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Fabrication and Characteristics of High-performance Doped - SnO_2 Thin Films for Explosive Gas Sensor

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Long term stability, sensitization in air, and gas sensing behaviors of tin oxide films were investigated with doping of antimony and palladium. The tin oxide films were prepared on a Corning glass by reactive rf sputtering method and tested for detection of hydrogen gas. Sb-doping improved a long-term stability in the base resistance of SnO_2 film sensor. A small amount of Pd doping caused the optimum sensor operating temperature to reduce and also enhanced the gas sensitivity, compared with the undoped SnO_2 film. Gas sensitivity depended largely on the film thickness. The important sensitization reactions for sensor operating were $(O_{2ads}) + e^- \text{----> } 2(O_{ads})^-$ on the surface of SnO_2 film at elevated temperature in air and a followed reaction of hydrogen atoms with $(O_{ads})^-$ ions.

Key words : Tin oxide, Thin film, Gas sensitization, Doping

I. Introduction

Thin films of tin oxide have drawn a increasing interest once again during last decade in view of their promising application to a high performance sensor integrated in a silicon chip with current solid-state technologies.[1] Thin film sensors fulfill the requirements of low cost due to mass production, high sensitivity, and miniaturization. Thin films are fairly suitable for gas sensing, because they have a large surface to volume ratio and of fast adsorption-desorption processes on their surfaces. Thin film sensors can also simplify the sensor fabrication variables by controlling film thickness and result in reproducible fabrication, compared with sintered sensors.[2] For the sintered gas sensor, neck size connecting adjacent grains is also an important factor which determines the gas sensitivity.[3] Nevertheless, the neck size is not simply controlled since the neck size can be changed by various experimental conditions such as particle size used, sintering temperature, and sintering time etc. Recently, tin oxide films have been prepared by various deposition techniques and investigated on gas sensing characteristics.[4,5] To improve the gas sensing characteristics, small amounts of additives such as Pd and Pt were added to tin oxide films. However, effects of additives and film thickness on gas sensing characteristics of tin oxide have been scantly studied.[6,7] As well, tin oxide sensors still bear a problem of long-term stability. The experimental results of such investigations are present and discussed in this work.

II. Experimental Procedure

1. Film preparation

Undoped and doped tin oxide films were prepared on Corning 7059 glasses by reactive rf-magnetron sputtering technique. Those films were obtained by sputtering four kinds of metal targets of Sn, Pd-Sn, Sb-Sn, and Pd-Sb-Sn under a plasma status of argon-oxygen gas mixture with a planar magnetron. The substrate was kept floating and rotating in the system. The distance between substrate and target was about 9.5 cm. Before starting the deposition, the base pressure inside the sputtering chamber was brought down to less than 10^{-6} torr. The substrates were heated to 400°C and maintained for about 1 hour for outgassing. The target surface was cleaned by sputter etching in argon at a pressure of 2 mtorr for about 10 min. Argon and oxygen gas were injected to the reaction chamber in flow of 10 sccm (standard cc/min) and 5 sccm through mass flow controllers, respectively The operating pressure was kept at 1.5 mtorr with the help of a throttle valve The films started to be deposited by supplying rf power of 30 watt.

2. Sample selection and characterization

The film thickness was measured using scanning electron microscope (SEM) and Ellipsometer. Microstructure of the deposited films was studied by transmission electron microscopy (TEM). Doping contents of Pd and Sb in the film were analyzed by Auger electron spectroscopy (AES). The doping contents of Pd and Sb in the film were quasi-quantitatively analyzed by AES.

The films deposited at 400°C were basically SnO_2 polycrystalline and consisted of microcrystals less than ~100Å in size. However, tin oxide films deposited at room temperature were nearly amorphous and found to be insensible to hydrogen gas. For the study on gas sensing behaviors, the films prepared at 400°C were selected.

