Surface reactivity of SnO_2 obtained by sol–gel type condensation: interaction with inert, combustible gases, vapour-phase H_2O and air, as revealed by electron paramagnetic resonance spectroscopy

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Electron paramagnetic resonance (EPR) studies have been carried out on lattice oxygen vacancies produced by the interaction of carbon monoxide with SnO_2 obtained by sol–gel type condensation. Under a 0.5% CO–argon reducing atmosphere the vacancies can transfer electrons to Sn^{4+} producing Sn^{2+} centres. In air the lattice defects interact with molecular oxygen in a manner which depends on whether the gas reducing treatment was performed under dry or moist conditions. Defects that undergo oxygen interaction at the SnO_2 surface, reduce O_2 to O_2^- or O^{2-}, depending on the temperature of the reaction with oxygen.

In previous work we have carried out EPR spectroscopic investigations into the surface reactivity of II–VI and IV–VI semiconductor metal oxides (ZnO, SnO_2), with flowing streams of inert, combustible gases (CO, H_2), vapour-phase H_2O and air. The investigations were performed on high purity commercial material (ZnO)[1–4] and on a metal oxide obtained by drying the corresponding hydrous form (SnO_2).[5]

The need to produce materials suitable for devices, and to study and characterise such materials, prompted us to search for alternative synthetic procedures. This need appeared to be particularly so for SnO_2 as it is widely used as a base material for gas sensors.[6–8]

We obtained the oxide by hydrolytic condensation of a tin(IV) alkoxide precursor; by this method SnO_2 can be in either the form of a powder, as used in the present investigation, or as a thin film suitable for devices.[9]

It is known that lattice defects of oxygen arise from the interaction of combustible gases with the SnO_2 surface;[7] ionisation of such defects and injection of their electrons into the conduction band lead to EPR active species.[10] Furthermore, paramagnetic forms of reduced oxygen should occur through the interaction of molecular oxygen with lattice defects.[11] For these reasons EPR seemed to be the most appropriate technique to study both defects and surface reactivity of SnO_2, which forms the basis of the present work.

Experimental

Preparation of SnO_2

SnO_2 was obtained by sol–gel condensation of $Sn(OEt)_4$, obtained from the $Sn(OBu^t)_4$ precursor. $Sn(OBu^t)_4$ was prepared by the procedure described by Hampden-Smith *et al.*[12]

$Sn(OBu^t)_4$ (2 g) dissolved in absolute EtOH (40 ml) gave a solution of $Sn(OEt)_4$ which was added dropwise, with rapid stirring at room temperature, over 1 h, to the hydrolysis solution of 95% EtOH (60 ml)–H_2O (15 ml). After the addition was complete, the solution was stirred continuously for 14 h at room temperature under a dry N_2 atmosphere and during this stage condensation of the alkoxide occurred. A sample of the gel was removed for analysis by scanning electron microscopy (SEM). After drying the gel (see below) SEM analysis showed that the powder obtained was composed of spherical shaped submicron sized particles (Fig. 1), characteristic of the sol–gel preparation technique.[13]

The gel was recovered by centrifugation, washed twice with distilled water and dried *in vacuo* (10^{-2} Torr) at room temperature for *ca.* 5 h. The dried gel was then heated to 473 and then

