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(Ti, Sn) SOLID SOLUTIONS AS FUNCTIONAL MATERIALS FOR GAS SENSING

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Abstract

Metal-oxide semiconductors are widely used as functional materials for gas sensing because of their chemoresistive effect when interacting with ambient gases. For this work, nanosized $\text{Ti}_x\text{Sn}_{1-x}\text{O}_2$ have been synthesised at increasing Ti molar ratio ($x = 0, 0.1, 0.2, 0.25, 0.3, 0.5, 0.7, 0.8, 0.9, 0.95, 1$) and extensively investigated through a wide variety of characterizations. It turned out that the merging process of the two single oxides formed new compounds with improved gas responses compared to pure TiO_2 and also to pure SnO_2 . Moreover, all investigated physico-chemical characteristics resulted tuneable through the titanium content in the solid solution. Each characterization carried out onto $\text{Ti}_x\text{Sn}_{1-x}\text{O}_2$ solid solutions made it possible to identify two classes of materials with SnO_2 -like or TiO_2 -like behaviours, the best CO response being on the intersection of the two species of materials. Moreover, a very interesting analysis on the generally accepted electrical transport model through polycrystalline semiconductors has been carried out. Indeed, the comparison with experimental evidences has highlighted a conduction mechanism not previously considered.

1. INTRODUCTION

Wide-gap semiconductor oxides have been extensively investigated because of their wide range of technological applications, such as heterogeneous catalysis, photocatalysis, piezoelectricity, optoelectronics, photovoltaic conversion and gas sensing [1-5]. Moreover, the recent emphasis given to synthesis and engineering of structures with dimensions at nanometric scale have opened the way to novel electrical, mechanical, chemical and optical properties [6-8]. On the other hand, to work on structures at nanometric scale is interesting in order to study the unique physical properties that come from size reduction up to these dimensions [9,10].

The interest to the wide-gap semiconductor oxides in gas sensing began after Seyama et al. [11] evidenced their property of modifying electrical behaviour when interacting with ambient gases. Starting with this peculiar mechanism, a lot of features determine the sensor performances, but certainly the grain size reduction at nanometric level is one of the main factors enhancing their detection properties [12-14], both for large specific surface offered and for the influence in reducing the surface charge density. Indeed, when the particle dimensions scale down below a critical value, the phenomenon of the unpinning of Fermi level occurs, thus improving the sensing performance of these materials [15].

Apart from the grain size reduction, a lot of other complex factors affect the gas sensor performance which, in turn, is determined by the reception and transduction function along with the fabrication procedure (thin or thick film, porosity, particle agglomeration, etc.) [16]. The selection of the functional material, the synthesis procedure, crystal size and shape, the addition of foreign elements with the role of sensitizers or conductivity modifiers are some of the factors influencing the sensor response.

Understanding the mechanisms through which the sensor response is modified by each of these factors makes the semiconductor oxide suitable to be prepared with tuneable physical-chemical characteristics, thus enabling the fabrication of sensor devices with specific functionality.

This work aims to clarify some of these aspects. For this purpose, the functional materials have been analyzed by means of a wide variety of characterizations: structural and morphological (Thermo-gravimetric analyses (TG-DTA), transmission and scanning electron microscopy (TEM and SEM) and X-ray diffraction), electrical (surface barrier potential behaviour and gas sensing properties) and finally physical-chemical ones to investigate the electronic properties (diffuse reflectance UV-Vis-NIR and absorbance FT-IR spectroscopies). Indeed, particular interest for the microscopic understanding of the gas sensing mechanisms is devoted to identify the defect types

and the surface reactions that induce changes in the conductivity under different atmospheres. IR and UV-Vis spectroscopies are potentially the most suitable techniques for this task.

A large class of semiconductor materials based on metal oxides like SnO₂, TiO₂, ZnO, In₂O₃, WO₃ and MoO₃ are used in the fabrication of solid state devices for gas sensing. Moreover, mixed metal oxides and solid solutions have been considered for the superior performances shown in comparison to the single oxides [17-21]. The system Ti_xSn_{1-x}O₂ is particularly attractive because the two single oxides, tin dioxide and titanium dioxide, show several similarities in structural as well as in electronic properties. Indeed, both SnO₂ and TiO₂ exhibit tetragonal crystal symmetry with the space group P4₂/mm and two molecular units per primitive unit cell, with similarities also in the electronic structure [22]. Due to these properties, they can easily form a solid solution. Moreover, they are wide-gap *n*-type semiconductors due to stoichiometric defects, mainly oxygen vacancies acting as electronic donor levels, although with energy positions more deep inside the band gap for TiO₂. In spite of similarity in their structural and electronic properties, they exhibit some peculiar differences, such as electrical transport properties and gas sensing behaviour.

