Characterization of tin oxide films gas sensor by in situ conversion electron Mössbauer spectrometry (CEMS)

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119Sn conversion electron Mössbauer spectrometry was applied to analyse tin oxide films in order to clarify the sensitization mechanism to a hydrogen gas. The reduced Sn(II) species was detected in the presence of mixed oxides and doped Pd in tin oxide films. Spillover effect of hydrogen is discussed between these metal mixed tin oxide films. In situ CEMS at working temperatures of the gas sensor showed no reduced tin species, but Mössbauer parameters of Sn(IV) oxides changed in coincidence with the temperature, which specifies the gas sensing function.

1. Introduction

Tin oxides with a certain additive have been used for detecting various inflammable gas. The addition of catalysts such as Pd and Pt promoted the dissociation of hydrogen or hydrocarbons [1]. The property of sensor is affected by many factors such as the defects of oxide structure, grain size, grain boundary, morphology as well as the additive. The earlier study using conventional transmission Mössbauer spectroscopy [2] confirmed the production of reduced tin (II) species in tin (IV) oxide by the introduction of CO after the evacuation at high temperature. In our previous report [3], manganese mixed tin oxide and nickel mixed tin oxide films doped with Pd showed several ten times higher sensitivity to alcohol and hydrogen than tin oxide doped with Pd. Bismuth mixed tin oxides have a high selectivity to CO although the sensitivity was low [4].

There are two possible mechanisms for sensitization, that is, electric sensitization and chemical sensitization [5]. When tin oxide with Pd is exposed to inflammable gas, adsorbed oxygen on Pd is released, which results in decrasing the potential barrier and releasing the attracted electrons to the surface back into the bulk of tin oxide. In the former case, the state change of tin cannot be expected at low temperature. In the latter case, however, the state change should be observed if the spillover of inflammable gas occurred at a certain temperature.

In order to clarify the interaction mechanism between inflammable gas and tin oxide or supported other oxides, the change of chemical state of tin in these oxides were studied by 119Sn Mössbauer spectrometry (CEMS) at room temperature and at the working temperatures of gas sensing.

2. Experimental details

Tin oxide based films were prepared on an aluminium nitride plate by spray pyrolysis of methanol solution of SnCl₂ and other metal chloride [3]. CEM spectra were observed by a backsatter gas flow detector [6], in which a heater was included. In situ 119Sn CEMS was also applied to chemical state analyses of tin oxides gas sensor at working temperature up to 500°C in flowing 1% isobutane, 5% CO, or 5% CH₄ and He balance gas. About 10 MBq of 119mSn (BaSnO₃) source and 1 GBq of 57Co(Rh) were used. IS and Doppler velocity were calibrated using BaSnO₃ and α-Fe for 119mSn CEM spectra, respectively.

3. Results and discussion

3.1. Ex situ measurement of tin oxides for gas sensor

CEM spectra of several kinds of tin oxides films doped with Pd were measured after hydrogen treatment and shown in fig. 1. The electrical resistance of tin oxide film decreased with temperature in vacuum, but increased at 310°C and decreased again at 400°C in air [7]. In CEM spectra of tin oxide film (30 nm thick) heated at 400°C in vacuum of 13.3 Pa, Sn(II) species of IS = 2.75 mm/s and QS = 2.17 mm/s was found to be produced in the tin oxide film. Reduced Sn(II) species could not be detected in tin oxide film annealed at 400°C in 5% H₂+N₂ atmosphere for 1 h, but in the presence of Pd a shoulder appeared at IS = 1.7-2.1 mm/s. A partial reduction of tin oxide was found to result from the release of lattice oxygen through migrations of atomic hydrogen decomposed at Pd sites.
Manganese mixed tin oxide and nickel mixed tin oxide films doped with Pd showed several ten times higher sensitivity against hydrogen than tin oxide film doped with Pd [3]. Manganese mixed tin oxide films (Mn:Sn = 5:1, ∼200 nm thick) with and without Pd coating in a part or a whole did not show a large change in the $^{111}$Sn CEM spectra after the hydrogen treatment. But only in the ESR spectrum of Mn mixed tin oxides with Pd, a broad signal was observed [7]. It reduced in a strong interactions of Mn$^{2+}$ ($I=5/2$) ions. Hydrogen was decomposed at Pd site and migrated towards MnO$_2$ grains through tin oxide. In this case, manganese oxide reacts as an acceptor of hydrogen under the presence of Pd.

In both CEM spectra of nickel mixed tin oxide films with and without Pd after hydrogen treatment, reduced tin species were observed. Reduced peaks were composed of a doublet with IS = 1.59-1.89 mm/s and QS = 1.2-1.5 mm/s and a singlet with IS = 1.4-1.5 mm/s. Since the parameters were different from those of Ni$_x$Sn$_2$ (IS = 1.77 mm/s, QS = 1.27) [8], and contained 0.1 wt. % hydrogen, a doublet may be assigned to nickel tin hydride and a singlet to metallic tin doped in nickel such as Ni +3%Sn alloy (IS = 1.4 mm/s) [8]. Nickel oxide was found to play a role of activator together with Pd metals and acceptor phase.

The chemical state of tin in tin oxide films varied depending on the presence or absence of activator and acceptor on the supported oxide. The phenomenon of spillover is an important symptom of the close interaction between doped metal and supported oxide. The spillover hydrogens reside in the surface on the second phase of supported oxide, partially diffuse into it and reduce the bulk of the metal oxide, and partially are recombined.

3.2. In situ measurement of tin oxides for gas sensor

In situ CEM spectra were measured for bismuth mixed tin oxide (Bi:Sn = 1:5) films in 5%CO + 95%He and 5%CH$_4$ + 95%He atmospheres [9] at various temperatures. Reduced Sn(II) species could not be detected but the peaks of Sn(IV) was a little affected by an interaction with incoming gas. Mössbauer parameters of a doublet of Sn(IV) oxide changed in the function of working temperature as shown in fig. 2. A larger decrease in isomer shift (IS) was observed with increasing temperature than a second order Doppler shift of 0.03 mm/s at 500°C. This suggests that the
state of Sn(IV) became more ionic by the interaction with each gas. It was at 200°C and 350°C that tin oxide interacted with CO and CH₄, respectively. The splitting (QS), and FWHM of this species also changed, depending on gas and temperature. These changes supported the resistance change of bismuth tin oxide sensors in each gas atmosphere. CEM spectra of tin oxide doped with Pd were also measured in a 1% iso-butane atmosphere [10]. The Mössbauer parameters started to decrease at 350°C, since this film was not so sensitive. These parameters are found to reflect a dynamic reaction with each gas.

4. Conclusions

¹¹⁹Sn CEMS was applied to the observation of interaction between gas and tin oxide. It was found that CEMS has a possibility to evaluate gas sensor materials. Two types of electronic sensitization and chemical sensitization as gas sensing mechanisms are depending on additives in tin oxide. The intermediate compounds on the process of gas sensing were detected by CEMS and the gas sensing mechanisms were characterized. In situ CEMS showed that IS, QS and FWHM of Sn(IV) in Bi mixed tin oxide film started to change at 250°C in CO atmosphere and at 400°C in CH₄ atmosphere. In situ CEMS is found to be useful for characterization of gas sensor mechanism by using inflammable gas as a quenching gas of He gas flow counter.

References