

Experimental studies of O₂–SnO₂ surface interaction using powder, thick films and monocrystalline thin films

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Abstract

Surface properties of solids and the interactions between molecules and solid surfaces are important for many technical applications. They also involve a range of physical and chemical phenomena of fundamental scientific interest. The importance of oxygen chemistry at SnO₂ surfaces follows from the fact that SnO₂ is used as an active material in gas sensor applications. The operation principle of these sensors is usually based on measurable conductance response of the material, which is understood in terms of reactions of gas molecules with different oxygen species adsorbed onto the surface. The role of the lattice oxygen, but in particular, the bridging oxygen atoms on SnO₂ surfaces, is also active. Detailed understanding of the reaction mechanisms of various oxygen species at SnO₂ surfaces is important, as it offers a way to improve the sensitivity and selectivity of the sensors.

Oxygen adsorption–desorption kinetics at the SnO₂ surface is studied experimentally using O₂-temperature-programmed desorption (TPD) method together with conductance measurements in the case of SnO₂ powder and polycrystalline thick films made from the powder. In addition, CO-TPD is studied and the transient behaviour of various oxygen species is considered. Molecular beam epitaxy (MBE) was also used to fabricate polycrystalline and monocrystalline thin films with the SnO₂(101) face on single crystal sapphire substrate. Simultaneous surface potential and conductance measurements during heating and cooling in different ambient atmospheres were used to characterize the monocrystalline SnO₂(101) surface after various surface treatments.

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1. Introduction

The importance of oxygen chemistry at SnO₂ surfaces follows from the fact that SnO₂ is used as the active material in gas sensor applications. The operation principle of these sensors is usually based on measurable conductance responses in the bulk material, which are understood, e.g., in terms of reactions of gas molecules with O₂[−] and O[−] ions adsorbed onto the surface [1]. The role of lattice oxygen, but

in particular, the bridging oxygen atoms on SnO₂ surfaces, is also active [2]. Detailed understanding of the reaction mechanisms of various oxygen species at SnO₂ surface is important, as it offers a way to the development of sensitivity and selectivity of the sensors [3–6].

A powerful tool for penetrating the surface reaction mechanisms is to carry out the measurements under transient conditions. In this work, the transient temperature-programmed desorption (TPD) measurements of oxygen and carbon monoxide adsorption–desorption kinetics at SnO₂ surfaces are performed. We also studied the influence of oxygen on the surface potential of monocrystalline thin film with SnO₂(101) face. Simultaneous conductance measure-

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ments together with either TPD or surface-potential measurements give more insight into the surface phenomena.

In an earlier work [7], we have studied the kinetics of various oxygen components at SnO₂ surface using kinetic Monte Carlo method and reported an initial conductance increase when a polycrystalline sample is heated up and a conductance decrease in a temperature region above about 280 °C. Similar behaviour has been observed also experimentally [3,8]. It is given a suggestion for the conductance decrease that it is related to a change of lattice (bridging) oxygen amount at SnO₂ surface [2,4].

Temperature-programmed desorption studies of oxygen adsorption–desorption behaviour at SnO₂ surfaces have been reported earlier by several authors [9–12]. Yamazoe et al. [9] reported desorption of four kinds of oxygen species on the basis of their TPD experiments with a heating rate of 20 °C/min, i.e., O₂ at 80 °C, O₂[−] at 150 °C, O[−] (or O^{2−}) at 450–600 °C and lattice oxygen above 600 °C. Only two of these predicted species, namely O[−] (or O^{2−}) and lattice oxygen, were observed after SnO₂ was treated with oxygen at 400 °C followed by cooling to room temperature (RT) in vacuum. Thus, the fully oxidized surfaces gave these two desorption temperature regions (species), whereas in the case of partially reduced surfaces (after H₂ exposure) only desorption region of lattice oxygen was observed [11].

The measurement of the O₂-TPD from an SnO₂ powder together with simultaneous measurement of the conductance response of the same powder (in the form of thick film) is a new approach in this study. Conductance measurements in high vacuum made it also possible to avoid the effect of humidity on the conductance response of the samples made of the powder. Monocrystalline SnO₂ thin films made by molecular beam epitaxy (MBE) for gas-sensing studies are also a very new approach in this study. For example, they make it possible to study a specific crystal face like the SnO₂(101) face in this study. Surface-potential (Kelvin probe) measurements made on monocrystalline film surfaces give also more exact results as compared to results obtained on polycrystalline sample surfaces [13].

