Mössbauer studies on tin-bismuth oxide CO selective gas sensor

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Tin-bismuth (Sn-Bi) oxide films prepared by spray-pyrolysis techniques were characterized by in situ conversion electron Mössbauer spectrometry in an atmosphere of CO and CH₄. The isomer shift of Sn⁴⁺ in Sn-Bi oxide decreased at 250 °C and 400 °C in CO and CH₄ atmospheres, respectively. An electrical resistance change was also observed at about 250 °C in CO atmosphere, which showed a selective behavior towards CO gas in comparison to CH₄ and C₂H₅OH gases. These results show that CO gas interacted with bulk as well as with the surface of Sn-Bi oxide at low temperature. The increase in the sensitivity of CH₄ and C₂H₅OH at temperatures around 400 °C at the expense of selectivity towards CO was interpreted in terms of surface as well as bulk interactions, and also the catalytic enhancement by reaction of decomposed products from CH₄ and C₂H₅OH.

I. INTRODUCTION

It is known that semimetal oxide films such as SnO₂ and ZnO have received significant commercialization in such fields as transparent conductors and gas sensors. The resistances of semimetal oxides are changed in different gaseous environments. These phenomena are used for the detection of various gases. The addition of p-type semiconductors to n-type semiconductors increased the electrical resistance, but improved the sensitivity to inflammable gases. The sensitivity of SnO₂ towards certain inflammable gases increased by adding other metal oxides together with a catalyst such as Pd. Films of SnO₂ are polycrystalline in nature and retain the tetragonal, rutile structure, with oxygen at the corners of a tetrahedron.

Bismuth oxide (Bi₂O₃) exists in at least four polymorphic states. The structure of Bi₂O₃ can be stabilized by suitable additives, heat treatments, and rapid quenching techniques. According to x-ray structural and NQR data, the Bi₂O₃ unit cell contains two crystallographic and chemically nonequivalent positions for Bi atoms. The BiO₃ polyhedra in A and B sites are distorted by different amounts. Position A is assigned to the NQR spectrum corresponding to a large quadrupole coupling constant (QCC) and a small asymmetry parameter of 10%, while position B corresponds to a smaller QCC and a large asymmetry parameter with a value of 38%. A local magnetic field on Bi in Bi₂O₃ was detected and was due to the partial removal of spin-orbit degeneracy as a result of the incomplete pairing of electrons of Bi atoms. These unpaired electrons enter the conduction band with Bi atoms acting as donors. SnO₂ and Bi₂O₃ have band gaps of 2.6 and 1.6 eV, respectively. By adding Bi₂O₃ to SnO₂, the band gap of SnO₂ can be modified for sensor applications. Earlier studies showed that patterns of catalytic reactions are related to the kinds of oxygen species involved, e.g., lattice oxygen and/or adsorbed oxygen. In olefin oxidation over Bi₂O₃·2MoO₃, lattice oxygen is a primary source of the O atoms required in olefin oxidation over Bi₂O₃·2MoO₃. Various types of oxygen species are reported on ZnO and SnO₂ by many workers. Most gases interact locally with anions of adsorbed oxygen (O⁻ and O₂⁻), which normally exist in equilibrium at the surface of oxides.

The adsorbed oxygen in the form of O₂ and O₂⁻ are normally adsorbed or desorbed below 150 °C, while O⁻ and O₂⁻ are adsorbed or desorbed above 150 °C. Lattice-oxygen species are important for gas sensing and selective reactions at higher temperatures. Points defects, such as oxygen vacancies and interstitial ions in the surface region, have a pronounced effect on oxygen adsorption. These vacancies may not only lower the work function in the near surroundings but also cause strain on the solid surface.

The SnO₂ based sensors are not selective to any reacting gas, because adsorbed oxygen in the form of anions was available to reacting gases. The Bi₂O₃ has a lower amount of adsorbed oxygen. Sn-Bi oxide was prepared by mixing SnO₂ with Bi₂O₃ for our studies because Sn-Bi oxide is considered to have less accumulation of chemisorbed oxygen and also can supply lattice oxygen for reaction selectivity and sensitivity. The scarcity of adsorbed oxygen can prevent Sn-Bi oxide from lowering reaction selectivity.

II. EXPERIMENTAL DETAILS

The Sn-Bi oxide films with various compositions were prepared by vacuum evaporation and spray pyrolysis methods with subsequent annealing in air. Films were prepared by spraying a 0.1 M methanol solution of SnCl₄·4H₂O and BiCl₃ with different molar ratios at regular 30 s intervals onto quartz glass or aluminum-nitride ceramic sheets heated to about 370 °C. These films were completely oxidized in air for several hours at 590 °C. Silver electrodes were printed on oxide films by vacuum evaporation, and these films were further annealed for 2 h at 590 °C.