Due to its inherent characteristics, the TiO₂-SnO₂ system has been widely investigated with the aim to determine the crystallographic properties, the phase diagram and to study the spinodal decomposition [23-26]. Conventionally, the solid solution Ti_xSn_{1-x}O₂ is obtained from SnO₂ and TiO₂ via solid-state reaction, calcined at temperatures up to 1600 °C, or high energy ball milling [27,28]. Recently, with the aim to use the TiO₂-SnO₂ as photocatalyst or as functional material in gas sensing, synthesis methods suitable to produce the functional material at nanometric scale (e.g. co-precipitation, molten salt method, sol-gel or thin film) have been adopted [29-33].

In this work the Ti_xSn_{1-x}O₂ system has been studied both from a fundamental point of view and as functional material for gas sensing. The basic idea has been to synthesise several materials, through sol-gel route via cross-condensation, at increasing Ti molar ratio for understanding how the material properties would be modulated. From this perspective, a fundamental property in gas sensing is the grain dimension, in this system widely tunable by varying the stoichiometry ($0 \leq x \leq 1$) of the synthesised powders. This particular feature and some others have been already analyzed in two previous papers [34, 35]. However, further characterization, presented in the present work has pointed out possible correlations between electrical and spectroscopical measurements, through the proposed interpretation.

2. EXPERIMENTAL

2.1 Powder preparation and analysis

SnO₂, TiO₂ and Ti_xSn_{1-x}O₂ (0.1 ≤ x ≤ 0.95) powders were synthesised via sol-gel route under atmospheric conditions from reagent-grade starting materials and solvents, used as received.

SnO₂ synthesis - Pure tin oxide powders were prepared according to procedure described in [36]: to a *n*-butanol solution 0.7 M of Sn(II)2-ethylexanoate a given amount of deionized water was added drop-wise and the mixture was stirred at room temperature during 3 h. The molar ratio of water to Sn was 4 and the pH of the solution was adjusted to be 1 with HNO₃. The resulting gel was dried overnight at 95°C and subsequently calcined at 550°C for 2 h.

TiO₂ synthesis - Ti(IV) *n*-butoxide (Aldrich, 97%) was dissolved in absolute ethanol (0,23 M) and added drop by drop to a solution of ethanol/water 1:1 vol under rapid stirring. After stirring, the suspension was filtered to obtain a white precipitate which was dried in air (100°C) for 16 h. Finally, the powders were calcined at 450°C in air for 2 hours [37].

Ti_xSn_{1-x}O₂ synthesis - Required stoichiometric proportions of Sn(II)2-ethylexanoate (Aldrich, ~95%) and Ti(IV) *n*-butoxide (Aldrich, 97%) have been dissolved in a hydroalcoholic solution while stirring and maintaining the reaction environment at T = 50°C. The total cation-concentration have been kept rigorously at [Mⁿ⁺]_{tot} = 0.1 M for each preparation. Diluted HNO₃ (pH~1) was slowly added to the Ti⁴⁺/Sn⁴⁺ solution to slightly modify the hydrolysis rate of Sn-OR bonds with the aim to achieve the simultaneous formation of Ti-OH and Sn-OH inorganic functions and their further “one-pot” cross-condensation. The resulting colloids were separated from mother-waters by filtration, washed with diethyl ether and dried in air at 100°C for 15 hours. The resulting white powders were calcined at 550 °C for 2 h to achieve the final oxides. The yield of synthetic process for Ti_xSn_{1-x}O₂ is in the range of 95-98% for each stoichiometry of interest.

In order to study the structural and the morphological evolution of the nanopowders with temperature, each precursor was further calcined at 650, 850 or 1050 °C for 2 h.

Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) (Netzsch STA 409) using alumina crucibles under air flow conditions were performed on dried powders to study the thermal decomposition of the precursors. Thermal behaviour of the xerogels were explored with the heating rate of 20 °C/min up to a temperature of 800°C.

X-Ray Diffraction (XRD) analyses were performed using a Philips PW 1830 vertical diffractometer with Bragg-Brentano geometry (Cu K α radiation, 40 kV, 30 mA) provided with a graphite monochromator along the diffracted beam. Diffraction patterns were collected over the range 10–120° (2 θ) with steps of 0.02° and 10 s of dwell time. The unit cell parameters were estimated through the program for Rietveld analysis (structure profile refinement) FullProf (release

2011) [38], while the crystallite size was estimated, according to Debye-Scherrer formula, $L = k\lambda/(\beta \cos\theta)$, where λ is the wavelength of the X-ray radiation, k is a constant taken as 0,89, β is full width at half maximum height and θ is the diffraction angle.

The microstructure of the powders was observed by transmission electron microscopy (TEM, model H-800, Hitachi, at an accelerating voltage of 200 kV). Selected area diffraction pattern (SADP) measurements were also performed during TEM analysis.