2. Experimental

2.1. TPD and conductance

Both thick and thin film samples were used in the study of the interaction of oxygen with SnO₂ surfaces. Temperature-programmed desorption experiments (O₂-TPD) together with conductance measurements for SnO₂ thick films were carried out in a quartz chamber in vacuum (pressure down to 10^{−7} mbar) at temperatures 25–800 °C. Tin dioxide sample used in the experiments was a commercial powder of pure tin dioxide supplied by Merck Ltd. The surface area of the SnO₂ powder was 6 m²/g measured according to the standard Brunauer–Emmett–Teller (BET) method. Adsorption gases, oxygen (99.998%)

and CO (99.97%) were supplied by AGA Ltd. (Sweden) and the small moisture content of the gas was removed using a molecular sieve before the exposure. Gas flows were regulated with mass flow controllers (Bronkhorst). A split of the product flow was taken through a short pipe into a quadrupole mass spectrometer (Carlo Erba Q.T.M.D).

Prior to every TPD run, the excess gas was removed by evacuation until no residual gases were detected in the gas atmosphere. TP190 temperature controller (Carlo Erba Instruments) was used to control the heating rate that was kept constant (10 and 30 °C/min) during the experiments. Blank tests were carried out with an empty reactor and no desorption peaks or reactions were detected.

For the TPD measurements, ca. 1 g of SnO₂ powder was packed in a quartz chamber. Prior to TPD measurements, the sample was first heated at 550 °C in vacuum for 2 h. Then, a gas was adsorbed at a lower temperature and the sample was cooled down to RT, e.g., in vacuum. Finally, the TPD chromatogram was measured from RT up to 800 °C. In the oxygen adsorption experiments, oxygen (20 ml/min) was adsorbed onto the powder surfaces at different temperatures (550 °C, 300 °C and RT) for 10 min. In the case of the highest adsorption temperature the sample was cooled down to RT slowly either in an oxygen flow or in vacuum. We also performed carbon monoxide adsorption tests in which CO (20 ml/min for 10 min) was adsorbed on SnO₂ surfaces at RT in three subsequential measurement runs. Between the measurements the sample was heated at 550 °C in vacuum for 2 h, and cooled down to RT in vacuum.

The conductance of SnO₂ was measured simultaneously during the O₂-TPD run by using a thick-film sample fabricated on alumina substrate. An approximately 15 μm thick SnO₂ layer was screen-printed on top of thick-film gold electrodes first screen-printed on alumina substrate. The gap between the electrodes was 200 μm wide. Tin dioxide paste used in the screen printing was prepared from the same tin dioxide powder that was used in the TPD measurements. The paste was made by mixing SnO₂ powder with organic vehicle containing 94.7 wt.% terpeneol, 4 wt.% ethyl cellulose and 1.3 wt.% antrox. The solid content in the paste was about 60 wt.%. The sample was annealed for 1 h with 10 min at a peak temperature of 850 °C.

A computerized measurement system was used to measure both temperature and conductance during the TPD runs. Temperature was measured with a type-K thermocouple that was placed inside the furnace close to the vacuum chamber. The voltage of a thermocouple was measured with a HP3458A multimeter. The conductance of the SnO₂ sample was determined by measuring the current through the sample with an HP 3457A multimeter. Constant 10 V was fed to the sample from HP 6628A power supply during the measurement.

2.2. Surface potential and conductance

Surface potential and conductance changes as a function of temperature in different ambient conditions were studied

