Influence of the Particle Size on the Surface Reactivity and Gas Sensing Properties of SnO₂ Nanopowders

Marie-Isabelle Baraton¹ and Lhadi Merhani²

¹SPCTS-CNRS, Faculty of Sciences, 123 Avenue Albert Thomas, F-87060 Limoges (France), baraton@unilim.fr
²CERAMEC R&D, 64 Avenue de la Libération, F-87000 Limoges (France)

The surface reactivity of a powder depends on the chemical composition of its surface and on the presence of defects. In the case of nanosized powders, the surface reactivity is enhanced by the increased defect concentration on the surface. On the other hand, the gas sensing properties of a semiconductor material are strongly related to the surface reactivity. In this article, it is shown, by Fourier transform infrared spectrometry, that SnO₂ semiconductor nanoparticles are very sensitive toward CO and that the decrease of the particle size greatly enhances this sensitivity. Comparison is made between particles having an average size of 15 and 8 nm. Surface reactions at the origin of the CO detection mechanism are discussed as a function of the particle size.

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1. Introduction

The general public awareness of environmental issues has led the decision-makers to define more drastic regulations for air quality monitoring and to set the thresholds of acceptable pollutant concentrations at very low values. As a result, the demand for reliable and low-cost gas sensors capable of detecting gas concentrations at sub-ppm levels has drastically increased. For combustible gases, chemical gas sensors based on semiconducting materials certainly meet the cost requirements. However, their sensitivity has to be improved for their use in air quality monitoring applications.

In previous works,¹,² it has been demonstrated that, compared to their micron-sized counterparts, the nanosized powders when used in the fabrication of chemical gas sensors by optimized screen-printing technology greatly increase the sensitivity of the devices. The sensitivity enhancement can be explained by the higher surface area exposed to the gases to be detected and by the possible formation of a space-charge region in the whole grain as the grain diameter becomes comparable to the Debye length.³ On the other hand, it is known that, for catalysts, the decrease of the particle size to the nanometer range leads to a higher surface reactivity thanks to a higher concentration of surface defects.

In order to investigate the consequences of a further decrease of the particle size, we have studied two tin oxide (SnO₂) powders with different average grain diameters in the nanometer range (15 and 8 nm). By Fourier transform infrared (FTIR) spectroscopy, we have compared the chemical species on the surface of the two kinds of tin oxide nanoparticles. Moreover, we have simultaneously investigated the variations of the electrical conductance of the nanomaterial. Indeed, when carbon monoxide (CO) is adsorbed at the material surface, the conductance variations generated by surface chemical reactions translate into variations of the infrared energy transmitted by the tin oxide sample. All the information obtained from the infrared spectra of the tin oxide nanopowders under various gaseous environments can therefore be correlated to the behavior of the real sensors.

2. Fundamental Principles

2.1 Chemical sensors

Semiconductor sensors detect gases via variations of their resistance (or conductance). Among semiconductor sensors, families have been identified depending on the form of energy at the origin of input signal.⁴ In chemical sensors based on semiconducting metal oxides, a chemical reaction occurs at the material surface between oxygen species and the gas to be detected, thus modifying the semiconductor resistance. Tin oxide (SnO₂) is certainly one of the most popular materials for the fabrication of chemical gas sensors and therefore has been extensively studied (see for example Ref. 5) and references therein). It is generally admitted that the variations of the SnO₂ resistance allowing the detection of combustible gases is caused by a reaction of the combustible gas with oxygen adsorbed as negatively charged species (ionsorbed species) on the tin oxide surface. The concentrations of the different types of ionsorbed oxygen species, such as O₂⁻, O⁻ and O²⁻, depend on the temperature. While the O⁻ species are the most reactive ones in the 300–500°C range,⁵,⁶ the O₂⁻ species become preponderant at lower temperatures (100–200°C). The oxygen ionsorption causes electron transfer from the surface of the grain toward the adsorbed species, thus leading to the formation of an electron-depleted surface layer (space-charge region). As a result, the resistance of a n-type semiconductor is increased due to the enhancement of the potential barrier at the grain boundaries.