The film thickness of samples was calculated from the weight difference before and after deposition of the film. The thicknesses of films were about 200 nm. Changes in electrical resistance of these films were...
measured by two-point electrode methods at various temperatures in various ambient atmospheres containing inflammable gases, such as CO, CH₄, H₂, and C₂H₅OH vapors. These gases were either passed or injected inside the 10-ℓ steel chambers at a known concentration. Tin states in the Sn-Bi oxide films were measured with a conversion electron Mössbauer (CEM) spectrometer, which was composed of a conventional Mössbauer spectrometer with a backscatter type of gas flow counter. The CEM spectra at room temperature and high temperatures up to 500 °C were measured by using a 95% He + 5% CH₄ or 95% He + 5% CO gas mixture at a flow rate of ≈5 ml/min as the counting gas. The temperature was precalibrated and regulated within the temperature range of ±5 °C. A 100 MBq (or 3 mCi)¹¹⁹Sn(BaSnO₃) source was employed with gamma rays perpendicular to the surface of the samples. The data were fitted, assuming the shape of the curve as two Lorentzians. Isomer shifts (ISs) were also calculated by taking into consideration different intensity ratios for the Sn⁴⁺ doublet state in Sn-Bi oxide films.

III. RESULTS

A. Electrical properties

Sn-Bi oxide films, with compositions of 15% to 75% Bi, showed resistances on the order of 0.4 - 1.1 M Ω/cm² at room temperature. The resistance of the film increased as the Bi content increased.

The electrical resistances of Sn-Bi oxide were measured in various inflammable gases (≤1000 ppm) such as CH₄, CO, H₂, and C₂H₅OH vapors in air at 250 °C. Appreciable changes in resistance were observed with CO. Other gases showed little or no change in resistance. Thus, Sn-Bi oxide film shows a selective behavior towards CO.

Operating temperatures (T_m) of SnO₂ for CO gas were around 450 °C. The T_m of SnO₂ can be altered or modified using certain suitable dopants. The T_m values for the SnO₂ films doped with Bi₂O₃ were also reduced to 250 °C, resulting in a selectivity for CO gas with a Sn:Bi ratio of 5:1. Lower percentages of Bi in Sn-Bi oxide film showed higher sensitivity as well as selectivity. With the increase of Bi content over 20% in Sn-Bi oxide films, the sensitivity towards various gases decreased. Sn-Bi oxide (5:1) was selected for Mössbauer studies because this ratio showed good response to gases and also preserved selectivity at low temperatures towards CO gas. Figure 1 shows the variation of resistance of Sn-Bi oxide film with temperature in different gas environments. As the temperature is increased, the resistance of the Sn-Bi oxide (5:1) film decreased up to 300 °C in air, increased up to 400 °C, and then decreased again. The initial decrease in resistance is caused by desorption of OH⁻ and O₂⁻ ions adsorbed at the surface of the Sn-Bi oxide. The increase in the resistance is caused by the shift in the equilibrium of reversible adsorption and desorption of O⁻ and O²⁻ ions. The number of electrons decrease because electron transfer to the chemisorbed oxygen resulted in an increase in the potential barrier due to build-up of the positive space-charge region at the surface. The reactive affinity of different gases is different towards adsorbed oxygen. The change in resistance for Sn-Bi oxide films below 300 °C for CO gas (1002 ppm in air) was very large. Due to the reaction of gas with chemisorbed oxygen, the positive space charge is suppressed, resulting in a return of electrons to the lattice, and thereby, resistance of the Sn-Bi oxide film decreases. The reacting CO is desorbed in the form of CO₂ because of the greater affinity of CO towards adsorbed oxygen anions. Some of the lattice oxygen also diffuses at the surface to compensate for the consumed adsorbed oxygen anions. The diffusion of oxygen at the surface caused larger perturbations in the lattice and bulk. These changes were also reflected in the CEM spectra after CO adsorption, which are discussed later. A change in resistance for CH₄ gas was observed at temperatures above 400 °C. As temperature increased in an atmosphere of C₂H₅OH, the sensitivity increased, as shown in Fig. 2. The increase in sensitivity towards C₂H₅OH can be attributed to the enhancement of

FIG. 1. Variation of electrical resistance of Sn-Bi (5:1) oxide films with temperature for (a) Air, (b) CH₄ (989 ppm in air), and (c) CO (1002 ppm in air).

