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Characterization of tin oxide films prepared as gas sensors by conversion electron Mössbauer spectrometry

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Mn and Ni oxides incorporated tin oxide films, prepared by a spray pyrolysis technique and treated in hydrogen atmospheres, were characterized by conversion electron Mössbauer spectrometry and electron spin resonance to study the gas-sensing mechanism of tin oxides by the addition of metal oxides. Although the chemical state of Sn in undoped tin oxide film did not change after treatment with 5% H_2 at 400 °C, the reduced Sn species was detected in the tin oxide films doped with Pd. In Sn–Mn oxide films with the addition of Pd, the chemical state of Sn did not change, but the state of Mn changed on exposure to H_2. In Sn–Ni oxide films with and without Pd, the chemical states of Sn and Ni were strongly affected by H_2. A mechanism of hydrogen spillover effect on the tin oxide films is discussed.

1. Introduction

Semiconductors of metal oxides such as tin oxide and zinc oxide are used for detecting inflammable gases. The sensitivity and selectivity of these semiconductors have been improved by the addition of catalysts such as Pd or Pt, which can promote the dissociation of hydrogen or hydrocarbons [1]. The high degree of dispersion of catalyst in metal oxides is an essential requirement to achieve the higher sensitivity and selectivity. The general reaction on the solid surface is considered to be as follows [2]. When an inflammable or reducing gas such as H_2 or CO interacts with the surface of a semiconductive metal oxide, the amount of adsorbed O_2 in the form of anion decreases, which results in a decrease of the potential barrier of the top surface and an increase in carrier density by releasing the carrier electrons back into the bulk, causing a change in the electrical resistance. The gas can be detected easily by monitoring the change of electrical resistance. Matsushima *et al.* [3] reported that interaction between metal additives and tin oxide in tin oxide-based gas sensors could be discussed based on results obtained by X-ray photoelectron spectroscopy, and that, although the electric interaction is very important in Ag-doped tin oxide sensors, it is important only at low temperature in the case of Pd-doped tin oxide sensors. There are two possible mechanisms of sensitization, electrical and chemical.

The phenomenon of spillover was first noticed in 1957 by Kuriacose [4]. Bond *et al.* [5] reported that CO is first chemisorbed on Pd and then spills over to tin oxides, producing a faster reduction of tin oxide in the presence of Pd than in its absence. In earlier studies using Mössbauer spectroscopy and infrared spectroscopy, Thornton and Harrison [6] reported that the partial reduction of Sn(IV) oxide to Sn(II) species was recognized by the chemisorption of CO on tin oxide.

In our previous report [7], manganese oxide–tin oxide and nickel oxide–tin oxide films doped with Pd, showed several tens times higher sensitivity against alcohol and H_2 than tin oxide film doped with Pd. Although functions of the doped metal and of the semiconductive oxide cannot be simply separated, the phenomenon of spillover is evidence of the close interaction between doped metal and supported oxide. Hydrogen atoms formed by a dissociation of molecular hydrogen on metal particles may easily migrate to another phase of the metal oxide, which has acceptor sites for H_2. The spiltover H_2 may reside on the surface of the second phase of metal oxide, diffuse into it, and partially reduce the bulk of the metal oxide [8]. In order to clarify the interaction mechanism of H_2 on tin oxide films, and manganese or nickel oxide incorporated tin oxide films with and without Pd, the change of chemical state of these oxides was observed by ^{119}Sn Mössbauer spectrometry (CEMS) and electron spin resonance spectrometry (ESR).

2. Experimental procedure

Undoped tin oxide films with a thickness of 30 nm, prepared on a glass plate were heated in air, 5% H_2 atmosphere or in vacuum. Mn oxide–tin oxide film and Ni oxide–tin oxide film with a thickness of about 200 nm were prepared by spray pyrolysis from methanol solutions of tin chloride and manganese or nickel chloride with a mole ratio of 1:5, respectively [7]. Some of tin oxide films were prepared by spraying partially on one side or wholly with 0.01 M palladium chloride solution and preheating in air at 400 °C for 2 h before heating in various atmospheres.