When a combustible gas, such as carbon monoxide, is subsequently adsorbed, oxidation reactions proceed and the electrons trapped by the ionsorbed oxygen species return to tin oxide grains, thus decreasing the height of the potential bar-
rrier and the material resistance:

\[ \text{CO} + \text{O}_2^- \rightarrow \text{CO}_2 + \frac{1}{2} \text{O}_2 + e^- \]
\[ \text{CO} + \text{O}^- \rightarrow \text{CO}_2 + e^- \]
\[ \text{CO} + \text{O}^2- \rightarrow \text{CO}_2 + 2e^- \]

It is obvious that, when the grain size becomes comparable to the depth of the space-charge region, the electrical conduction is no longer controlled by the grain boundaries, but by the grain itself. For example, in the case of tin oxide, it has been demonstrated that the sensitivity of the sensors drastically increases when the particle diameter is decreased down to a critical value around 6 nm.\(^3\) Below this critical grain size, the sensitivity of the SnO\(_2\) sensors rapidly decreases. Because it has been calculated that the Debye length of SnO\(_2\) is \(D = 3\) nm at 250°C,\(^7\) it seems that the highest sensitivity of the sensor is reached when the SnO\(_2\) particle diameter corresponds to \(2D\).

From an electrical point of view, it is therefore clear that a decrease of the particle size down to \(2D\) should benefit to the sensor sensitivity. However, it must pointed out that, while the particle size reduction is an essential factor for a sensitivity increase, it is not sufficient as the grain size must be retained during the entire sensor fabrication process.

It is known that, when decreasing the size of a particle, the concentration of surface defects greatly increases leading to a higher surface reactivity of the nanoparticles compared to their micron-sized counterpart. Therefore, it can be expected that the oxidation reactions taking place at the surface of the semiconducting particles will be favored by a decrease of the particle size and, as a consequence, the resistance variations should be enhanced.

2.2 FTIR spectroscopy as a tool for electrical characterization

To simultaneously study the surface reactions and the resulting conductance variations of semiconducting nanoparticles, Fourier transform infrared (FTIR) spectroscopy appears to be a quite successful technique.\(^8\) The method for characterization of the surface chemical species and surface reactivity has been described earlier\(^9\) and the correlation between the variations of the transmitted infrared energy and those of the conductance has also been explained elsewhere.\(^8\) Only a reminder is given below.

Due to the high surface-to-bulk ratio of nanoparticles, the chemical species located at the very first layer of the nanoparticles contribute in a non-negligible way to the infrared absorption spectrum. Even though the interatomic vibrations of the bulk are very intense compared to those of the surface species, it is possible to discriminate vibrations originating from the bulk due to the surface species. Therefore, the chemical composition of these surface species can be determined. On the other hand, by controlled adsorption of appropriate probe-molecules, the reactive surface sites can be identified and their respective acido-basicity can be qualitatively evaluated. In addition, reactive adsorption or co-adsorption of selected molecules can be followed \textit{in situ} either versus time at any fixed temperature or versus temperature.

Independently from the interatomic vibrations, the free car-

riers of a semiconducting material also contribute to the ab-
sorption by the sample in the total infrared range.\(^10\) The sample absorption over the total infrared range can be estimated from the total infrared energy transmitted by the sample. Therefore, the variations of the transmitted infrared energy (\(E_{\text{IR}}\)) are directly related to the variations of the free carriers density and to the variations of the conductance.

As a consequence, it can be easily understood that FTIR spectroscopy allows the simultaneous chemical and electrical analysis of a semiconducting nanopowder. Indeed, when a gas is adsorbed on the semiconducting sample, surface chemical reactions can be studied while the induced variations of the transmitted infrared energy are measured. A direct correlation is therefore obtained between the chemical reactions occurring at the surface and the resulting variations of the sample conductance.

3. Experimental

3.1 Apparatus and materials

Such FTIR analyses require a specific setup attached to the spectrometer. It consists in a vacuum cell specially designed to fit into the sample compartment of the spectrometer. Inside the cell, a small furnace allows heat-treatment of the sample from room temperature up to 500°C. The cell is connected to vacuum pumps via a nitrogen trap and to gas cylinders through a precision valve system. Details on the equipment can be found in.\(^9\)

For the FTIR analyses, 30 mg of tin oxide nanopowder \((n-\text{SnO}_2)\) are slightly pressed on a stainless grid (Gantois, St Dié, France). Besides allowing a mechanically stable thin pellet to be obtained, this grid ensures a homogeneous thermal distribution in the tin oxide pellet. The pressure to which \(n-\text{SnO}_2\) is submitted during the sample preparation is adjusted at its minimum possible value in order to avoid any variations in the crystalline phase and/or the stoichiometry.\(^11\)

The tin oxide nanosized powders were synthesized at the Technische Universität Clausthal (Germany) by evaporation of compressed micro-crystalline powder with the pulse radiation of a Nd:YAG-laser and subsequent condensation of the vapor in a controlled atmosphere.\(^11\) The two batches used for the present experiments have an average particle diameter of 15 and 8 nm. The XRD analyses show that both nanopowders are crystallized under the quadratic phase. Oxygen (99.999% pure) and carbon monoxide (99.9% pure) have been provided by Air Products Corp.