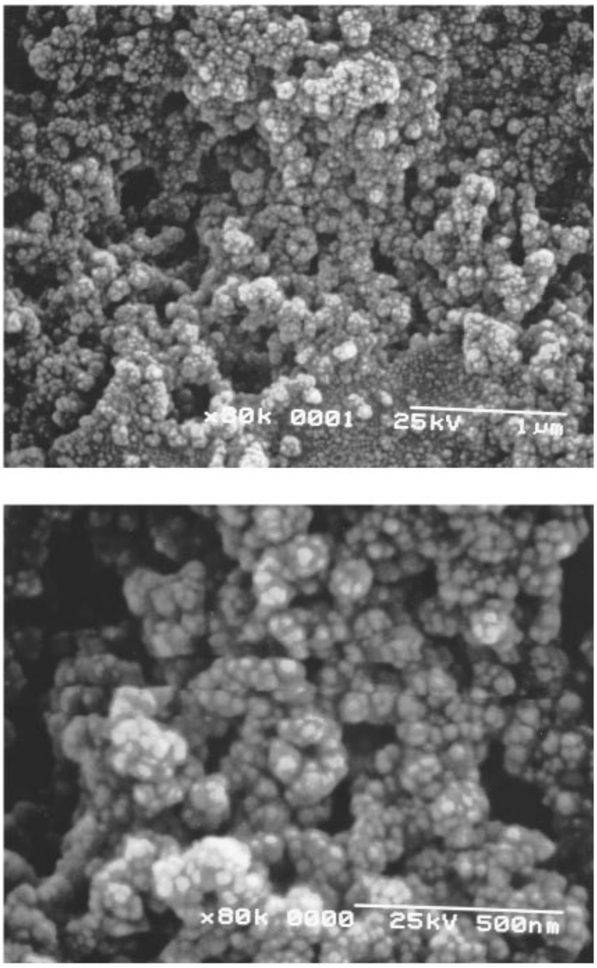

Fig. 1 Scanning electron micrographs of SnO_2 from $Sn(OBu^t)_4$

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to 673 K under flowing air ($100\,\mathrm{ml\,min^{-1}}$) for 8 and 4 h, respectively. Such treatments dehydrated the oxide without dramatically reducing the surface area.

Thermogravometry (TG) performed under nitrogen on the dried gel with a heating rate of $5\,^{\circ}\mathrm{C\,min^{-1}}$ from 323 to 1173 K, showed four major mass losses: from 323 to 373 K (33%), from 373 to 673 K (5%), from 673 to 773 K (0.5%) and from 773 to 1173 K (1%).

The major mass loss, observed between 323 and 373 K, is mainly due to the hydrolytic condensation of residual water from the synthesis, or to physisorbed water, its amount varying depending on the time the previous treatment *in vacuo* was performed. Temperature programmed desorption (TPD) studies on SnO_2 in the literature[14] have demonstrated that losses at higher temperatures can be attributed to chemisorbed species, presumably hydroxy groups, located on different crystal planes of the oxide with different bond strengths, and that at higher temperatures a simultaneous desorption of oxygen becomes active. At 673 K, the temperature chosen for the thermal air conditioning of the oxide (see later), most of the hydroxy groups were lost. Different TG measurements, performed under an air stream on the dried gel, at 473 and 673 K, showed that the expected water losses occurred completely in about 20 min.

Surface area measurements performed after treatment under flowing air, for 8 h at 473 K and then for 4 h at 673 K, gave values of 165 and $75\,\mathrm{m^2\,g^{-1}}$, respectively. The decrease is in good agreement with previously reported trends of surface area *vs.* temperature for SnO_2 gels from $SnCl_4$.[15,16]

The oxide showed broad X-ray powder diffraction (XRD) peaks corresponding to the cassiterite phase of SnO_2.

Apparatus

XRD data were collected on a Siemens D500 diffractometer, operating with Bragg–Brentano geometry and with Cu-Kα radiation ($\lambda_{\alpha 1} = 1.540\,56$ Å, $\lambda_{\alpha 2} = 1.544\,39$ Å).

SEM was performed with a Hitachi S-2400 apparatus, supplied with a windowless type microprobe (Kevex) and images were obtained using secondary electrons.

BET surface area measurements were performed on a Coulter SA 3100 instrument, after outgassing the samples at 303 K for 5 h.

EPR spectra were recorded at 123 K on a conventional Varian E 109 apparatus equipped with variable-temperature accessory, working at X-band frequency and using 5 mW microwave power and 5 G modulation amplitude. The *g* values were measured by standardization with diphenylpicrylhydrazyl (DPPH). The amount of paramagnetic species was calculated by double integration of the resonance line area, taking care that the powder always filled the sensitive cavity region to the same extent.

XPS measurements were performed in a SSI M-Probe spectrometer (base pressure $= 5 \times 10^{-7}$ Pa) equipped with a monochromatized Al-Kα source (1486.6 eV). The energy scale was calibrated with reference to the $4f_{7/2}$ level of a freshly evaporated gold sample, taken as 84.0 eV. The 1s level of adventitious carbon was taken as the internal reference at 284.6 eV and for every sample the binding energy reproducibility was always checked (0.1 eV). XPS runs were performed on the powdered samples pretreated under the same conditions as for the EPR measurements. All the treatments were performed in a quartz reactor connected directly to the XPS analysis chamber so as to avoid contamination or surface modification of the treated samples due to exposure to air.

Experimental procedures and spectroscopic measurements

The interactions of SnO_2 with dry or wet flowing gases were performed in a quartz apparatus suitable for both gas-flow and EPR measurements, and were subdivided into three steps.