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^{119}Sn CEM spectra of every sample prepared were observed at room temperature. γ-rays from 40 MBq ^{119m}Sn(Ba_2SnO_4) were irradiated perpendicular to the sample surface and the electrons re-emitted after Mössbauer effect were detected with a back-scattered proportional counter [9]. The Doppler velocity was calibrated using Ba_2SnO_4 as an isomer shift standard and the position of α-Fe splitting peaks as velocity scales.

3. Results and discussion

3.1. Electrical properties of tin oxide film

Electrical properties of tin oxide film of 30 nm thickness were measured in ambient air and in a vacuum of about 13.3 N m^{-2} as shown in Fig. 1. The electrical resistance of the thin tin oxide film was lower in vacuum than in air, and decreased with increasing temperature because the carrier electron density in n-type semiconductor increases with temperature. The potential barrier of the surface on the tin oxide is high because the adsorbed oxygen extracts carrier electrons from the tin oxide film. When the temperature of the tin oxide increases, the adsorbed O_2 escapes from the tin oxide surface by releasing the attracted electrons to the substrate, which results in an increase of electron density, thus decreasing the height of the potential barrier. Whereas the decrease in electrical resistivity was caused only by the temperature increase of electron density in vacuum, the electrical resistance increased at about 310 °C and again decreased at 380 °C in air. CEM spectra of tin oxide film heated at 400 °C in ambient air and in vacuum at 13.3 N m^{-2} are shown in Fig. 2.

Isomer shift (IS) and quadrupole splitting (QS) of the tin oxide film were − 0.02 and 0.37 mm s^{-1}, respectively, due to Sn(IV) oxide in ambient air and 2.75 and 2.17 mm s^{-1}, respectively, due to Sn(II) species in addition to Sn(IV) oxide in vacuum. The IS and QS of the resultant Sn(II) species produced on the surface were a little different from those of black SnO (IS = 2.71 mm s^{-1}, QS = 1.45 mm s^{-1}) and red SnO (IS = 2.60 mm s^{-1}, QS = 2.20 mm s^{-1}) powders, and SnO (IS = 2.95 mm s^{-1}, QS = 2.45 mm s^{-1}), which were observed for the sample treated by evacuation at 330 K for 12 h and then reacted with CO at 1.33 kN m^{-2} [5]. The CEM spectra showed that a partial reduction of tin oxide on the top surface was induced by the release of lattice O_2 by evacuation. At a temperature higher than 300 °C, the adsorption and desorption of O_2 in the lattice and surface of tin oxide occurred. The temperature where an electrical resistance between in air and in vacuum differ most, can become an optimum temperature for detecting inflammable gases because O_2 contributes to the oxidation of reductive gases such as H_2, CO, CH_4, and alcohol by metal oxides.

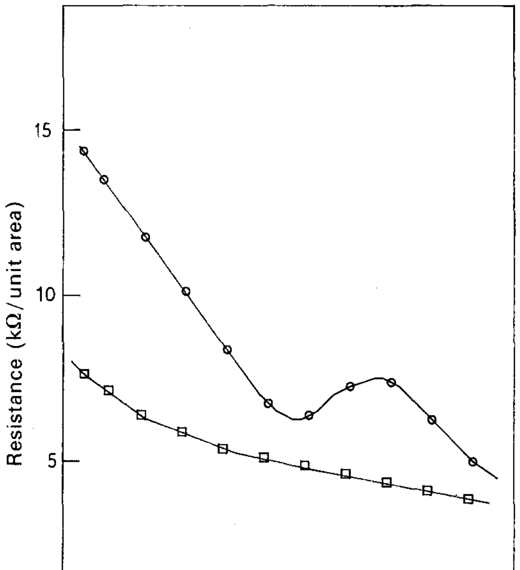

Figure 1 Effect of heating temperature on the resistance of tin oxide film (30 nm thick) (○) in air, and (□) in vacuum (13.3 N m^{-2}).