To measure the gas sensitivity, a chamber of 50×50×50 cm^3 in volume was constructed. A heater was installed in center of the chamber. The hydrogen gas was introduced into the chamber through a flowmeter and stirred well by a fan. The sensor, which was attached to the silver paste as electode, was put on the heater. The gas sensitivity, S was defined as $S=(R_{air}-R_{gas})/R_{air}$ (%) in this study.

where, R_{air}: sensor resistance in air

R_{gas}: sensor resistance under detecting gas

The resistance changes of the sensor were measured by the multimeter and voltage detection method.

III. Results

1. Long-term stability in base resistance of SnO_2 films

SnO_2-based gas sensor for explosive gases is generally sustained at the high temperature of ~300°C to function effectively in air. Because the sensor operating mechanism is the change of the base resistance before and after exposing to detecting gas, it is important to stabilize the base resistance of sensor at the high temperature in air for the long term reliability of sensor. Figure 1 shows the change in the base resistance of the pure SnO_2 film as a function of the holding time in air. The films were maintained at 300°C, a typical sensor operating temperature. The base resistance of undoped SnO_2 film was very unstable in long term. The unstability in the base resistance of tin oxide film is arised from its conduction mechanism, where the electrical conduction is dominated by nonstoichiometry associated with oxygen vacancies as follows.

$$Sn^{+4}\,2e'_{\beta}\,O^{-2}_{2-\beta} \quad (V_o = V_o + 2e^-) \tag{1}$$

The oxygen vacancies react with an ambient oxygen gas, so the vacancy concentration varies toward an equilibrium, and thus the resistance. The equilibrium concentration of the oxygen vacancies depends on the ambient oxygen partial pressure and the temperature as follows.

$$O_o = \frac{1}{2}O_2(g) + V_o \tag{2}$$

$$[V_o] = K_{eq}(T)\cdot P_{O_2}^{-\frac{1}{n}} \tag{3}$$

On the other hand, Sb(7.53 wt%)-doped SnO_2 film showed a long-term stability of the base resistance in figure 1. The conductivity of the Sb-doped film is adequately explained by controlled valency mechanism instead of nonstoichiometry, as follows.[7]

$$Sn^{+4}_{1-x}\,e'_x\,Sb^{+5}_x\,O^{-2}_2 \tag{4}$$

This means that the conductivity of Sb-doped SnO_2 film can be stabilized and controlled by the amount of antimony without large regarding of oxygen vacancy concentration, subsequently make the film have a long-term stability in the base resistance, and consequently in gas sensitivity.

2. Sensitizations of SnO_2-based films

Figure 2 shows the resistance changes of Sb-doped tin oxide film with the heating temperature in pure nitrogen atmosphere The base resistance of the sample exponentially decreased with increasing temperature for the first heat-treatment. The drastical decrease of sample resistance with increasing temperature was attributed to not only the semicunducting characteristics of tin oxide, but also the desorption of the already ad-

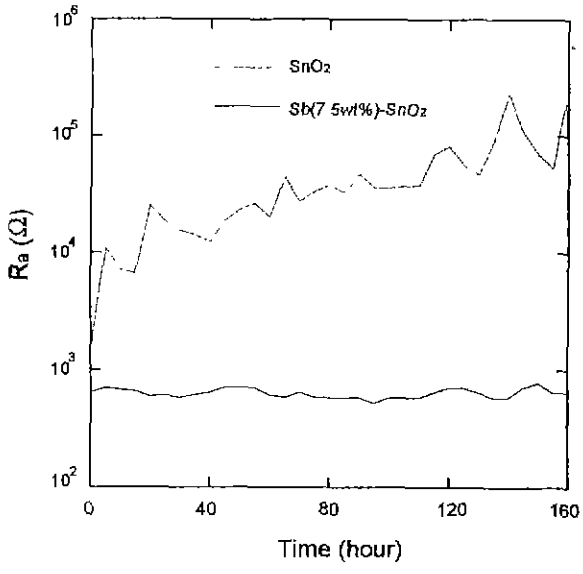

Fig. 1. Change of base resistance of as-deposited SnO_2 films with operating time (sensor operating temperature, 300°C).