(i) First SnO_2 powder samples (*ca.* 1 g) were treated at 673 K for 4 h in a dry air stream ($100\,\mathrm{cm^3\,min^{-1}}$) and the related EPR spectra were recorded. This procedure was performed before any further treatment with the different gases, in order to obtain a stoichioimetric composition of the SnO_2 surface.

(ii) The interaction between the oxide and the dry or wet gases was then performed (the different processes are summarized in Table 1). SIAD gases were employed in pure (argon, air) and mixed (0.5% CO–argon, 0.5% CO–air) forms. Gases were moistened by bubbling the flowing gas through water in an ice-bath (H_2O about 0.6%). The experimental procedure for the interaction required three steps: (*a*) the gas was passed over the sample at room temperature at a flow rate of $100\,\mathrm{cm^3\,min^{-1}}$) for 5 min. Then the temperature was increased at a heating rate of $50\,^{\circ}\mathrm{C\,min^{-1}}$ up to the temperature selected for the treatment (298, 373, 473, 573, 673 or 773 K). The heating stages of the processes were performed also using a dry atmosphere, even if studying the interaction with moist gases, in order to avoid water absorption at temperatures lower than selected (compare procedures B and B′ in Table 1); (*b*) dry or moist flowing gases were contacted with samples at the selected temperatures for 30 min and (*c*) the samples were rapidly cooled (about 5 min) at room temperature and the EPR spectra were taken. Cooling was performed under a dry, inert atmosphere in order to avoid interaction with oxygen at temperatures lower than the contact temperature (compare procedures E and E′ in Table 1).

(iii) After interaction with the gases, the samples were successively exposed to a stream ($100\,\mathrm{cm^3\,min^{-1}}$) of dry air for 10 min at room temperature, to investigate the interaction of the previously reduced samples with oxygen.

The EPR spectra of SnO_2 were generally recorded under the same atmosphere as the treatment. When air was present the spectra were taken after evacuating the air, in order to avoid, due to line broadening, non-detection of an EPR signal from a possible paramagnetic surface species. Such line broadening is well known, and is brought about by the magnetic interaction occurring from collisions of oxygen with surface species. As an exchange interaction occurs, this effect is commonly termed exchange broadening, and can be used to distinguish between surface and bulk paramagnetic species.[17]

Results

SnO_2 was pretreated in a dry air stream at 673 K for 4 h before any further contact with other gases, in order to make the SnO_2 surface as stoichiometric as possible. No EPR resonance lines were observed on such pretreated SnO_2.

Interaction with dry argon and dry 0.5% CO–argon

Treatment with flowing dry argon (procedure A in Table 1) at all temperatures did not change the spectrum.

If a stream of dry 0.5% CO–argon was used, in the tempera-

Table 1 Experimental procedures for the interaction of SnO_2 with dry and wet gases[a]

process	(*a*) heating RT→*T*	(*b*) treatment *T*	(*c*) cooling *T*→RT
A	dry Ar	dry Ar	dry Ar
B	wet Ar	wet Ar	dry Ar
B′	dry Ar	wet Ar	dry Ar
C	dry CO–Ar	dry CO–Ar	dry CO–Ar
D	dry CO–Ar	wet CO–Ar	dry Ar
E	dry CO–air	dry CO–air	dry CO–air
E′	dry CO–air	dry CO–air	dry Ar
F	dry CO–air	wet CO–air	dry Ar

[a] RT = room temperature, *T* = treatment temperature.