FIG. 2. Variation of sensitivity with C₂H₅OH concentration for Sn-Bi (5:1) oxide films at various temperatures.
conductivity by decomposed products of C$_2$H$_5$OH at the surface and the bulk of the oxide in the vicinity of 390°C.

B. Structure and chemical state

Figures 3 and 4 show the in situ CEM spectra for Sn-Bi oxide (5:1) films in 5% CO + 95% He and 5% CH$_4$ + 95% He atmospheres at various temperatures, respectively. Sn-Bi oxide films were exposed for one day at each temperature during measurements. The state of Sn$^4+$ was a little affected by the interaction with incoming gases, especially CO gas. A decrease in IS was observed with increasing temperature, as shown in Fig. 5.

The adsorbed oxygen atoms in the tin oxide and lattice oxygen atoms in bismuth oxide matrices are partially responsible for the surface and bulk reactions, and for respective or concurrent changes in IS and resistance. Interaction of CO is limited by adsorption, and the reaction is also limited by desorption in the form of CO$_2$. These short-range interactions of CO with the Sn-Bi oxide system resulted in a large change in IS. The second-order Doppler shift (SDS) for Sn compounds between room temperature and 400°C is changed by about 0.03 mm/sec. The contribution from SDS in our results contains 30% at highest in IS. A larger variation was observed in the resistance as compared to other gases. The long-range interaction of CH$_4$ can be thought of as a physisorption rather than chemisorption at temperatures below 400°C. The dissociation of CH$_4$ does not take place on the surface of the oxide materials at lower temperatures than 400°C. The changes in the IS by reaction of CH$_4$ were also small at lower temperatures. These changes in IS supported the electrical resistance changes.

In the CEM spectra of Sn:Bi oxide (5:1) films, doublet peaks with large quadrupole splitting (QS) for Sn atoms were observed, as shown in Fig. 6. The large QS can be
attributed to many defects in the lattice of Sn-Bi oxide matrices.

If all of the six positions of oxygen in the corners of an octahedron are occupied at the correct positions, this leads to a vanishing value of the electric-field gradient tensor (EFG) at the tin-atom lattice point, and hence the QS is zero. If all of the O-Sn-O bond angles are either $\pi$ or $\pi/2$, QS is not observed. But if there is a deformation or conformational change due to the repeated twinning of oxygen octahedra around tin atoms, a distorted (noncubic) charge distribution and nonvanishing EFG tensor will appear, resulting in a QS.

From peak intensity ratio ($P_i$) of the Sn$^{4+}$ doublet in the Sn-Bi oxide films during interaction with CO and CH$_4$ gases, the corresponding values of $\theta$ were calculated. Assuming the asymmetry parameter of the electric field gradient (EFG) to be zero, $P_i$ is given by the following formula:

$$P_i = 1 + \cos^4 \theta/(1 + \sin^2 \theta),$$

where average angle ($\theta$) is the angle between propagation of the incident gamma rays and the direction of the principal axis in the EFG. The change of $\theta$ in a CO atmosphere was larger than with a CH$_4$ atmosphere. These changes in $\theta$ also supported the rearrangement of the Sn-Bi oxide lattice by reaction with CO or CH$_4$ gases.

### IV. DISCUSSION

CO reacts with chemisorbed oxygen in the ion radical state. Bi sites served as adsorption centers for CO at Bi sites on the surface.

CEM spectra showed large changes in the IS, QS, and FWHM during interaction with CO due to the conformational changes in bond angles and/or rotation about one or more symmetry axes without bond breakage. In the initial stages of reaction at low temperatures, the perturbation region was small and localized in a particular region. After reaction of incoming gas with chemisorbed oxygen, the perturbation region increased with an increase of temperature. As temperature increased, many lattice oxygen atoms try to diffuse to the surface, forming anions and reacting with incumbent CO. Large perturbations in electron density resulted in a large variation in the IS.

The decrease in IS was due to a change in the configuration around Sn atoms by reduction of the bismuth-oxide matrix in the initial stages of the reaction. A reaction mechanism can be visualized in which only surface adsorbed oxygen atoms do not take part in the reaction, but lattice oxygen atoms also take part. The partial reduction of Bi$_2$O$_3$ also results in the movement of lattice oxygen to the surface to form anions and causes lattice distortion, or changes, in thermal entropy. Some oxygen atom deficiencies in the Bi-oxide lattice can be shared by oxygen atoms in Sn oxide. Thus, the electron density surrounding the Sn atom will be reduced, which results in a decrease in the IS.