with SnO₂ thin films. Epitaxial 30 nm and 100 nm thick thin films were deposited on a single crystal sapphire substrate (1 cm²) with (r-cut) surface orientation, by using a molecular beam epitaxy (MBE) system V80M. The system was equipped with Leybold–Heraeus electron beam gun for Sn evaporation. The target was made from metal tin (99.99%) or hot pressed SnO₂ (99.9%). Reactive deposition process was used for film deposition. The oxygen was introduced by Oxford Plasma RF plasma cell. Mixture consisting of 80% O₂ and 20% Xe was used to provide a stable plasma discharge. The typical oxygen pressure during deposition was $\sim 10^{-4}$ mbar. The deposition system was equipped with a boron nitride coated graphite heater, which allowed high temperature processes at high oxygen pressure. Before deposition the substrate was first cleaned ex situ by boiling it in nitric acid and then in situ by exposing it to oxygen plasma for 5 min. The SnO₂ films were deposited at temperatures between 260 and 460 °C with the deposition rate 0.02–0.1 nm/s. After deposition, the samples were cooled down in vacuum ($<10^{-6}$ mbar). Crystal structure of the films was characterized by reflection high-energy electron diffraction (in situ) (RHEED) and XRD. Depending on the growth parameters the crystalline structure was found to be either monocrystalline or polycrystalline. Surface orientation with (101) face of the SnO₂ films was found in all cases. Films with monocrystalline structure were used in the surface potential studies. For the surface potential and conductance measurements the samples were cut in smaller size and on top of the film Pt electrodes were evaporated so that the surface area of the SnO₂ thin film was finally around 5*5 mm².

Surface potential changes of SnO₂ thin films were investigated using vibrating capacitor (Kelvin) method. Graphite rod of 2 mm in diameter was used as the reference electrode. For the measurements, sample was put in a separate sample holder with integrated Pt resistor for heating and electrical contacts for the conductance measurements. Constant 1 V was fed to the sample during the conductance measurements while during the surface potential measurements it was disconnected. A Pt heating element in the sample holder was also used as a temperature sensor to find out the temperature of the films. The difference of the temperatures between the heater and the surface of the film was determined by using a calibrated Pt thin-film resistor that was fabricated on top of a similar sapphire substrate.

3. Results and discussion

The observed desorption of oxygen species depend greatly on how the oxide surface is treated prior to the TPD run [9]. In our experiments where oxygen was adsorbed at 550 °C, desorption was observed only at high temperatures (ca. 550–600 °C depending on the heating rate) in both cases where the sample was cooled down in oxygen flow or in vacuum. However, in the case of cooling

down in oxygen containing atmosphere in Fig. 1 an additional tail is seen in the chromatogram at around 650 °C. This additional peak can be seen more easily in Fig. 1 in the case where oxygen was adsorbed at 300 °C and cooled down in vacuum in which case, however, the amount of desorbed oxygen was quite small. Fig. 1 shows also TPD results of a sample on which oxygen was adsorbed at RT after it was heated at 550 °C in vacuum for 2 h and cooled down in vacuum. Here desorption was observed only at around 100 °C. This desorption product was earlier assigned to O₂⁻ adsorbates on the surface and the high temperature peaks to O⁻ (or O²⁻) by Yamazoe et al. [9]. Finally, in all cases, except in the case where oxygen was adsorbed at RT, it is possible to see in Fig. 1 oxygen desorption starting to increase again at about 750 °C. This observation was also reported recently by Gaillard et al. [12]. At such high temperatures one can suppose desorption from the lattice.

Fig. 2 shows results of the conductance measurements together with O₂-TPD runs. Two subsequent runs were made: first after adsorption of oxygen at 550 °C and cooling down to RT in the same atmosphere and the second immediately after cooling down to RT in vacuum after the first run without any treatment. Heating rate of 10 °C/min was used in these measurements. At low temperatures in the first run the conductance was very low, comparable to the noise level of the measurement system (around 10⁻¹⁰ S) so it is difficult to say what kind of influence the low temperature desorption has on the conductance. Conductance remains low until 350 °C and after that temperature it starts to increase rapidly. This behaviour is quite different as compared to the conductance measurements done in dry atmospheric conditions, where first conductance maximum is usually seen at around 280 °C for a sample that is supposed to be dry and oxidized before heating [14]. A reason for the conductance decrease above about 280 °C in atmospheric conditions could be the residual humidity that is still present on the tin-dioxide surface even after treatment at elevated temperatures in dry synthetic air. In the temperature range around 400 °C in Fig. 2 conductance increase is slowing down, but before 500 °C it starts again to increase. This correlates well with the desorption results in Fig. 2

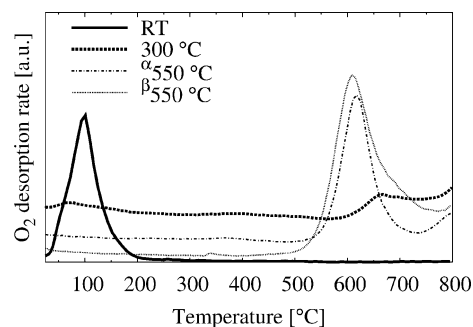


Fig. 1. Thermal desorption rate of oxygen as a function of temperature at a heating rate of 30 °C/min from SnO₂ powder sample treated at different oxygen adsorption temperatures. Superscripts α and β denote cooling in vacuum and in O₂ flow after the adsorption, respectively.