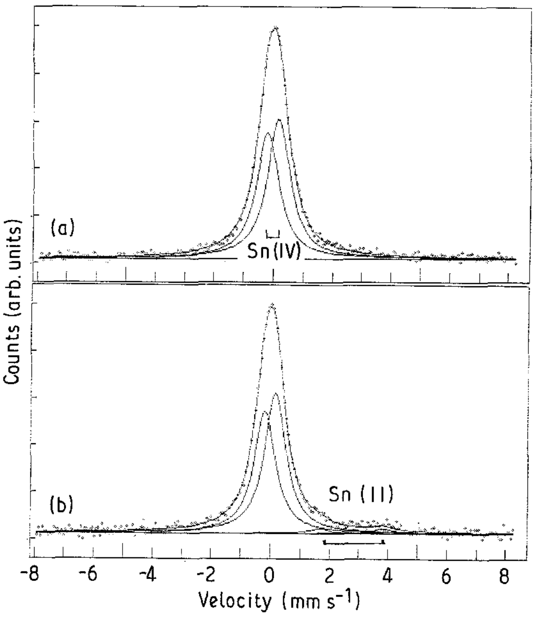

Figure 2 CEM spectra of tin oxide film (30 nm thick) heated at 400 °C for 1 h (a) in air, and (b) in vacuum (13.3 N m^{-2}).

3.2. Effect of Pd doping on tin oxide film

CEM spectra of tin oxide films with Pd on one side or the whole, annealed in 5% H_2 + 95% N_2 atmosphere at 400 °C for 1 h, are shown in Fig. 3. Although tin oxide film without Pd did not change on annealing in the H_2 atmosphere, shoulders appeared at IS = 1.7 and 2.1 mm s^{-1} with Pd on one side and the whole, respectively. The results support the idea that hydrogen molecules are decomposed at the Pd site to form atomic hydrogen, which migrates and instigates the partial reduction of Sn(IV) oxide.

3.3. Manganese–tin oxide film

Manganese–tin oxide films, partially or wholly covered by palladium chloride, were heated in air at 400 °C and annealed in 5% H_2 + 95% N_2 at

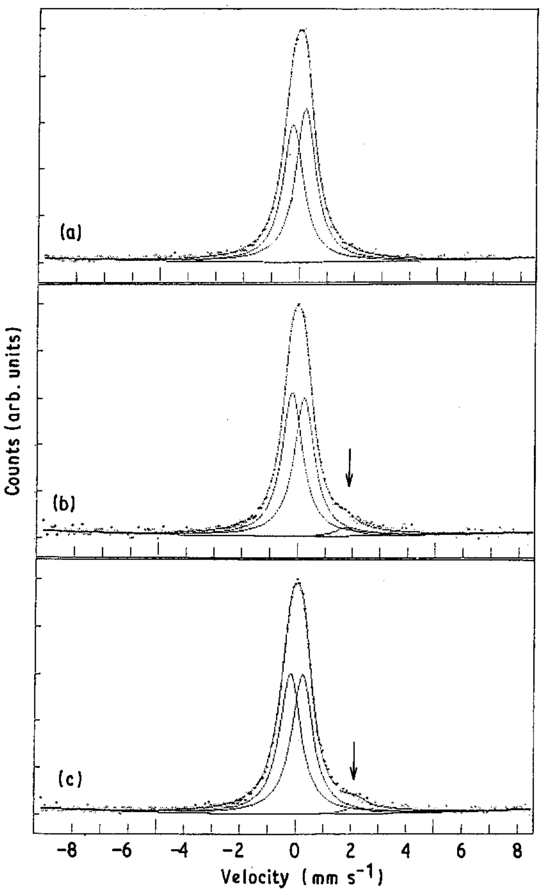

Figure 3 CEM spectra of tin oxide film heated in 5% H_2 + 95% N_2 atmosphere at 400 °C for 1 h. (a) Tin oxide film without Pd. (b) Tin oxide film with Pd deposited on one side. (c) Tin oxide film covered with Pd.