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The sensitivity towards gases other than CO was less at 230 °C, and very small changes were observed in IS, QS,
FIG. 7. Variation of "full width at half maximum" (F/2) with temperature for Sn-Bi (5:1) oxide film exposed to (95% He + 5% CH₄) and (95% He + 5% CO) gas.

and FWHM in the CEM spectra of Sn oxide exposed in a CH₄ atmosphere. It is considered that CH₄ is physisorbed below 400 °C, and that dissociation of CH₄ takes place above 400 °C.

It is known that the electric field acting on the nucleus consists of two parts; one is a static field determined by the mean position of the Sn atoms, and the other a dynamic field connected by thermal motion. The change in the average position of the tin atoms and the amplitude of the thermal vibrations due to the movement of lattice oxygen will result in a decrease in the QS. The QS in Sn-Bi oxide films gradually decreased due to interactions with CO and CH₄. The changes were approximately of the same magnitude for CO and CH₄, although they occurred at lower temperature for CO than for the CH₄ atmosphere.

When full line width at half maximum (FWHM) were compared for interactions of Sn-Bi oxide with CO and CH₄ gases in Fig. 7, the increase up to 400 °C was larger with CO as compared to CH₄. This may be affected by changes in the values of distortion at A and B sites in the bismuth-oxide structure. A decrease in the CO and CH₄ atmospheres was observed for temperatures greater than 400 °C. This can be attributed to a decrease in lattice distortions, and also a decrease in thermal entropy and orientation. Part of the increase in FWHM is influenced by the dynamic field of the lattice, which leads to natural broadening of the resonance line due to a partial contribution from SNS.

Large changes in the average angles (θ) of CEM spectra with temperature were also observed in CO gas atmospheres, as shown in Fig. 8. It shows that a large amount of rearrangement takes place in the lattice. A change in the environment around Sn atoms can be attributed to rearrangements of the Bi—O bond and O-Bi-O angle due to the release of lattice oxygen. In the case of interactions with CH₄, the value of θ was almost constant with the increase in temperature. This suggests that there were few changes in surface rearrangements of Sn-Bi oxide.

Asymmetry in the intensity of the two components of

the Sn⁴⁺ doublet in Sn-Bi oxide may be partially related to conformational changes and to anisotropy of the Lamb-Mössbauer factor (i.e.,Goldanskii-Karyagin effect; if temperature is decreased the intensity ratio for the doublet approaches unity) as observed in dimethyl tin difluoride.

The Sn-Bi oxide film was sensitive and selective towards CO. But at high temperature, the sensitivity towards CH₄ and C₂H₅OH were higher, as shown in Fig. 2. The C₂H₅OH also interacts locally with the oxygen ions adsorbed at the surface by forming reaction products such as CO, CO₂, H₂, and H₂O, which are electron donors, because the decomposition of C₂H₅OH is considered to take place above 390 °C into basic constituents.

As weak chemisorption predominates at lower temperatures, the surface coverage of donor species is small and resistance changes are small. As temperature increases, the fraction of strongly adsorbed donor species increase, and large electrical resistance changes are observed. These anomalies can be attributed to appreciable surface reactions at higher temperature for CH₄ and C₂H₅OH with Sn-Bi oxide film, resulting in an increase in sensitivity.

V. CONCLUSIONS

The characteristics of Sn-Bi oxide films have been investigated in different ambient atmospheres of CH₄, CO, H₂, and C₂H₅OH. Changes in the electrical resistance of the Sn-Bi oxide film were observed in a CO atmosphere at about 250 °C. The result showed high sensitivity and selectivity to CO as compared to C₂H₅OH and H₂. But the sensitivity towards C₂H₅OH and CH₄ increased as temperature increased. These surface and bulk reactions were enhanced by decomposition and desorption products as an electron donor. The reaction mechanism was also discussed on the basis of the characterization of the Sn⁴⁺ state of Sn-Bi oxide films as compared with that of tin-oxide films using in situ CEM spectrometry. Lattice oxygen, in addition to surface adsorbed oxygen at higher tem-
perature, plays an important role in the larger variation of the Mössbauer parameters (i.e., IS, QS, and FWHM) as well as changes in electrical resistance. We have shown for the first time that the data observed from the in situ CEM spectrometry can support the electrical resistance data as well as models of absorption and desorption of inflammable gases, especially CO.

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