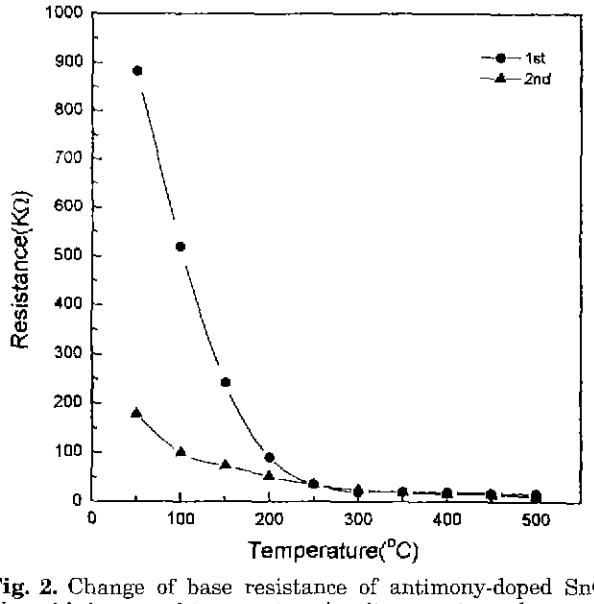

Fig. 2. Change of base resistance of antimony-doped SnO_2 film with increased temperature in nitrogen atmosphere.

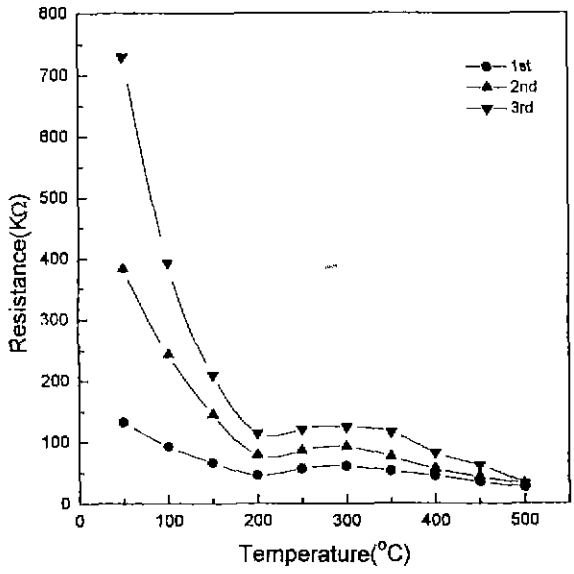

Fig. 3. Change of base resistance of antimony-doped SnO_2 film with increased temperature in oxygen atmosphere.

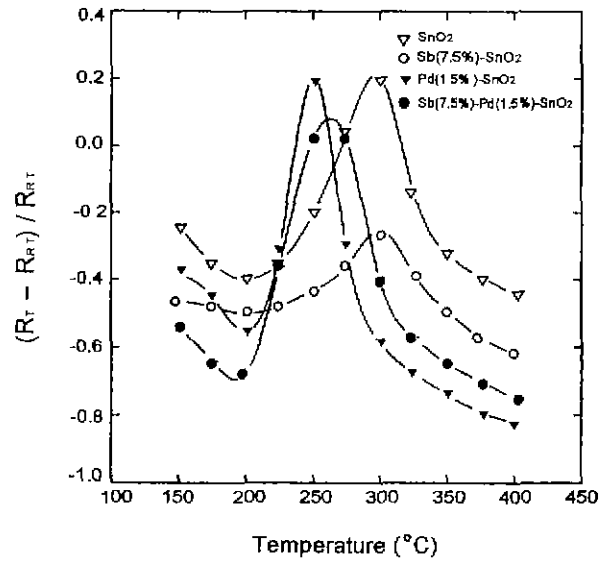

Fig. 4. Resistance-temperature relationships in air for various films.

sorbed oxygen on the film surface during the sample preparation in air atmosphere. In the second heat-treatment, the sample showed a gradual decrease of base resistance with increasing temperature, mainly due to its semiconductor behavior. The present sample was tested in pure oxygen atmosphere after the heat-treatment in nitrogen atmosphere. Figure 3 shows the resistance changes of the sample with heating temperature in pure oxygen atmosphere. The resistance variations with temperature in oxygen atmosphere were somewhat different compared with those in pure nitrogen atmosphere. The sample resistance steadily increased with the increasing temperature in the first heat-treatment. However, the sample resistance showed a sigmoid variation with temperature, and this behavior was stabilized after several repeating heat-treatments. This sigmoid variation with temperature is thought to be related with oxygen adsorption on the sample surface compared with one in nitrogen atmosphere of figure 2.