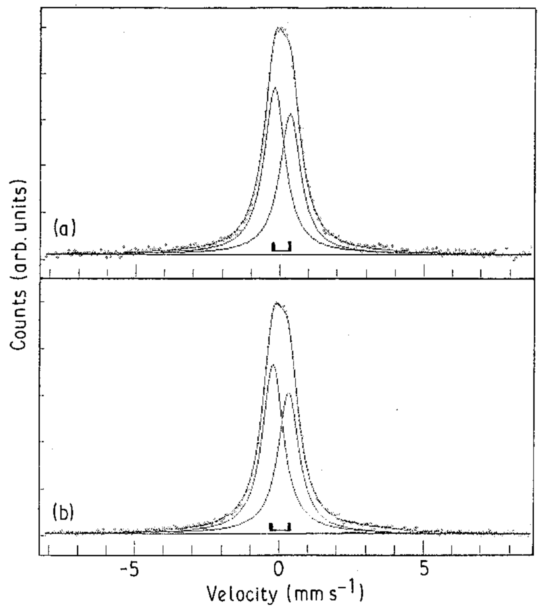

Figure 4 CEM spectra of manganese–tin oxide film (a) without Pd and (b) with Pd treated in 5% H_2 atmosphere at 400 °C for 1 h.

400 °C for 1 h. CEM spectra of the samples are shown in Fig. 4. The Mössbauer parameters were IS = 0.02 mm s^{-1}, QS = 0.54 mm s^{-1} for a doublet of Sn(IV) in manganese–tin oxide films. Orientation of Sn(IV) oxide in manganese–tin oxide film was different from that of tin oxide film prepared by physical vapour deposition. The peak intensity ratios (R) of the doublet of Sn(IV) in manganese–tin oxide and undoped tin oxide films were 1.18 and 0.90, respectively, which corresponded to $\theta = 58°$ and 52°, respectively. Assuming the asymmetry parameter of the electric field gradient (EFG) was zero, θ was calculated using the relation

$$R = (1 + \cos^2\theta)/(2/3 + \sin^2\theta) \qquad (1)$$

where θ is the angle between propagation of incident γ-rays and direction of the principal axis in the EFG. These results suggested that the direction of the principal axis of EFG of the latter sample was arrayed more perpendicular to the film surface than that of the former.

None of these samples showed any change in ^{119}Sn CEM spectra after the hydrogen treatment. ESR spectra of samples scraped off a glass plate are shown in Fig. 5. No signals were observed in ESR spectra of both manganese–tin oxide treated in air or in an H_2 atmosphere. But a broad signal was observed for manganese–tin oxide doped with Pd, treated in an H_2 atmosphere. The broad signal suggested that Mn^{2+} (nuclear spin, $I = 5/2$) ions produced by the H_2 reduction interacted strongly with each other. When the manganese–tin oxide sample was measured using thermal analysis, the weight decreased gradually with increasing temperature. The weight loss of manganese–tin oxide in 4.5% H_2 atmosphere was 12.8 wt % after heating at 620 °C whereas O_2 occupies 32.8 wt % in this sample. H_2 was adsorbed at the Pd sites and migrated towards MnO_2 grains. The change in the electrical conductivity of manganese–tin oxide is considered to be caused mainly by the change in the chemical composition of manganese oxide grains among the tin oxide grains in bulk, rather than by the change of the surface of tin oxide grains.