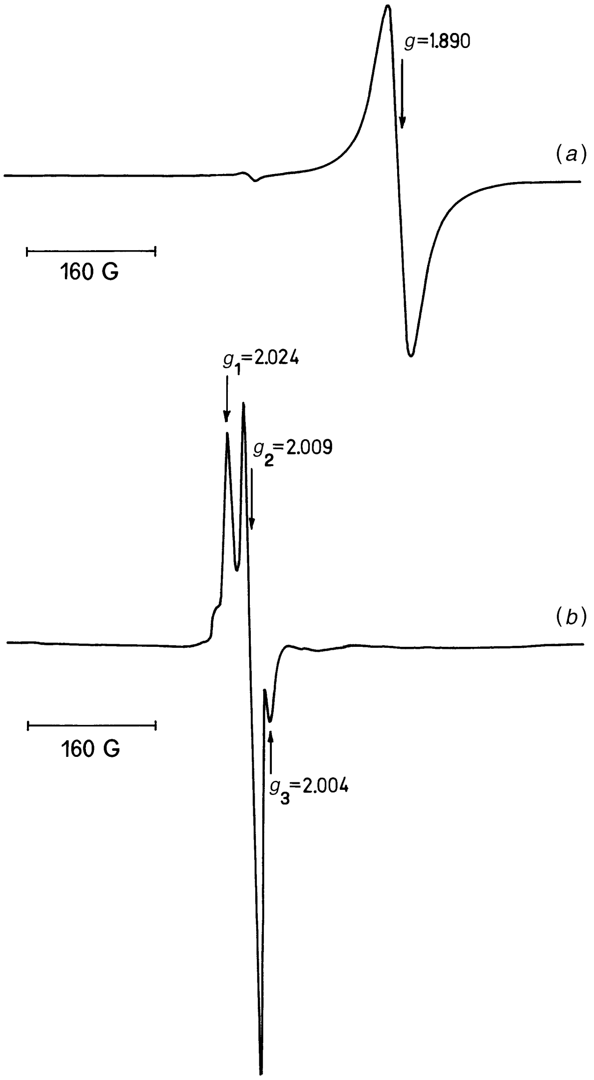

Fig. 2 (*a*) EPR spectrum, recorded at 123 K, of V_O^+ defects found on SnO_2 treated under dry 0.5% CO–argon at 298–773 K; (*b*) EPR signal, recorded at 123 K under an argon atmosphere, of $Sn^{4+}-O_2^-$ centres found on SnO_2 treated under dry 0.5% CO–argon at 298–773 K, then under an air stream at room temperature

ture range 298–773 K (procedure C in Table 1), symmetrical resonance lines were observed at $g=1.890$. Resonances were similar to those of singly ionized oxygen vacancies $(V_O^+)^{10}$ and corresponded, in their *g* tensor values, to 'shallow' defects[18] [Fig. 2(*a*)]. The amount of V_O^+ ranged from *ca.* 10^{16} spin g^{-1} at room temperature up to 5×10^{16} at 773 K [Fig. 3(*a*)].

Each sample was successively exposed to a stream of dry air at room temperature for 10 min in order to investigate the species at the surface obtained by reacting O_2 with the reduced samples.

A decrease in intensity of V_O^+ lines was observed and the resonances of residual V_O^+ ($V_O{}^+{}_{res}$) disappeared at 673 K [Fig. 3(*a*)]. Moreover new strong resonance lines with three well separated *g* component values ($g_1=2.024$, $g_2=2.009$, $g_3=2.004$) became evident, besides the signals of residual V_O^+ [Fig. 2(*b*)]. Comparison with literature data[10] enabled the new lines to be attributed to $Sn^{4+}-O_2^-$ centres located at the surface of the oxide. In agreement with this attribution, the lines of $Sn^{4+}-O_2^-$ were not observed if the EPR spectra were recorded in air due to exchange broadening as discussed above (see spectroscopic measurements).

The amount of $Sn^{4+}-O_2^-$ centres increased with the temperature of the dry 0.5% CO–argon treatment from 2×10^{17} to 3×10^{18} spin g^{-1} [Fig. 3(*b*)]; specifically the number of $Sn^{4+}-O_2^-$ centres was always much higher than the original V_O^+ centres, more than doubling that of vacancies for temperatures lower than 473 K. Above this temperature the amount of $Sn^{4+}-O_2^-$ increased dramatically reaching concentrations of ten to a hundred times that of V_O^+.