Diffuse reflectance UV-Vis spectra were run at RT on a Varian Cary 5 spectrophotometer. For the analysis, the powders calcined at 550 °C were placed in a quartz cell, allowing thermal treatments in controlled atmospheres up to 800 °C. Spectra were run at RT after treatment at 550 °C in vacuum and in dry oxygen and after treatment in CO at increasing temperatures up to 500 °C. Spectra are reported with the Kubelka-Munk function [$f(R_\infty) = (1-R_\infty)^2/2 R_\infty$, where R_∞ = the reflectance of an 'infinitely thick' layer of the sample] [39] in the ordinate scale.

2.2 Film deposition and characterization

The sensing films, composed of the functional materials, whose synthesis methods have been above described, were deposited through screen printing technique onto miniaturized alumina substrates, each one provided with a heater element and interdigitated contacts. This technology has been adapted for the fabrication of sensing layers composed of nanosized particles. Indeed, a correct material preparation is a crucial point and many factors have been considered, including grain shape and size, size distribution, intragranular porosity, and surface conditions. In this frame, one of the main advantages of using this technology for production of sensing layers is the actual separation of the processes to obtain the functional material and the film deposition, thereby reaching the optimization of the two processes independently of one another. The thick-films are prepared from pastes obtained by adding to the functional material an organic vehicle, consisting of a mixture of rheological agents in volatile solvents to ensure the correct viscosity for screen-printing, and a small amount of a bonding agent, a glass frit or an oxide, which promotes the film adhesion to the substrate. The thickness of the deposited layers vary from a few to ~20 μm , depending on certain parameters, such as size of the particles in the functional phase, paste viscosity and other parameters, typical of the screen-printing technique. The last steps include the drying thermal processes (150-200 °C) to remove the organic media, and firing (650-950 °C) in controlled atmosphere, in which the residual organic vehicle burns and the resultant inorganic films, through physical and chemical transformations, achieve the desired electrical and micro-structural

properties. Further details on the fabrication process can be found in [40]. The morphology of the films was observed using scanning electron microscopy (SEM, model EVO 40, Carl Zeiss).

For electrical characterizations the sensors were placed in a sealed test chamber maintained at a fixed ambient temperature of 25 °C. Indeed, as described in a previous work [41], the ambient temperature is directly influencing the sensor behaviour, even if the working temperature of the sensor is kept almost constant.

The flow-through technique was used to test the electrical properties of the sensing layers. The measurement of conductance was carried out maintaining a flow rate of 0.5 l/min using synthetic air as carrier gas in dry or wet (RH = 40%) conditions. Dynamical responses of sensing films were obtained in presence of mixture of different gases by varying the operating temperature from 350 to 650 °C. The sensor response is defined as ratio between the conductance in presence of the target gas and the conductance in air.

The direct determination of the height of the surface potential barrier at a fixed temperature is carried out using the method of temperature-stimulated conductance measurements, firstly described by Clifford and Tuma [42], according to which the conductance is measured as a function of time, after a change of temperature so fast that it is possible to assume the constancy of the barrier while the conductance changes due to the variation of free carriers. Afterwards, conductance measurements were performed by changing the temperature between 300 and 900K at the heating rate of 3 K/min. Now, through Morrison's equation [43], which factorizes the surface and bulk contributions, the heights of the potential barrier as a function of temperature can be calculated from the measured conductance values.

All the electrical characterizations here shown have been performed onto sensing films fired at 650 °C and named with the abbreviation ST followed by the percentage of titanium in the solid solution. Moreover, for the sake of simplicity, all measurements here reported were carried out in dry air to avoid interference with water vapour.

3. RESULTS

3.1 Powder analysis

3.1.1 Thermal characterization

In Fig 1 the comparison of the DSC curves of all the analyzed materials is reported. The first step of the decomposition of the dried precursors consists of an endothermic peak occurring between 80 and 140 °C corresponding to the loss of surface adsorbed water in the dried powders. The decomposition proceeds with a first sharp exothermic event which peak can be observed at temperatures ranging from 120 to 180°C assignable to the decomposition of nitrates [44]. Indeed, the phenomenon has been observed in all samples, except than in pure TiO₂, according to the addition of diluted HNO₃ in the synthetic process in the preparation of all samples except pure titania. The process carries on with two other exothermic events occurred at variable temperatures, dependent on Ti molar ratio and ranging from 280 to 315°C for the first peak and from 345 to 400°C for the second one. The first can be assigned to the combustion process of some organic compounds residue of the synthesis process, while the second to a decomposition of the xerogel (expressible as (Ti_xSn_{1-x})(OH)₄ → (Ti_xSn_{1-x})O₂ + 2 H₂O) and a simultaneous crystallization. For x = 0.5 the two peaks merge together indicating that the crystallization process is the most hindered with respect to the other compositions, as confirmed by X-Ray diffraction analysis.