3.4. Nickel–tin oxide film

Nickel–tin oxide films were prepared by the same procedure as manganese–tin oxide films. CEM spectra of nickel–tin oxide film treated in 5% H_2 + 95% N_2 gas at 400 °C for 1 h are shown in Fig. 6. The Mössbauer spectra consist of a doublet and a singlet produced by H_2 treatment or a doublet (IS = 0.0 mm s^{-1}, QS = 0.3 mm s^{-1}) of Sn(IV) oxide. The parameters of the tin species produced were IS = 1.59–1.89 mm s^{-1} and QS = 1.2–1.5 mm s^{-1} for a doublet and IS = 1.4–1.5 mm s^{-1} for a singlet. The relative peak intensities of these doublets and singlets for the nickel–tin oxide film with Pd were larger than that obtained for the nickel–tin oxide film without Pd. Even if Pd was not present on the nickel–tin oxide film surface, the chemical state of Sn changed with the exposure of the film to H_2 because nickel oxide works as an auto catalyst. This conclusion is also supported by thermal analysis measurements of nickel–tin oxide powder scraped off the glass plate showing that the weight decrease began at 370 °C and ended at 420 °C, with up to 22% weight loss in a 5% H_2 + 95% He atmosphere, whereas O_2 occupied 23.8 wt % in this nickel–tin oxide, as shown in Fig. 7. When the electri-

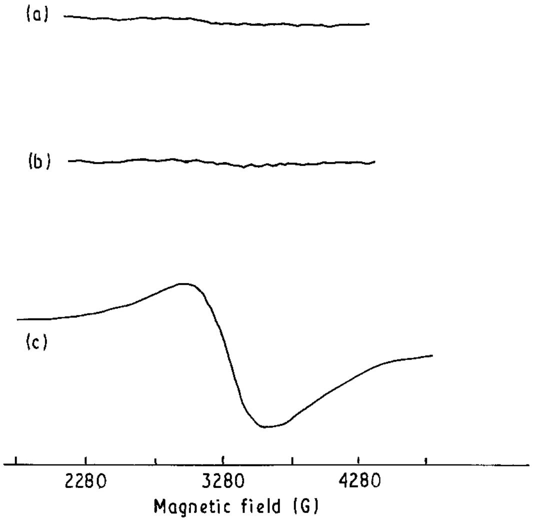

Figure 5 ESR spectra of manganese–tin oxide (5:1 mole ratio) with and without Pd annealed in air or in 5% H_2 atmosphere at 400 °C for 1 h. (a) Manganese–tin oxide film heated in air. (b) Manganese–tin oxide film heated in 5% H_2. (c) Manganese–tin oxide film with Pd heated in 5% H_2.

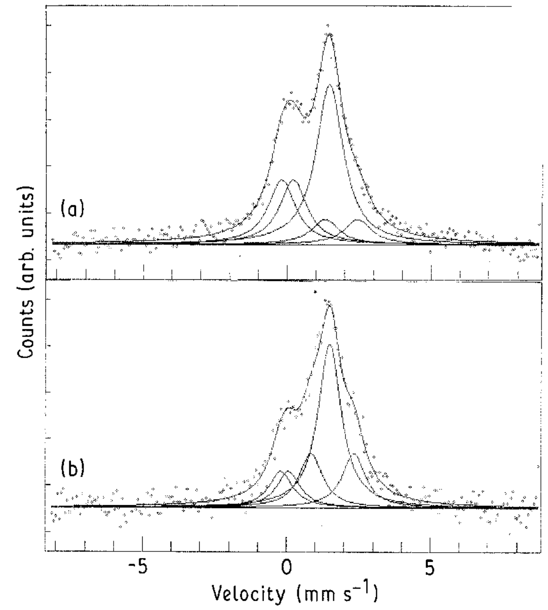

Figure 6 CEM spectra of nickel–tin oxide film (a) without Pd and (b) with Pd, treated in 5% H_2 + 95% N_2 atmosphere at 400 °C for 1 h.