The Fourier transform infrared spectrometer (Perkin-Elmer, Spectrum 2000) is equipped with a MCT cryodetector. All the spectra are recorded \textit{in situ} in the 7800–450 cm\(^{-1}\) range with a 4 cm\(^{-1}\) resolution. To optimize the signal-to-noise ratio, 128 scans have been accumulated for each spectrum. Under those conditions, it takes about 2 minutes to record a spectrum.

3.2 Procedure

The thermal treatment, referred to as activation, usually performed before surface characterization consists in heating the sample under dynamic vacuum.\(^9\) This activation is necessary to remove all impurities physisorbed or weakly chemisorbed on the surface, thus activating the surface sites. But, such a thermal treatment under vacuum is a reducing
treatment and, as a consequence, is not suitable for semiconducting materials. Therefore, in the case of tin oxide, we modified the activation procedure to avoid oxygen desorption and we conducted the experiments the following way. The pellet of pressed SnO₂ nanopowder was placed inside the furnace of the vacuum cell and evacuated at room temperature (1 Pa). Five kPa of oxygen were then introduced in the cell and the SnO₂ pellet was heated at 400°C for one hour. This heat-treatment under O₂ actually corresponds to the pretreatment undergone by the real sensors before operation. To eliminate all the gaseous impurities which could have possibly desorbed from the SnO₂ sample during the heat-treatment (e.g. humidity and other surface contaminants), the cell was quickly evacuated at 400°C and a new dose (5 kPa) of fresh oxygen was introduced. The sample was then cooled at room temperature under O₂.

The pre-treated SnO₂ pellet is then used to simulate the gas sensors. For the real sensors prepared from 15 and 8 nm SnO₂ particles, it has been determined that two sensitivity maxima for CO detection occur around 120 and 350°C and therefore, these two temperatures have been taken into account in our gas sensing experiments. After the pre-treatment, the SnO₂ pellet was heated again at the temperature chosen for the gas sensing experiments (120°C or 350°C). At the selected temperature, oxygen was quickly evacuated and replaced with a dose of CO (1 kPa). After a 10-minute contact, CO was evacuated before the addition of a new dose of CO₂ thus starting a new measurement cycle. These CO doses (1 kPa) can be also added in presence of O₂ (5 kPa) to simulate the working conditions of the real sensors in air. In this latter case, oxygen was introduced for 10 (or 20) minutes followed by the addition of CO for 10 minutes before quick evacuation of the cell. At each step of the experiments, both the infrared spectrum and the infrared energy transmitted by the sample were recorded.

4. Surface Analysis

The infrared spectra of the two SnO₂ nanopowders pre-treated at 400°C and recorded at room temperature are presented in Fig. 1. Differences between the two spectra can immediately be noted in the highest wavenumber range.

The absorption bands in the 3800–2500 cm⁻¹ wavenumber range are assigned to \( \nu(\text{OH}) \) stretching vibrations of surface hydroxyls groups. These OH groups originate from the hydrolysis of the nanoparticles surface which takes place as soon as the nanoparticles are in contact with atmosphere, outside the synthesis chamber. As a general rule, the \( \nu(\text{OH}) \) absorption frequency depends on the nature of the atom to which the OH group is bonded and on the coordination of this atom within the surface. Therefore, in the case of SnO₂, the multiplicity of the \( \nu(\text{OH}) \) bands indicates that, on the surface, tin atoms are present in different coordination states. The broad band centered around 3100 cm⁻¹ on both spectra is assigned to the \( \nu(\text{OH}) \) vibration of OH groups associated with either adjacent OH groups or with water molecules (hydrogen bond) not totally eliminated by the pretreatment. This broad band also includes the \( \nu(\text{OH}) \) stretching vibrations of these water molecules possibly adsorbed.

The difference between the 3750–3400 cm⁻¹ regions of both spectra is emphasized in Fig. 2. Well-defined bands clearly appear in the 15 nm-SnO₂ spectrum whereas, in the spectrum of the 8 nm-SnO₂ powder, the bands are poorly resolved. Even though this poor resolution can be partly due to the large intensity of the broad band centered at 3100 cm⁻¹ and partly overlapping the 3750–3400 cm⁻¹ region, a larger bandwidth can be easily observed in the 8 nm-SnO₂ spectrum for all bands in this particular region. However, all these bands present in the 15 nm-SnO₂ spectrum can also be seen in the 8 nm-SnO₂ spectrum in a more or less evident manner. No additional bands which could have revealed different species are observed.