3.1.2 Micro-structural characterization

For establishing the crystalline phase evolution of the powders with temperature, X-ray diffraction at room temperature was carried out. The calcined materials exhibited a single-phase rutile-like (space group *P 4₂/mnm*) for all Ti/Sn molar ratios, as already reported in [35], except for x = 1 (pure titania), which instead exhibited anatase structure, space group *I 4₁/amd*. It is well known that, heating TiO₂ powders, when non added with foreign ions able to inhibit the crystalline phase transformation from anatase to rutile (the most stable polymorph), such transition, in case of sol gel preparation, occurs between 650 to 850 °C [37]. On the other hand, it must be highlighted that a minimum content of tin (5%) was sufficient to manifest rutile phase, independently from the calcination temperature.

To verify that the Ti_xSn_{1-x}O₂ powders were synthesised with the declared stoichiometry, the XRD Bragg's reflection of the (110) and (101) planes of the materials calcined at 1050°C were taken into consideration. In fact, at this temperature no phase transformations occur and all samples exhibit a proper stage of crystallization. In Fig. 2 it can be observed the increasing of 2θ angle in 101 diffraction peak by increasing the Ti content in Ti_xSn_{1-x}O₂, thus establishing that each synthesised material shows sufficient agreement with the declared stoichiometry. Moreover, it is also evident that the full width at half maximum of the peaks broads in the halfway compounds because of a decreasing of crystallinity related with an increasing of structural defects. Indeed, the

solid solutions are metastable because the samples have been heated at temperatures within the miscibility gap, which suggests the occurrence of phase separation in form of spinodal decomposition of the solid solution in tin-rich and titanium-rich oxide phases. In fact, in the powder with $x = 0.7$, when calcined at 850 or 1050 °C, the phenomenon appears. Specific results have been previously reported in [45] and are in agreement with the literature on the subject [24,25].

Table 1 lists the cell parameters estimated using the Rietveld method: a and c , volume, Bragg R factor, grain size, x coordinate of oxygen atoms, along with Me–O apical and basal bond distance for samples heated at 1050°C. Figs. 3A and 3B show a comparison between the estimated values of the a and c cell parameters and those reported by Yuan and Virkar in [24]. The agreement is on the whole good; however, while the a parameter fits quite good, the c parameter exhibits a slight deviation around the Ti molar ratio of $x = 0.5$. Once again, it must be taken into account that the halfway compounds suffer of shortage of crystallinity due to an increase of structural defects .

TEM observations performed on the powders showed morphologies consisting in nanoparticles for all samples calcined at 550°C. As an example, in Fig. 4 a TEM micrograph of the powder with $x = 0.3$ with the corresponding SADP of the precursor heated to 550 °C is shown. The powder was made of agglomerated nanoparticles whose size, at the magnification of the micrograph is not measurable, but, evaluated through XRD analysis using Scherrer's equation, was estimated 4.4 nm. The crystallite size of the other powders resulted 7.8 nm for $x = 0.1$ and 11.7 nm for $x = 0.9$, whereas it decreases in the halfway compounds down to 4.4 nm for $x = 0.3$ and $x = 0.5$. SADP analysis confirmed the presence of very fine polycrystalline materials in all rutile structures. Pure titania is the only one to exhibit anatase phase.

3.1.3 UV-Vis spectroscopic characterization

In Fig. 5, a comparison between diffuse reflectance UV-Vis spectra of SnO₂ (section A) and TiO₂ (section B) after treatment in O₂ at 550 °C (curves a) and after treatment in CO at 400 °C (curves b) is reported. For SnO₂, the switching from oxygen to CO causes changes in the shape of the VB-CB absorption edge, in particular a broadening of the absorption edge is observed. This broadening is ascribable to a stoichiometry seriously perturbed by oxygen loss, that causes the formation of a defect state distribution near the bottom of the conduction band. Actually, photoemission studies on SnO₂ low index surfaces, prepared by vacuum procedures, show the presence of defect states above the valence band maximum associated with Sn²⁺ ions [46,47]. Moreover, electronic structure calculations performed for reduced (110) surfaces predict the presence of defect states (associated with Sn²⁺ ions) at the bottom of the band gap, for low density of oxygen vacancies, and a broad

distribution of defect states filling the entire band gap, when all the bridging oxygen at the surface are removed [48-50]. For TiO_2 , the changes induced by the switching from oxygen to CO are negligible: in particular, no changes of the absorption edge related to the band gap are observed. Only a very weak and broad absorption on the low wavenumber side is formed. This absorption is related to the presence of Ti^{3+} ions and assigned to a metal-metal charge transfer transition between Ti^{3+} and Ti^{4+} ions, also known as polaronic transition.