cal resistance of this film treated in an H_2 atmosphere was measured from room temperature to 4 K, the resistance decreased with decreasing temperature. This suggested that the hydrogen-treated nickel–tin oxide film had a metallic property. ESR of nickel–tin oxide film without Pd showed the high intensity of a broad signal, as shown in Fig. 8. Spin density is considered to decrease in the presence of Pd because the film was nearer to the metallic state. The doublet and the singlet produced by H_2 treatment in CEM spectra can be assigned to nickel–tin alloys, which were different from Ni_3Sn_2 (IS = 1.77 mm s^{-1}, QS = 1.27 mm s^{-1}) and Ni + 3%Sn (IS = 1.4 mm s^{-1}) [10]. Because about 0.1 wt % hydrogen was detected in the sample scraped off the coated glass by gas chromatography, a doublet may originate from the nickel–tin hydride. When the nickel–tin oxide reduced in H_2 was heated again in air at 400 °C, a doublet of Sn(II) with a very low intensity remained, although the singlet was converted to peaks of Sn(IV) species.

3.5. Hydrogen spillover on tin oxide materials

The types of spillover mechanism, reviewed by Conner *et al.* [11], represent three cases where spillover may occur: (A) metal (activator) on a support, (B) metal (activator) on a support with an admixed support (acceptor), and (C) metal (activator) on a support

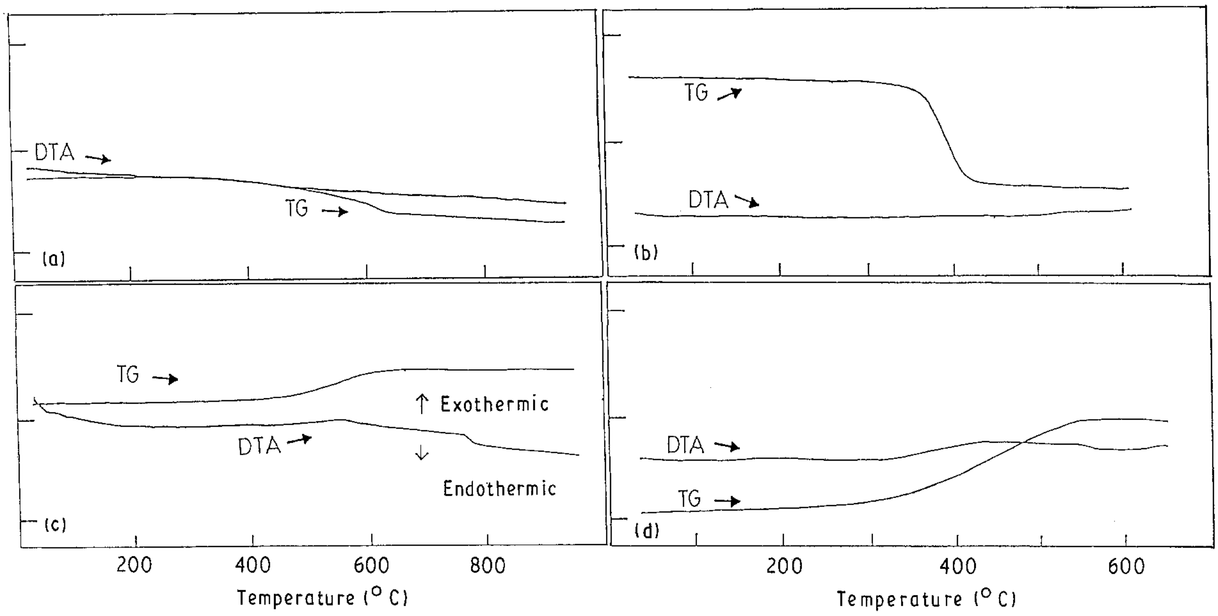

Figure 7 Simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) for samples of manganese–tin oxide and nickel–tin oxide. Heating rate 10 °C min^{-1}. (a) Manganese–tin oxide in 4.5% H_2 + 95.5% He atmosphere. (b) Nickel–tin oxide in 4.5% H_2 + He atmosphere. (c) Manganese–tin sample reoxidized in air after H_2 treatment as in (a). (d) Nickel–tin sample reoxidized in air after H_2 treatment as in (c).