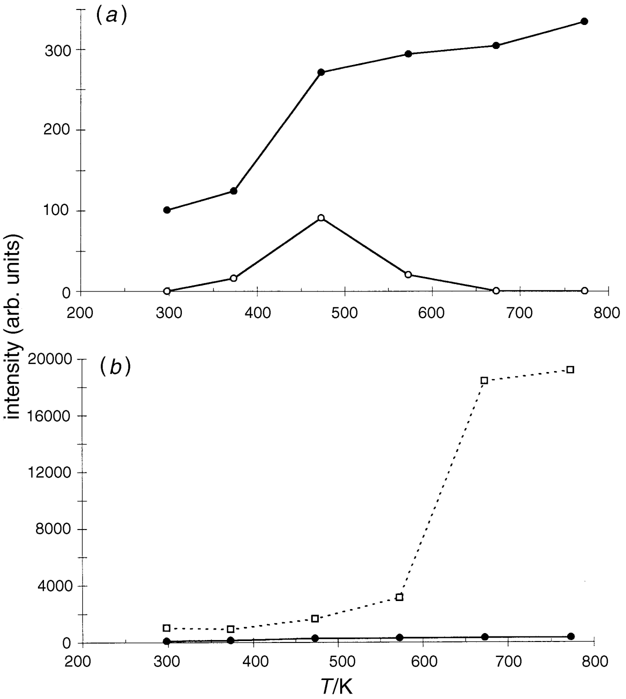

Fig. 3 (*a*) Temperature dependence of V_O^+ defects (●) and $V_O{}^+{}_{res}$ defects (○) on SnO_2 treated with dry 0.5% CO–argon; (*b*) trends *vs.* temperature of V_O^+ defects (●) on SnO_2 treated with dry 0.5% CO–argon and of $Sn^{4+}-O_2^-$ centres (□) from successive air treatment at room temperature

Interaction with moist argon and moist 0.5% CO–argon

Treatments with moist argon (procedures B and B′) led to the formation of V_O^+ centres. The number of defects increased up to 573–673 K (Fig. 4). Above this temperature the number of vacancies differed depending on the procedure used {B [Fig. 4(*a*)] or B′ [Fig. 4(*b*)]}. The differences lay in a larger decrease of defects above 573 K for samples treated by procedure B′ in which the moistened gas was injected at the treatment temperature, while with procedure B the sample underwent a heating stage from room temperature to the treatment temperature under moist flowing gas. Surprisingly these defects do not react with oxygen after exposure to a stream of dry air at room temperature.

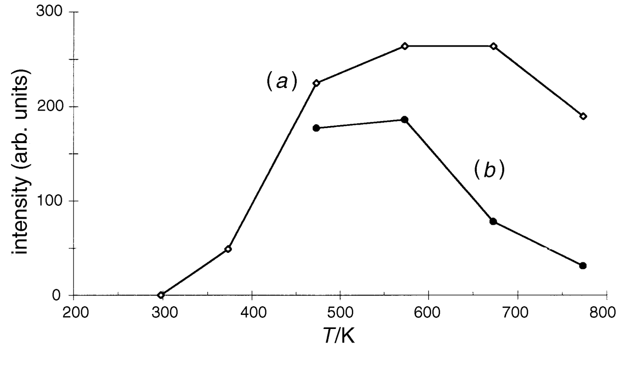

Fig. 4 Trends *vs.* temperature of V_O^+ defects formed by moist argon treatment by procedure B [curve (*a*)] and procedure B′ [curve (*b*)]

Under a moist 0.5% CO–argon stream (procedure D) $V_O{}^+$ defects were produced [Fig. 5(*a*)]. The oxygen vacancies obtained at temperatures lower than 573 K did not react with oxygen when contacted with a stream of dry air at room temperature. Treatment at higher temperatures produced defects reactive towards oxygen, giving a large amount of $Sn^{4+}-O_2{}^-$ centres [Fig. 5(*b*)].

It thus appeared that when treatment with the moist gas was performed at $T > 573$ K, the behaviour of the oxide is not dissimilar from that observed under dry CO–Ar.

Interaction of CO with dry and wet 0.5% CO–air

The EPR spectra of samples treated under dry 0.5% CO–air stream, recorded under an argon atmosphere, showed resonance lines of $Sn^{4+}-O_2{}^-$ on the SnO_2 surface for treatments in the range 323–773 K and a few ionized vacancies at 473 and 523 K.

The trends of both $V_O{}^+$ and $Sn^{4+}-O_2{}^-$ centres as a function of the temperature of the 0.5% CO–air stream are shown in Fig. 6. If the cooling process was performed under dry CO–air (procedure E) more $Sn^{4+}-O_2{}^-$ centres were observed at all treatment temperatures than for cooling under dry argon (procedure E′).