For all the mixed $\text{Ti}_x\text{Sn}_{1-x}\text{O}_2$ oxides, the switching from oxygen to CO causes a lowering of the energy at which the systems start to absorb radiation (Fig. 6). On one hand, for the powders with $x = 0.1, 0.2$ and 0.3 (Fig. 6 sections A, B and C, respectively) this effect is related to a broadening of the band-gap absorption and, so, to the presence of a broad distribution of defect states in the band gap, as observed for SnO_2 . On the other hand, for the systems with $x = 0.5, 0.7$ and 0.9 (Fig. 6 sections D, E and F, respectively) the broadening of the band-gap absorption is not observed, but treatment in CO causes the increase of an absorption near to the VB-CB edge, at about 21000 cm^{-1} (2.6 eV). Furthermore, for system with $x = 0.9$, differently from the other mixed oxides, the absorption related to the presence of Ti^{3+} ions appears at wavenumbers lower than 14000 cm^{-1} , as observed for TiO_2 .

The assignment of the absorption at 21000 cm^{-1} (2.6 eV) observed for systems with $x = 0.5, 0.7$ and 0.9 is not straightforward. Actually, it could be assigned to an electronic transition from the valence band to empty states present in the band gap, just about 2.6 eV above the valence band maximum. Alternatively, it could be assigned to electronic transition from deep levels (just about 2.6 eV under the conduction band) to the conduction band. As a matter of fact, the results of the electrical characterization performed on the films and reported in the following allow to assign this absorption to transitions from deep levels. Nevertheless, this absorption shows an increase in its intensity increasing the Ti content reaching its maximum for ST-90 and disappears in TiO_2 . Thus, it is reasonable related to the presence of tin, but in situation of high dilution in TiO_2 .

3.2 Film characterization

3.2.1 Morphology

For all materials the morphology consists in nanoparticles with moderate grain coalescence, as the content of titanium in the solid solution increases. The main feature consists in a different morphology offered by the materials with $x \leq 0.25$ for which the nano-particles arrange around a core to form spherical agglomerates. Figs. 7 shows this behaviour for ST10, SnO_2 , ST20 and ST25

showing a similar morphology. The other materials ($x \geq 0.3$) lose the spherical shape of the agglomerates as the Fig. 8 shows for ST70 sensing layer, representative of the other samples.

3.2.2 Electrical characterization

Two types of electrical characterizations have been performed: i) dynamic responses of sensing films obtained in presence of mixture of different gases; ii) conductance and intergranular energy barrier measurements as a function of temperature, in presence of different atmospheres. The first type of measurement obviously aims to determine the sensor performance, i.e. response to specific gases, stability in time, selectivity, influence of humidity, etc..

The second one is more suitable to understand the mechanism of conduction, which is generally accepted that in metal oxides is controlled by electron flow through a huge series of surface barriers that develop at intergranular point contacts, due to the presence of charged surface states. Whereas, the basis of sensing mechanism consists in a variation of the intergranular barrier with subsequent change of conductance as an effect of the chemical reactions occurring at the surface of the oxide in contact with the different atmospheres.

In a previous work [35] it was shown that the $Ti_xSn_{1-x}O_2$ sensing films split into two broad behaviour tendencies: pure SnO_2 and a few solid solutions with a low x exhibit a SnO_2 -like behaviour, while, for $0.3 \leq x \leq 1$, a TiO_2 -like one, the drastic change appearing in correspondence to $x = 0.2$, a borderline material between SnO_2 and TiO_2 . Several measurements show this type of feature: among the electrical measurements, the shape of the Arrhenius plots, the conductance values, the shape of the energy barriers and the CO responses vs. temperature. However, the spectroscopic measurements especially highlight some differences between the two types of materials. This can be viewed, for UV-Vis measurements in the previous paragraph and for IR spectroscopy in [34].

In Fig 9A, 9B, and 9C, the Arrhenius plots for pure SnO_2 , ST10, and ST70 in dry air and in 500 ppm of CO in dry air are reported. Two main observations can be made: i) in dry air, the conductance decreases increasing the titanium content in the solid solution up to three orders of magnitude; ii) the shape of the Arrhenius plots changes as a minimum content of titanium is added to tin dioxide. Moreover, starting from ST30, shape and conductivity are identical for all the other compositions ($0.3 \leq x \leq 1$). Finally, ST20, similarly to ST25, are samples with a borderline behaviour, maintaining some features of SnO_2 -like materials, but having acquired some of the TiO_2 -like ones.

