller, E. J. Am. Chem. Soc. 1938, 60, 309–319. doi:10.1021/ja01269a023
35. Haber, J.; Stone, F. S. Trans. Faraday Soc. 1963, 59, 192–206. doi:10.1039/tf635900192
36. Barsan, N.; Schweizer-Berberich, M.; Göpel, W. J. Anal. Chem. 1999, 365, 287–304. doi:10.1007/s002160051490
37. Kohl, D. Sens. Actuators, B 1989, 18, 71–113. doi:10.1016/0250-6874(89)80728-X

License and Terms

This is an Open Access article under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The license is subject to the Beilstein Journal of Nanotechnology terms and conditions: (http://www.beilstein-journals.org/bjnano)

The definitive version of this article is the electronic one which can be found at: doi:10.3762/bjnano.8.12