It is known that the decrease of the particle size leads to the increase of the defect concentration on the particle surface.¹³
This increase may have consequences on the electronic distribution in the surface tin atoms to which the OH groups are bonded, thus modifying the force constants of these O–H bonds. In the present case, we observe that the decrease of the SnO₂ particle size from 15 to 8 nm generates the broadening of the ν(OH) bands. This can be explained by a broader distribution of the force constants of the different OH bonds around the average value due to a larger and random distribution of the surface defects around the surface tin atoms.

The presence of a higher concentration of surface defects indicated by the ν(OH) band broadening should lead to a higher surface reactivity of the 8 nm-SnO₂ powder compared to that of the 15 nm-SnO₂ powder. As a consequence the sensitivity of the 8 nm-SnO₂ powder should be higher.

In the 1500–800 cm⁻¹ region (Fig. 3), the absorption bands have been assigned to the δ(OH) bending vibrations of the surface hydroxyl groups and/or to the vibrations of adsorbed oxygen species.\(^{14,15}\) Two bands are specific of each spectrum: the 1061 cm⁻¹ band which appears only in the 15 nm-SnO₂ powder spectrum and the 1182 cm⁻¹ band only appearing in the 8 nm-SnO₂ powder spectrum. Because the ν(OH) frequencies are identical for both powders, the δ(OH) frequencies should not be different. We can therefore conclude that these two bands are most probably due to adsorbed oxygen species. According to the literature,\(^{16,17}\) a band at 1190 cm⁻¹ would be assigned to O²⁻ species adsorbed on Sn⁴⁺ sites whereas a band at 1045 cm⁻¹ would rather be assigned to O²⁻ species adsorbed on Sn²⁺ sites. On the other hand and still according to the literature,\(^{16}\) intermediate values of the absorption frequencies might indicate the presence of defects. It is worth noting that the assignments of these bands to ionsorbed oxygen species are rather difficult due to the fact that the \(^{16}O/\(^{18}O\) isotopic exchange has not yet given any clear result. In the present case, the two different absorption frequencies (1182 and 1061 cm⁻¹) for the vibrations of ionsorbed oxygen suggest that the distribution of the cations and of the defect sites would not be the same on the 8 nm-SnO₂ powder surface as on the 15 nm-SnO₂ powder surface.

5. Sensing Properties

We compared the sensing properties of the two SnO₂ nanopowders toward CO at 120 and 350°C according to the procedure described in Section 3.2.

After the pre-treatment under oxygen at 400°C, the 15 nm-SnO₂ nanopowder was subjected to three subsequent CO doses in absence of O₂, followed by four subsequent doses of CO in presence of O₂ at 120 and 350°C. The variations of the infrared (IR) energy transmitted by the sample (E₀) versus gas exposures are reported in Fig. 4. As mentioned in Section 3.1, a decrease of the transmitted infrared energy is due to an increase of the absorption by the free carriers originating from the increase of the free carrier density, that is from an increase of the electrical conductance. Therefore, by analogy with the real sensor, the E₀ variations are referred to as the nanopowder response.

In Figure 4, it can be easily seen that, whatever the temperature, the addition of the first CO dose causes a strong E₀ decrease, thus indicating an increase of the conductance, which is in agreement with the response of the real sensor. However, the sample does not recover its original transparency after CO evacuation, meaning that the original oxidation state of the SnO₂ particles is not restored. The addition of the second and third CO doses at 350°C, still in absence of O₂, does not lead to further reduction, showing that the SnO₂ particles are already totally reduced by the first CO dose. At 120°C, a very weak decrease of the conductance can still be noted. The addition of 5 kPa of O₂ for 20 minutes completely restores the SnO₂ oxidation state at 350°C, while it leads to a very limited oxidation state recovery at 120°C. This can be explained by a higher oxygen diffusion rate at 350°C than at 120°C inside the lattice. When CO is added in presence of O₂, a reproducible response is observed whatever the temperature and the oxidation state of SnO₂ is restored after each oxygen addition. This is the proof that an oxidizing environment is necessary for normal operation of the sensor.