Passing to examine the heights of the potential barrier as a function of temperature, once again SnO₂ (Fig. 10 A) and ST10 (not shown here) exhibit the same features: after contact with carbon monoxide, a transfer of electrons from the surface to the conduction band occurs, thus decreasing the height of the barrier. In ST20 and in ST25, the barrier in CO remains just below the barrier in air, showing, as highlighted before, a borderline behaviour. Surprisingly, starting from ST30, the height of the barrier is higher in carbon monoxide than in air showing an opposite behaviour than usual. An example of this behaviour is reported in Fig. 10B and 10C for ST50 and ST70, respectively. On the other hand, it must be highlighted that the response to carbon monoxide, as described in the next paragraph, is particularly large for the halfway compounds characterized by the smallest grain size. Thereby, the explanation for this phenomenon must not be searched in the absence of reactivity to CO, instead in a more complex mechanism of sensing. Indeed, looking at the spectroscopic responses to CO in the medium IR region reported in [34], a completely different behaviour becomes manifest for SnO₂ and ST10, on one hand, and on the other one for samples with $0.3 \leq x \leq 0.9$, being the behaviour of ST20 borderline between the two groups of samples. In particular, in the MIR region, SnO₂ and ST10, after CO interaction, show the increase of a broad absorption with maximum at about 1500 and 2500 cm⁻¹, respectively, assigned to the photo-ionization of mono-ionized oxygen vacancies. On the contrary, samples with $0.3 \leq x \leq 0.9$ do not show any electronic absorption, but an erosion of the absorption edge related to the skeletal vibrational modes. The erosion of the metal-oxygen vibrational modes can be related to the loss of reticular oxygen near the surface during the reducing treatment in CO. The behavior of ST20 is borderline, since this sample shows both the broad band related to the photo-ionization of mono-ionized oxygen vacancies and the erosion of metal-oxygen vibrational modes.

Looking at the samples with $0.3 \leq x \leq 0.7$, another phenomenon appears, consisting in a decreasing of the energy barrier height in air due to the size of the nanoparticles (Figs. 10 B and C). Indeed, when the grain radius is smaller than the depletion layer width, the complete band bending cannot be fully developed. Consequently, the potential does not vanish on the centre of the nano-grain, and a partial flattening of the band bending takes place. On these materials, if the effect of the carbon monoxide was as expected, the band bending should be completely flattened. On the contrary, the barrier increases, but, at the same time, also the conductance increases due to an increase of the electrons in the conduction band coming from the chemical reaction on the surface of the semiconductor. A phenomenological explanation for this behaviour could be that the chemical reaction happens using surface lattice oxygen atoms rather than oxygen atoms ionosorbed on the semiconductor surface, generally claimed as responsible for the sensing mechanism. Further details on this aspect will be given afterwards in the discussion paragraph.

Another matter concerns pure TiO_2 for which no significant difference between energy barrier in air or in carbon monoxide was revealed (Fig. 10 D). Pure titania has been widely investigated gathering that it is characterized by a high density of the surface states leading to the pinning of Fermi level and thereby, the gas responses of titania-based sensors are strongly dependent on particle size [15]. It means that, when pure titania is in rutile form and consequently affected by an exaggerated grain coalescence, it becomes absolutely not reactive to the ambient gases. Thus, it is reasonable that the two energy barriers, in air and in CO, do not differ significantly, because very weak sensing process occurs.

3.2.3 Gas sensing properties

The most significant characteristic of the sensing layers prepared using the synthesized solid solutions is that the response to some gases, like carbon monoxide and methane, is particularly enhanced for certain compositions with $0.2 \leq x \leq 0.7$. Looking at the two single oxides, SnO_2 is a functional material very reactive to reducing gases, but, on the contrary, TiO_2 can be used only in anatase form when the particles are nanosized. The merging process of the two materials formed new compounds with much better performances than the two single oxides and with characteristics tuneable through the titanium content in the solid solution.

In Fig. 11 the response of the films to 50 ppm of CO (performed at the working temperature of 500 °C) has been plotted together with the crystallite size of the corresponding powders heated at 1050°C, both as a function of Ti molar ratio. For both curves the best fit is a quadratic function with a correlation coefficient $r^2 = 0.847$ for CO response, while r^2 for crystallite size was 0.958. It is evident that both phenomena are strongly dependent on the Ti molar ratio, but in the case of CO response with a greater error. Indeed, in this case two phenomena concur to the response: the content of titanium in the solid solution, but also the grain size, respect to which the dependence is linear. Looking at the CO response vs. Ti molar ratio, the material with $x = 0.25$ offers the highest response, being probably the material, even more than ST20, in which the contribution to the sensing process of both mechanisms is optimized. The two competing mechanisms are: reaction of CO with ionosorbed oxygen atoms (and hence Schottky barrier electron conduction) and reaction of CO with surface lattice oxygen atoms (and hence free electron conduction).