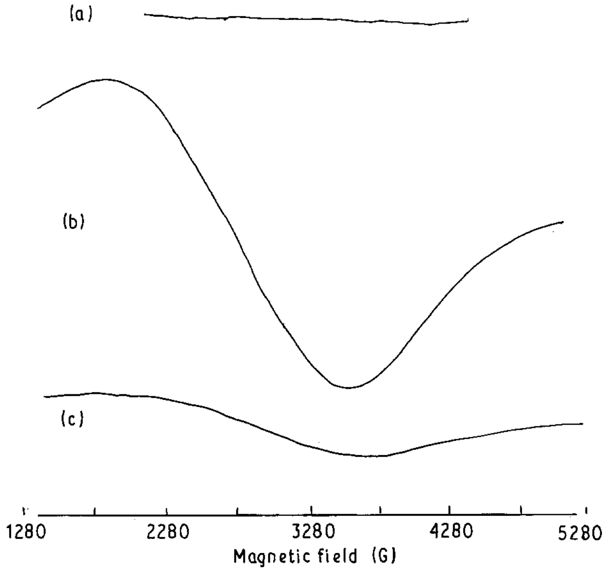

Figure 8 ESR spectra of nickel–tin oxide (5:1 mole ratio) with and without Pd treated in air or in 5% H_2 + 95% N_2 atmosphere at 400 °C for 1 h. (a) Nickel–tin oxide treated in air. (b) Nickel–tin oxide treated in an H_2 atmosphere. (c) Nickel–tin oxide with Pd treated in an H_2 atmosphere.

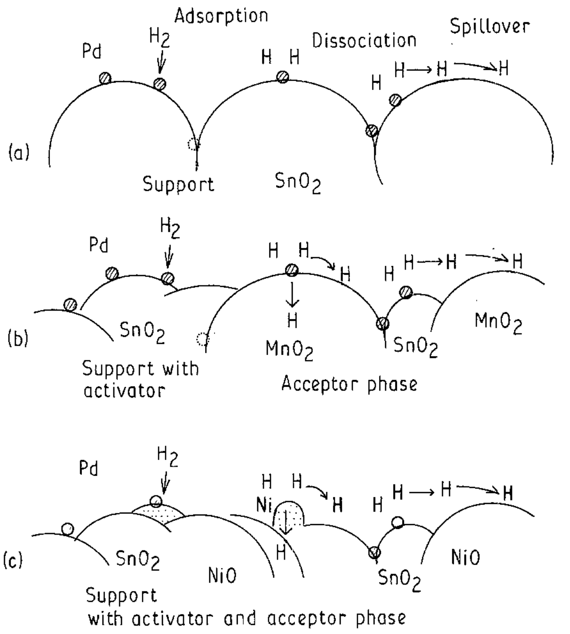

Figure 9 Schematic diagrams of three types of spillover. (a) metal (activator: Pd) on a support (tin oxide), (b) metal (activator: Pd) on a support (manganese–tin oxide) with an admixed support (acceptor: manganese oxide), (c) metal (activator: Pd and Ni) on a support (nickel–tin oxide) with a reactant (acceptor: nickel and tin oxide).

with a reactant (acceptor). Only tin oxide film with Pd used in this report belongs to type A. H_2 was adsorbed and activated on Pd, and spiltover H_2 was transferred on to the tin oxide surface. However, because there is no acceptor other than tin oxide in this case, spiltover H_2 cannot be trapped so strongly that the bulk reaction of tin oxide can take place. The chemical state of tin oxide varies very little, and spiltover H_2 ions recombine with each other or react with adsorbed O_2 in the form of anion on the top surface to form H_2 or water molecules.