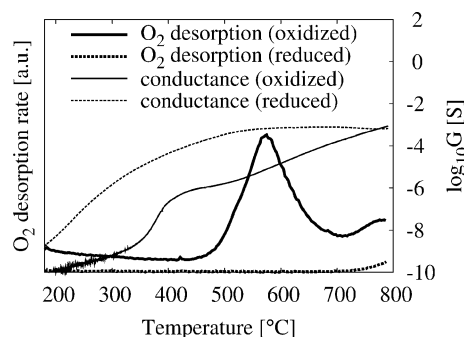


Fig. 2. Conductance and O_2 desorption rate of both oxidized and reduced SnO_2 thick-film and powder samples, respectively, as a function of temperature during heating at a rate of $10\text{ }^\circ\text{C/min}$.

where it is seen that the oxygen desorption rate starts to increase just below $500\text{ }^\circ\text{C}$. The second TPD run in Fig. 2 shows significantly higher conductance values as compared to those in the first run in the whole temperature range up to about $750\text{ }^\circ\text{C}$ where conductance values are equal. Also, below $100\text{ }^\circ\text{C}$, the conductance of the reduced sample is very low.

TPD results after CO adsorption on SnO_2 powder surfaces at room temperature are shown in Fig. 3. Three repeated TPD runs ((a),(b) and (c) in Fig. 3) were made for powder sample of about 0.7 g . Before the first run and between the runs the sample was heated at $550\text{ }^\circ\text{C}$ in vacuum for 2 h and after that cooled down to RT in vacuum. CO was then adsorbed on the surface at room temperature for 10 min. No oxygen was adsorbed during these three measurements. Curve (d) in Fig. 3 shows CO_2 desorption rate in the case where the powder sample of 1 g was heated at $800\text{ }^\circ\text{C}$ in vacuum for 2 h and after that oxygen was adsorbed on the sample surfaces at $550\text{ }^\circ\text{C}$, and then after cooling to RT in O_2 flow CO was adsorbed at room temperature for 10 min before the TPD run. It is possible to see two CO_2 desorption peaks in the TPD chromatograms in Fig. 3, first at around $80\text{--}100\text{ }^\circ\text{C}$ and second at around $200\text{ }^\circ\text{C}$. In the case of (d), there is only a strong broad peak at around $230\text{ }^\circ\text{C}$. According to Tamaki et al. [11], there are two possible adsorption sites (adsorbed oxygen and lattice oxygen) in which CO molecules could adsorb. Three major

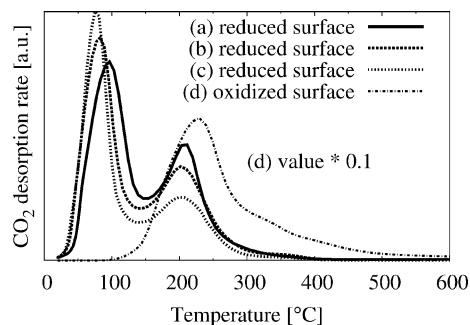


Fig. 3. Thermal desorption rate of CO_2 as a function of temperature at a heating rate of $30\text{ }^\circ\text{C/min}$ from SnO_2 powder sample after CO adsorption at room temperature on reduced surfaces (three repeated runs (a), (b) and (c), see text) and on oxidized surfaces (d), respectively.