It is well known that TiO_2 is one of metal oxides with higher catalytic activity for the formaldehyde oxidation [51]; for this reason $\text{Ti}_x\text{Sn}_{1-x}\text{O}_2$ samples have also been tested versus 1 ppm of formaldehyde in the range of temperature between 450 to 650 °C. In Fig. 12 a comparison between the responses in dry air to carbon monoxide (50 ppm) and formaldehyde (1 ppm) for ST10,

ST50 and ST90 is shown. It can be observed that for the materials with low x (here only $x = 0.1$ is shown), the response is increasing, decreasing the working temperature; starting from $x = 0.3$, the response exhibits a bell-shaped behaviour with temperature up to $x = 0.9$, for which only the formaldehyde response maintains the bell shape. Moreover, ST90 and Pure TiO_2 (in anatase form) have shown larger responses to 1 ppm of formaldehyde rather than 50 ppm of carbon monoxide. Actually, besides SnO_2 which shows low reactivity to HCHO, however, it is sufficient a low content of titanium in the solid solution to obtain very good responses to formaldehyde.

4. DISCUSSION

Focusing on the comparison of response to carbon monoxide and height of energy barrier, an unexpected phenomenon appears, for stoichiometry of composition $x \geq 0.3$. In summary, in the case of SnO_2 , ST10 and up to ST25, the sensors present a good response to CO and the increase of conductance is accompanied by the expected decrease in the barrier height due to the consumption of ionosorbed oxygen atoms. From a spectroscopic point of view, in the UV-Vis region, a broadening of the absorption edge related to the band gap is observed, indicating that the reaction between CO and ionosorbed oxygen causes the formation of a state distribution near the bottom of the conduction band (CB). The materials are therefore very reactive to CO from the point of view of surface electron exchange. Starting from ST30 the increase ~~in response of conductance with CO~~ is followed by an anomalous ~~decrease~~ increase in the barrier height.

It is possible to argue that the different behaviour of the samples with respect to the barrier height is a result of the contribution of two detection mechanisms: i) the chemical reaction happens between the analyte and ionosorbed oxygen atoms causing an electron transfer from the surface to the bulk and viceversa in turn causing a barrier modification; ii) the oxygen atoms involved in the detection mechanism are surface lattice oxygen atoms which bond electrons do not participate to the development of the spatial charge region and therefore of the intergranular barrier. Thus, it is reasonable that in the materials with $x < 0.3$, the prevalent gas detection mechanism is the usual one (through barrier modification), whilst for $x \geq 0.3$, it mainly happens through bond electrons which, after the reaction, enter CB without affecting the barrier height, but only bulk conductance. The case of TiO_2 in rutile form is not anomalous because of its very poor sensing capacity caused by the occurrence of too big grains.

Taking into account that for SnO_2 , ST10 and ST20 the consumption of ionosorbed oxygen by CO (decrease in the barrier height) causes the broadening of the band-gap absorption, for ST50 and

ST70 the absence in the UV-Vis spectra of the broadening of the band-gap absorption suggests less reactivity of CO with ionosorbed oxygen. For all molar ratios, the grains are small (according to the crystallite size) and the band bending cannot develop fully, therefore the change in atmosphere from air to CO does not change the band bending very much, and it only results in a shift of Fermi level. It is known from the literature [52] that an increase in oxygen partial pressure lowers the electrochemical potential of electrons, (the Fermi level goes down in the bandgap) thereby a strong reducing atmosphere is supposed to push the Fermi level in the other direction, towards conduction band bottom. The subsequent decrease in the distance between the Fermi level and the CB bottom leads to a rapidly increasing bulk conductance. In this range of molar ratio ($x \geq 0.3$), the reaction of CO with surface reticular oxygen (as revealed by IR analysis with the erosion of the metal-oxygen vibrational modes [34]) may lead to population of deep levels (Sn^{3+} , Sn^{2+}) which is consistent with a reticular (bulk) response, not due to surface ionosorption. As a matter of fact, the population of deep levels is put in evidence by UV-Vis analysis with the increase of an absorption at 21000 cm^{-1} (2.6 eV) near to the VB-CB edge. In this range of molar ratio, the method of barrier measurement through stimulated temperature jumps does not work, as the method assumes constant bulk conductance [42], whereas in this case, the increase in conductance is merely due to the Fermi level shift. Therefore, the anomalous barrier increase in the presence of CO with respect to dry air is just an artifact.

In the case of ST90 still the shift is present and the response to CO is still visible. When dealing with the pure TiO_2 sample, instead, no barrier modification is seen, no conductance variation and no spectral modification is observed in the presence of CO with spectroscopic analysis in the UV-Vis region. We think that this may be due to the large dimension of crystallites that lead to large grains and pinning of Fermi level can be responsible for no variation induced by atmospheric changes.