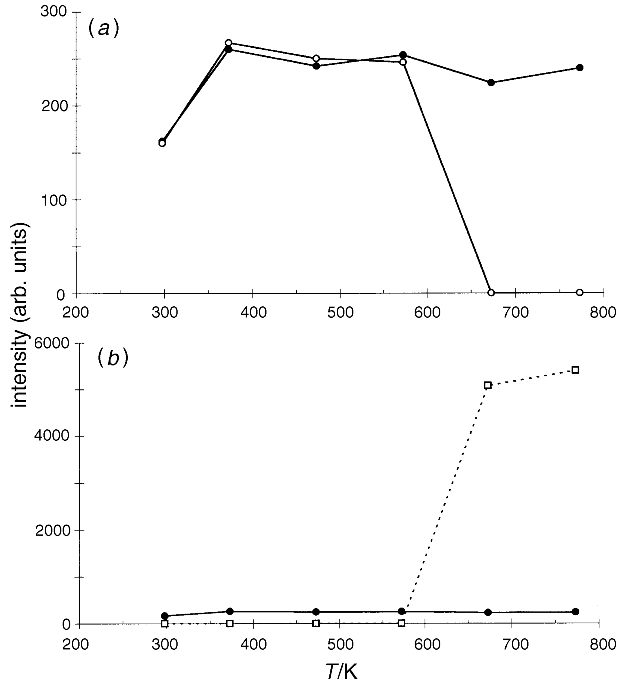

Fig. 5 (*a*) Temperature dependence of $V_O{}^+$ defects (●) and $V_O{}^+{}_{res}$ defects (○) on SnO_2 treated with wet 0.5% CO–argon; (*b*) trends *vs.* temperature of $V_O{}^+$ defects (●) on SnO_2 treated with wet 0.5% CO–argon and of $Sn^{4+}-O_2{}^-$ centres (□) from successive air treatment at room temperature

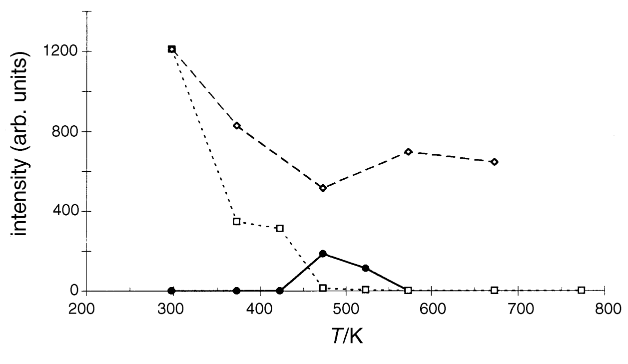

Fig. 6 Trend *vs.* temperature of $V_O{}^+$ defects (●) and $Sn^{4+}-O_2{}^-$ centres for SnO_2 treated under dry 0.5% CO–air at different temperatures by procedure E′ (□) and by procedure E (◇)

If the contact was performed under moist CO–air stream by procedure F, $V_O{}^+$ defects were observed only at 473 K, and no $Sn^{4+}-O_2{}^-$ centres appeared at any temperature.

Discussion

The reported results enable a rationale to be suggested for the surface reactivity of SnO_2 from sol–gel type condensation, after the material had undergone various flowing stream contacts.

Paramagnetic oxygen vacancies detected after interaction of SnO_2 with a CO–argon atmosphere, would originate from reactions (1) and (2),

$$CO + O_O \rightarrow CO_2 + V_O \tag{1}$$

$$V_O \rightarrow V_O{}^+ + e^- \tag{2}$$

where O_O indicates the oxide anions in lattice oxygen sites and V_O indicates bielectronic neutral oxygen vacancies. Single ionization of V_O produced localized paramagnetic defects $V_O{}^+$ and electrons that enter the conduction band [eqn. (2)].

The lack of increase in the number of the ionized oxygen vacancies formed at $T > 573$ K is difficult to rationalize, especially in the light of the exceptionally high number of $Sn^{4+}-O_2{}^-$ centres formed on SnO_2 samples treated with CO–Ar at $T > 573$ K and contacted with air at room temperature. We suggest that in addition to eqn. (1) and (2) an electron transfer [eqn. (3)] could also take place

$$Sn_{Sn}{}^{4+} + 2\ V_O{}^+ \rightarrow Sn_{Sn}{}^{2+} \tag{3}$$

Reaction (3) transfers electrons from the oxygen vacancies to $Sn_{Sn}{}^{4+}$ centres, reducing some of them to $Sn_{Sn}{}^{2+}$, and some examples of this process have already been reported.[19–22]

An XPS investigation we performed in the valence band region, on our material, after treatment with dry 0.5% CO–Ar atmosphere at different temperatures, gave unequivocal evidence that $Sn_{Sn}{}^{2+}$ centres are present at the surface. In fact a comparison of the valence band lines of our samples treated at different temperatures (Fig. 7), showed that by increasing the temperature, the peak at *ca.* 5 eV broadened, as expected in the presence of SnO and an additional shoulder due to SnO present together with SnO_2 appeared in the range 2–3 eV.[19–22]