types of surface species, unidentate carbonate, bidentate carbonate and carboxylate, were found formed in an infrared absorption study by Harrison and Guest [15] when polycrystalline SnO_2 was exposed to dry air containing low concentrations of CO. It was also found in the study that the surface bidentate carbonate and carboxylate, although quite stable at lower temperatures, slowly transform into surface unidentate carbonate at temperatures above about $130\text{ }^\circ\text{C}$. This may give an explanation for the observed TPD peak structure of curves (a), (b) and (c) in Fig. 3 where the lower temperature peak below about $130\text{ }^\circ\text{C}$ may be a superposition of the desorption of the bidentate carbonate and carboxylate species. The drift of the peak position to lower temperatures with increasing amount of desorption is characteristic for second order desorption as also the symmetric shape of the peaks [16,17]. However, there is no drift in the upper peak position in curves (a), (b) and (c) in Fig. 3 with changes of the amount of desorption which may be an indication of a first order desorption process [16,17]. The total amount of desorbed CO_2 is about the same in all three desorption runs on reduced surfaces in Fig. 3. Tamaki et al. [11] did not observe any low temperature desorption peaks in the case of partially reduced surface (after H_2 exposure). Similarly, in our case only the high temperature peak is seen in curve (d) in Fig. 3 where CO is adsorbed on the oxidized surface. The presence of only the unidentate carbonate species on the oxidized surface is an explanation for the observed desorption peak structure in the TPD run (d) in Fig. 3. No any desorption of water was found in the desorption experiments in Fig. 3.

Fig. 4 shows results of surface potential and conductance measurements as a function of temperature made on a 30 nm thick monocrystalline SnO_2 thin film. Measured values for conductance and contact potential difference (V_{cpd}) were taken after a stabilization period of around 30 min. Curve (a) represents a situation where the film was first reduced at $440\text{ }^\circ\text{C}$ in $1\%\text{ H}_2$ in N_2 for 30 min and then cooled down to $150\text{ }^\circ\text{C}$ in the same gas mixture. Then the flow was switched to $100\%\text{ O}_2$ flow. This change in the gas atmosphere at $150\text{ }^\circ\text{C}$

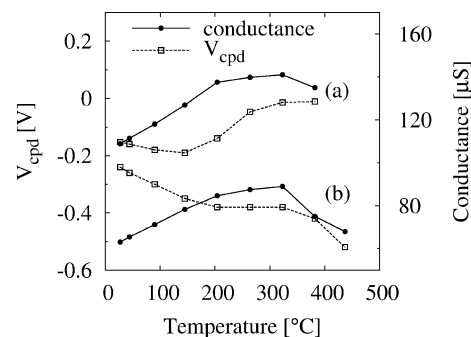


Fig. 4. Conductance and contact potential difference V_{cpd} as a function of temperature of a 30 nm thick monocrystalline SnO_2 thin film (a) in argon after exposure to $1\%\text{ H}_2$ in N_2 at $440\text{ }^\circ\text{C}$ followed by exposure to $100\%\text{ O}_2$ at $150\text{ }^\circ\text{C}$ and cooling down to RT in O_2 , and (b) in oxygen after exposure to $1\%\text{ H}_2$ in N_2 at $380\text{ }^\circ\text{C}$ followed by cooling down to RT in the same gas mixture.

had little or no influence on the conductance value, but V_{cpd} changed by about 0.2 V more negative. Sample was then cooled down to RT in O_2 atmosphere and dry argon was introduced to the chamber. This had no effect on the values of conductance and V_{cpd} . Then, the sample was heated stepwise up to 380 °C in Ar, as shown in Fig. 4. After about 150 °C, V_{cpd} starts to increase, which may indicate that negative oxygen species begin to leave the surface at this temperature. Conductance values show only a little correlation with the surface potential values. Maximum values are around 300 °C similarly with the maximum values in the case of polycrystalline thick-film samples in atmospheric air [8]. Yamazoe et al. [9] relate the decrease in conductance after about 300 °C to desorption of water from the surface that was exposed to hydrogen at 200 °C and cooled down to RT in the same atmosphere prior to the TPD run. In the case of curve (b) in Fig. 4, the sample was first heated up to 380 °C in 1% H_2 in N_2 and then cooled down to RT in the same atmosphere. Then, heating was conducted in 100% O_2 . Again, the change in the ambient atmosphere at RT had no effect on the values of conductance and V_{cpd} . During heating the surface potential decreases in two different temperature regions. First, from RT up to about 200 °C, V_{cpd} decreases by about 0.15 V and then by another 0.15 V between 300 and 440 °C. Conductance of the film now behaves very similarly with that in the case of (a). The conductance increase from RT up to the maximum value at about 300 °C is only by a factor of 1.3–1.4 in both curves (a) and (b), whereas in the case of a porous polycrystalline SnO_2 sample the conductance increases by many orders of magnitude in the same temperature range, as shown, e.g., in Fig. 2. This means that the energy barriers between grains in the porous polycrystalline samples are absent in the monocrystalline film. A reason for the conductance increase in curves (a) and (b) in Fig. 4 may relate to electron injection from the deeper energy level of the oxygen vacancy double donors into the conduction band at temperatures above RT [3]. Above 300 °C, the values of both conductance and V_{cpd} decrease in the case of curve (b) in Fig. 4. Again, it is possible to relate this behaviour to either water desorption from the surface [9] or to surface oxidation [18]. The large differences in the behaviour of V_{cpd} with temperature between curves (a) and (b) in Fig. 4 indicate that there are large differences in the surface phenomena between the two heating runs, but the conductance of the film is very insensitive to differences in the phenomena. This information may give some advice on how to continue the research with monocrystalline SnO_2 thin films.