5. CONCLUSIONS

Nano-sized $\text{Ti}_x\text{Sn}_{1-x}\text{O}_2$ powders were synthesised at increasing Ti molar fraction and their structural, morphological and optical characterization was performed. Through the screen printing technique the powders were deposited as thick films on alumina substrates for the electrical characterization.

The powders are single phase with a rutile-like structure and crystallite sizes in the range 4.4-11.7 nm. For all the thick films the morphology consists in nano-particles with moderate grain

coalescence. As for the sensing performances, the responses to CO of the solid solutions are higher than those shown by pure SnO₂ and TiO₂.

By combining the results of response to CO, height of the surface potential barrier and UV-Vis spectroscopy, it was possible to argue the contribution of two detection mechanisms: i) the chemical reaction involved in the sensing process occurs between CO and ionosorbed oxygen atoms. This causes an electron transfer from the surface to the bulk (conductance increase) and, as a consequence, the barrier height decreases; ii) the chemical reaction involved in the sensing process occurs between CO and surface lattice oxygen atoms which bond electrons that do not participate to the development of the spatial charge region and therefore of the intergranular barrier. It was possible to conclude that in the materials with $x < 0.3$, the prevalent gas detection mechanism is the usual one (through barrier modification), whilst for $x \geq 0.3$, it mainly happens through bond electrons which, after the reaction, enter the conduction band without affecting the barrier height, but only bulk conductance.

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Maria Cristina Carotta became Doctor in Physics at the University of Ferrara in 1973. From 1981 to 2010 she was researcher at the Department of Physics of the same University. Now she is researcher within CFR (Ferrara Research Consortium). Since 1983 she has focused her research activity on semiconductor physics, mainly on electrical, optical and transport properties of silicon and of semiconductor oxides for gas sensors. She is currently involved in research projects concerning the development and characterization of nanostructured thick-film gas sensors for industrial and environmental applications.

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Ambra Fioravanti got his degree in physics at the University of Ferrara in 2009. Since then she focused her studies on the electrical properties of semiconductor oxides for gas sensing, carrying on her activity at Sensors and Semiconductor Laboratory of the University of Ferrara. She is also involved in realization and characterization of nanostructured materials as well as of thick film gas sensors prepared through screen printing technology.

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Degree in “Tecnologie Fisiche Innovative” at the Physics Department – University of Ferrara in July 2002. In 2002 he collaborated with the Sensors and Semiconductor Laboratory in the characterization process of gas sensors, and since October 2002 he is been working in the laboratory as a technical assistant.

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CAPTIONS OF THE FIGURES

- Fig. 1 DSC curves of all $\text{Ti}_x\text{Sn}_{1-x}\text{O}_2$ precursors as a function of temperature
- Fig. 2 XRD Bragg's reflection of the (110) (A) and (101) (B) planes of the materials calcined at 1050°C . Reflections at higher Ti content show the splitting of $K\alpha_1$ and $K\alpha_2$ reflections.
- Fig. 3 Estimated values of the a (A) and c (B) cell parameters compared with those reported by Yuan and Virkar in [26].
- Fig. 4 TEM micrograph with SADP of $\text{Ti}_{0.3}\text{Sn}_{0.7}\text{O}_2$ calcined at 550°C for 2 h.
- Fig. 5 Diffuse reflectance UV-Vis spectra recorded at RT of (A) SnO_2 and (B) TiO_2 : curves a, after treatment in vacuum and oxygen at 550°C and curves b, after treatment in CO at 400°C .
- Fig. 6 Diffuse reflectance UV-Vis spectra recorded at RT of (A) ST-10, (B) ST-20, (C) ST-30, (D) ST-50, (E) ST-70 and (F) ST-90: curves a, after treatment in vacuum and oxygen at 550°C and curves b, after treatment in CO at 400°C .
- Fig. 7 SEM micrograph of the ST10 (A) and ST25 (B) film both heated at 650°C .
- Fig. 8. SEM micrograph of the ST70 film heated at 650°C .
- Fig. 9 Conductance vs. temperature in dry air of the following films: SnO_2 (A), ST10 (B), ST20 (C) and ST70 (D).
- Fig. 10 Energy barrier dependence on temperature in dry air for the following films: SnO_2 (A), ST10 (B), ST20 (C), ST50 (D), ST70 (E), and TiO_2 in rutile form (F).
- Fig. 11 Response to 50 ppm of CO (performed at the working temperature of 500°C) plotted together with the crystallite size, both as a function of Ti molar ratio.
- Fig. 12 Comparison between the responses in dry air to carbon monoxide (50 ppm) and formaldehyde (1 ppm) for ST10, ST50 and ST90.