In the case of manganese–tin oxide film doped with Pd, manganese oxide reacts as an acceptor of activated hydrogen and reduces to form Mn^{2+} species. However, the bulk of the tin oxide grains remains almost unchanged because Mn^{2+} cannot reduce Sn(IV). This phenomenon is classified as type B.

In the case of nickel–tin oxide film with and without Pd, it is considered that the films contain a support with activator (Ni and Pd metals partially reduced) and acceptor phase (NiO). The reduction of nickel oxide was followed by metallization of Ni. The Ni metal can react with tin oxide as the couple Ni/Ni^{2+} is known to work as a catalyst [11]. Because these reactions could proceed continuously in H_2, considerable intensive peaks of reduced Sn species were observed in CEM spectra. The electrical conductivity changes at every site, the surface, bulk and neck of the grains. The difference between the modified tin oxide films described above is shown in schematic diagrams of three types of spillover, in Fig. 9.

4. Conclusion

The correlation of gas sensing mechanism and the change of substrate in tin oxide films, was attempted by characterizing the chemical states of these materials. The spillover effect of H_2 was confirmed by CEMS and ESR. The chemical state of Sn was affected in H_2, depending on the metal ions added to tin oxide. Although it has been predicted, in general, that the chemical state of tin oxide changes at one or two surface layers and the bulk does not change, a change of tin oxide in the bulk (μm thickness) was observed. The addition of Pd to both manganese–tin oxide and nickel–tin oxide was effective for increasing the sensitivity towards inflammable gases to the same degree [7]. However, the surface interaction of the films with H_2 was found to be different among the modified tin oxide films. The tin oxides can be classified as follows from the view point of Pd catalysis to an H_2 trap: tin oxide, manganese–tin oxide and nickel–tin oxide are representative materials for case A of the primary spillover effect, case B of secondary spillover effects (activator and acceptor phases were separated from each other), and case C of secondary spillover effects (activator and acceptor were supported on the same grains), respectively.

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References

1. T. SEIYAMA, A. KATO, K. FUJIISHI and M. NAGATANI, *Anal. Chem.* **34** (1962) 1502; Toguchi, US Pat. 3603 954 (1970).
2. S. R. MORRISON, *Sensors Actuators* **12** (1987) 425.
3. S. MATSUSHIMA, Y. TERAOKA, N. MIURA and N. YAMAZOE, *Jpn. J. Appl. Phys.* **27** (1988) 1798.
4. J. KURIACOSE, *Ind. J. Chem.* **5** (1957) 646.

5. G. C. BOND, M. J. FULLER and L. R. MOLLOY, in "Proceedings of the 6th International Congress on Catalysis 1976", Vol. 1, edited by G. C. Bond *et al.* (The Chemical Society, London, 1977) p. 356.
6. E. W. THORNTON and P. G. HARRISON, *J. Chem. Soc.* **71** (1975) 461.
7. K. NOMURA, Y. UJIHIRA, S. S. SHARMA, A. FUEDA and T. MURAKAMI, *J. Mater. Sci.* **24** (1989) 225.
8. G. C. BOND, in "Spillover of Adsorbed Species", edited by G. M. Pajonk, S. J. Teichner and J. E. Germain (Elsevier Science, Amsterdam, 1983) pp. 1–16.
9. K. NOMURA and Y. UJIHIRA, *Bunsekikagaku* **33** (1984) T81.
10. H. Z. DOKUZOGUZ, H. H. STADELMA and L. H. BOWEN, *J. Less-Common Metals* **23** (1971) 245.
11. W. C. CONNER Jr, G. M. PAJONK and S. J. TEICHNER, *Adv. Catal.* **34** (1986) 1.

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