On the basis of the previous comments contact with air at

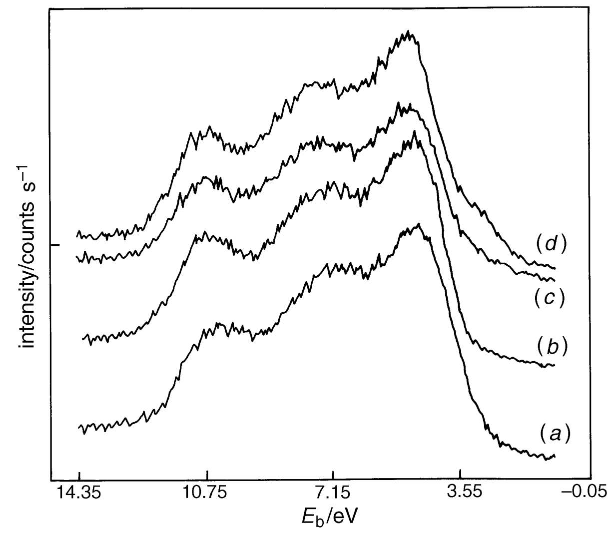

Fig. 7 Valence band XP spectra of SnO_2 (*a*) pretreated in an air stream at 673 K for 4 h, and after treatments with dry 0.5% CO–argon at 373 K (*b*), 573 K (*c*), 773 K (*d*)

room temperature, after treatment with CO–Ar, can be described by reactions (4)–(6) subsequent to reactions (1)–(3).

$$\mathrm{Sn_{Sn}}^{4+} + \mathrm{V_O}^{+} + \mathrm{O_2} \rightarrow \mathrm{Sn}^{4+} - \mathrm{O_2}^{-} \quad (4)$$

$$\mathrm{Sn_{Sn}}^{4+} + \mathrm{e}^{-} + \mathrm{O_2} \rightarrow \mathrm{Sn}^{4+} - \mathrm{O_2}^{-} \quad (5)$$

$$\mathrm{Sn_{Sn}}^{4+} + \mathrm{Sn_{Sn}}^{2+} + 2\,\mathrm{O_2} \rightarrow 2\,\mathrm{Sn}^{4+} - \mathrm{O_2}^{-} \quad (6)$$

Reactions (4)–(6) all point to the formation of $\mathrm{Sn}^{4+}-\mathrm{O_2}^{-}$ centres, the number of which is much higher than that of vacancies.

$\mathrm{O_2}^{-}$ bonds to $\mathrm{Sn_{Sn}}^{4+}$ by an electrostatic interaction, and we expect that the chemisorbed oxygen provides a Schottky barrier that hinders further transfer of electrons to molecular oxygen. This leaves a number of unreacted ionized vacancies, detected by EPR. Considering that the Weisz limit (10^{12}–10^{13} spin cm^{-2})[23] for chemisorbed $\mathrm{O_2}^{-}$ is reached by samples treated under CO–Ar at 773 K, it appeared clear that for lower treatment temperatures some of the vacancies were unable to react because of their probable subsurface location (residual vacancies). The defects produced by a CO–Ar atmosphere at temperatures $T > 673$ K have different reactivity compared to those formed at lower temperature and, by contrast with the latter, all disappeared on reaction with oxygen at room temperature [Fig. 3(*a*)]. This difference could be related to their location nearer the surface.

The formation of oxygen vacancies under a moist CO–Ar atmosphere requires critical evaluation. In fact, while it is easily understandable that CO could reduce the surface by abstracting some lattice oxygen and injecting electrons into the conduction band, it is not so clear how water interacts with, and reduces, $\mathrm{SnO_2}$.

We hypothesize that when moisture comes into contact with the oxide surface reactions (7) and (8) can occur.

$$\mathrm{H_2O} + 2\ \mathrm{Sn_{Sn}} + \mathrm{O_O} \rightarrow 2\ \mathrm{OH\ Sn_{Sn}} \quad (7)$$

$$2\ \mathrm{OH\ Sn_{Sn}} \rightarrow 2\ \mathrm{Sn_{Sn}} + \mathrm{H_2O} + \tfrac{1}{2}\mathrm{O_2} + \mathrm{V_O} \quad (8)$$

Reaction (7), leading to hydration of the $\mathrm{SnO_2}$ surface, is expected at room temperature while reaction (8) is expected to be favoured at high temperature.[14] If contact with a moist atmosphere was performed at room or moderate temperature, reaction (7) prevails, while at increased temperature, reaction (8) became more significant. The decrease in the number of defects using procedure B over B′ is due to a less effective hydration in the former; thus hydration step (7) seems a necessary requirement for the formation of oxygen vacancies by treatment with moist inert gas alone.