In parallel, the infrared spectra recorded at the different stages of the experiments show strong modifications of their baseline. These baseline modifications caused by variations of the background infrared absorption are due to changes in the free carriers density (that is, changes in the conductance). When the baseline modifications are not too strong, it is possible to perform the difference between two spectra recorded at two different stages of the experiment in order to highlight the surface chemical species which can be perturbed, created or eliminated during the considered experimental step. So, we performed the difference spectra corresponding to the evacuation steps (that is, the spectrum recorded just after evacuation minus the spectrum recorded just before evacuation) because, during this experimental step, the SnO₂ oxidation state is not strongly affected by quick cell evacuation and the modification of the spectrum baseline is not very important. These difference spectra actually give information on the species which are eliminated (negative bands), created or restored (positive bands) during evacuation. Apart from the negative bands centered at 2143 cm⁻¹ due to the elimination of gaseous CO, the

![Fig. 3 δ(OH) absorption range in the IR spectra of the pre-treated SnO₂ powders: a) 15 nm; b) 8 nm.](image-url)
only surface modification which can be observed at 120°C is the perturbation of the OH groups as indicated by the positive bands at 1250 and 965 cm$^{-1}$ (Figs. 5(a), (b)). But at 350°C in absence of O$_2$, a small amount of CO$_2$ is detected (negative band centered at 2340 cm$^{-1}$) proving that oxygen species are available at the surface of the SnO$_2$ particles for the CO oxidation (Fig. 6(a)). When CO is added at 350°C in presence of O$_2$, a larger amount of CO$_2$ is instantaneously formed (Fig. 6(b)) in addition to carbonate groups totally reversible by evacuation (negative bands at 1426 and 1372 cm$^{-1}$). Moreover, the OH groups are perturbed. At 120°C neither CO$_2$ nor carbonate groups can be identified. However, a weak response of the SnO$_2$ nanopowder toward CO is noted. This has been confirmed by the electrical measurements performed on the real sensors.$^{1,2}$

The same series of experiments were performed on the 8 nm-SnO$_2$ powder. The $E_{IR}$ variations are given in Fig. 7 at 120 and 350°C versus gas exposures. Unlike the case of the 15 nm-SnO$_2$ powder, a small amount of CO$_2$ is formed at 120°C in absence or in presence of O$_2$ (Fig. 8). This means that the oxidation of CO can take place at a lower temperature on the surface of these small particles. Carbonates are formed only at 350°C and in presence of oxygen (Fig. 9(b)). We also note that the recovery of the SnO$_2$ oxidation state at 120°C is faster on 8 nm-SnO$_2$ powder than on 15 nm-SnO$_2$ powder (Figs. 4 and 7). Like in the case of the 15 nm-SnO$_2$ powder and whatever the temperature, the response toward the first CO dose in absence of O$_2$ is very intense compared to that toward the second and third CO doses (Fig. 7). The perturbation of the OH groups is noted in all cases (Figs. 8
and 9), except at 350°C in absence of oxygen. All these results have been confirmed by similar studies on different tin oxide batches having the same average particle size (15 and 8 nm).

The oxidation of CO into CO2 on the 8 nm-SnO2 powder at a relatively low temperature can be related to the higher concentration of surface defects, thus leading to a higher surface reactivity. As a result, a higher response of 8 nm-SnO2 powder toward CO at 120°C is observed, which is in agreement with the electrical measurements performed on real sensors made of 8-nm and 15-nm SnO2 nanopowders. In addition, the faster recovery of the 8 nm-SnO2 powder oxidation state at 120°C is obviously due to the smaller particle size allowing a deeper oxygen diffusion in the core of the particle even at this low temperature.

On the infrared spectra, a perturbation of the surface OH groups is noted, particularly visible on the difference spectra (see for example Figs. 5, 6 and 8). As mentioned in the literature, this perturbation may play a role in the sensor response since it is the only effect observed on the 15 nm-SnO2 powder at 120°C. Obviously, the perturbation of the ν(OH) vibrational frequencies translates into a perturbation of the electronic distribution in the surface OH bonds, which may have consequences on the free carrier density at the surface and, thus, on the thickness of the depletion layer. Further experiments are needed to totally explain the role of the OH groups in the gas detection mechanism. It is worth mentioning that the involvement of the OH groups in the sensor response may be a key point in the understanding of the humidity effects.
6. Conclusions

By FTIR spectrometry, we have demonstrated that the surfaces of the 15 and 8 nm SnO₂ particles are not identical, thus proving that the decrease of the particle size can change the surface properties.

FTIR spectrometry is also proved to be an extremely valuable tool to investigate the sensing properties of nanosized powders and to correlate the gas detection mechanism with the chemical reactions occurring on the very surface of the semiconductor particles. In agreement with the electrical measurements performed on the real sensors, the 8-nm diameter SnO₂ powder appears to be the most sensitive material at temperatures in the 100°C range. It can therefore be concluded that the decrease of the particle size leading to a higher surface reactivity is fundamentally beneficial to the sensitivity of gas sensors.

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