In Fig. 5, it is shown that simultaneous conductance behaviour at different temperatures runs off 30 nm thick monocrystalline (denoted by m) and polycrystalline (denoted by p) thin-film samples measured in different ambient atmospheres after different sample pretreatments. Before the measurements, samples were first heated in dry argon (99.9999%) from RT up to 600 °C at a rate of 10 °C/min and, then, rapidly cooled down to RT. At first,

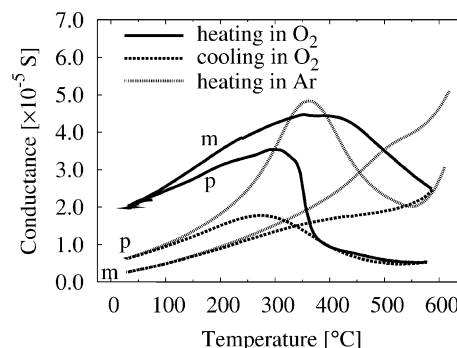


Fig. 5. Conductance as a function of temperature of 30 nm thick monocrystalline (m) and polycrystalline (p) SnO_2 thin films in dry oxygen and argon atmospheres. Before the first heating and cooling runs in oxygen samples were heated in dry Ar (99.9999%) from RT up to 600 °C at a rate of 10 °C/min followed by rapid cooling down to RT in the same atmosphere.

measurements were made in 100% O_2 with a heating and then cooling rate of 1 °C/min. Second measurements were made right after the first ones in dry argon at a heating rate of 10 °C/min.

There are some differences in the behaviour of conductance between the two samples in Fig. 5. The initial conductance increase of both films during heating up to 300 °C in O_2 is very similar to that in Fig. 4. This means that the energy barriers are absent also in the polycrystalline film. Both films have the same crystal orientation where the (101) face forms the film surface. There are some differences in the behaviour of conductance between the monocrystalline and polycrystalline films which are not easy to understand. Although the films were not reduced by H_2 in the pretreatment, the atmosphere during measurements did contain also some small amounts of humidity. However, it was found in Fig. 4 that the conductance behaviour of the monocrystalline film was very insensitive to different phenomena at the film surface. Therefore, it is not easy to make conclusions on the effects of humidity for the differences in the conductance behaviour between monocrystalline and polycrystalline films in Fig. 5.

4. Conclusions

Temperature-programmed desorption of oxygen from SnO_2 powder surfaces in vacuum together with simultaneous conductance measurements with thick films made from the same powder was studied after different pretreatments of surfaces. It was found that the conductance of oxidized thick films with temperature in vacuum behaves very differently as compared to the behaviour of SnO_2 thick films in atmospheric conditions containing at least residual amounts of oxygen and humidity. The conductance increase of oxidized thick films at high temperatures (>450 °C) in vacuum seems to relate to oxygen desorption from the SnO_2 surfaces (Fig. 2). However, at intermediate temperatures

(350–400 °C) where a rapid increase appears in conductance no change in the desorption of oxygen was found (Fig. 2). A large difference was found between the CO₂-TPD chromatograms measured after CO adsorption at room temperature on reduced and oxidized SnO₂ surfaces, respectively (Fig. 3). A comparison of the results obtained with polycrystalline and monocrystalline thin films with the (101) face (Figs. 4 and 5) with those reported in Refs. [6,19] may indicate the importance of the pretreatment of the surface for the behaviour on surface potential and conductance of the films with temperature. The preliminary research reported here with SnO₂ thin films made by MBE did give some advice for future research on the films.

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