The same reactions (7) and (8), suggested a rationale also for the behaviour of $\mathrm{SnO_2}$ contacted with a moist CO–Ar stream. In this case, the formation of oxygen vacancies unreactive to molecular oxygen was observed for treatments up to 573 K. The formation of $\mathrm{Sn}^{4+}-\mathrm{O_2}^{-}$, observed after treatment with air at room temperature of samples treated under moist CO–Ar at $T > 573$ K, can be ascribed to reactions (3) and (6), already occurring in the case of dry CO–Ar. It can be hypothesized that the coverage of $\mathrm{SnO_2}$ with hydroxy groups at $T < 573$ K pushes the vacancies into a subsurface region, making them unreactive towards oxygen.

The defects produced on $\mathrm{SnO_2}$ by interaction with 0.5% CO–air can at the same time react with molecular oxygen present in the surrounding atmosphere to produce $\mathrm{Sn}^{4+}-\mathrm{O_2}^{-}$. The stability of this species is temperature dependent and the signals of $\mathrm{Sn}^{4+}-\mathrm{O_2}^{-}$ rapidly decreased above 373 K. We concern ourselves only with the behaviour of samples cooled under a dry inert atmosphere as cooling under CO–air introduced artifactual $\mathrm{O_2}^{-}$ stabilised at a temperature different from the contact temperature.

Two explanations can be proposed for the $\mathrm{O_2}^{-}$ stability trend: $\mathrm{O_2}^{-}$ is converted to O^{-}, not seen in the EPR spectrum, and then to diamagnetic O^{2-}, in agreement with some literature reports;[7] however the presence of unreacted $\mathrm{V_O}^{+}$ defects at 473 and 573 K could alternatively suggest that at these temperatures the superoxide undergoes disproportionation to $\mathrm{O_2}$ and O^{2-} and the amount of O^{2-} is not sufficient to fill all the produced vacancies.

The behaviour of $\mathrm{SnO_2}$ under a 0.5% CO–air flowing stream in moist conditions showed, as expected, the total absence of $\mathrm{Sn}^{4+}-\mathrm{O_2}^{-}$ at temperatures lower than 473 K, unreactive $\mathrm{V_O}^{+}$ defects at 473 K and even the disappearance of oxygen defects at higher temperature.

Conclusions

The spectroscopic studies reported here have led us to conclude that $\mathrm{SnO_2}$, obtained by sol–gel condensation, stabilised two types of oxygen defects which differ in their reactivity.

One type, located at the surface, is reactive towards oxygen and fixes it at the surface of $\mathrm{SnO_2}$ in a reduced form, $\mathrm{O_2}^{-}$ or O^{2-}, depending on the treatment temperature; these defects were observed after treatment with a dry reducing CO–Ar atmosphere.

The other type, located in a subsurface region, does not react with oxygen. This was due to chemisorbed OH groups, when the defects were produced by treatment under moist inert or reducing atmosphere, to an original location in the subsurface region,[24] when they were residual defects after interaction with air of defects produced under a dry reducing atmosphere.

It was found that the first type of defects are able to transfer electrons to Sn^{4+} in the absence of air, reducing it to Sn^{2+}, which in the presence of air is reoxidised.

In CO–air the formation of oxygen vacancies, due to interaction of CO with the $\mathrm{SnO_2}$ surface, and the reaction of vacancies with molecular oxygen occur at the same time. Below 473 K, saturation of vacancies occurs owing to chemisorption of $\mathrm{O_2}^{-}$, while above 473 K saturation is *via* O^{2-}.

An almost identical process was found to be responsible for the saturation of vacancies observed in ZnO under similar conditions as studied here.[1–3]

Our conclusions confirm the hypothesis of Mattogno *et al.*[25] who suggested that no role is played by chemisorbed reduced oxygen species $\mathrm{O_2}^{-}$ or O^{-} in electronic exchange processes above 673 K.

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