It was reported[8] that at room temperature $(O_{2\,ads})^-$ species covers on the film surface, reaction (5) takes place with increasing temperature and above approximately 450 K $(O_{ads})^-$ ions are found as the prevailing species.

$$(O_{2\,ads})^- + e^- \longrightarrow 2(O_{ads})^- \quad (5)$$

The transition causes an increase of surface charge density with consequent increase of sample resistance. It was, therefore, concluded that the appearance of sigmoid variation was due to the surface reaction of oxygen adsorbate took place at certain temperature range against the semiconductor behavior of tin oxide.

Figure 4 shows resistance-temperature relationships for various tin oxide films in air. All the samples basically showed the sigmoid variations in the base resistance with temperature. Our thin films showed similar increase of the resistance above ~200°C, which is well consistent with the report mentioned above. Ogawa et al.[9] reported the same resistance-temperature characteristics as those of Fig. 4. Maximum resistance in the sigmoid variation of Fig. 4 is considered to have related with a saturated adsorption of $(O_{ads})^-$ ions and the decrease in the resistance at higher temperature after maximum is considered due to the characteristics of a degenerated semiconductor associated with lattice oxygen vacancies.[10] However, the maximum temperatures varied with the doping element. Pd-doped films showed a maximum resistance at ~250°C, whereas undoped and Sb-doped films occurred at ~300°C. Palladium doping into the SnO_2 film is believed to activate the dissociation of reaction (5) which is a thermal process. Yamazaki et al.[11] also reported that the change in the film resistance occurred as a result of the oxidation, which became effective above around 500 K, and the change increased greatly by the addition of small amount of Pd.

3. Gas sensitivities of SnO_2-based films

All sensitivity measurements were conducted after an annealing at 300°C for more than ~10 hours in air for stabilization. Figure 5 shows the sensitivity to hydrogen gas as a function of operating temperature for the various films. As shown in figure 5, the sensitivity increased with increasing the operating temperature and was maximized at 300°C for the undoped SnO_2 film sensor. On the other hand, the Pd-doped SnO_2 film sensor exhibited the maximum sensitivity at ~250°C. Sb-doped film showed a similar trend to the undoped SnO_2 film, but a reduced sensitivity. Figure 6 shows the sensitivity changes with H_2 concentration for the undoped and for the Pd-doped SnO_2 film sensor. The operating temperatures were

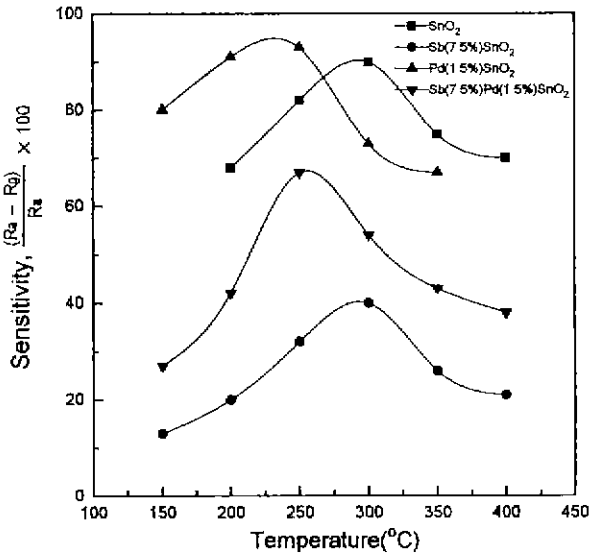

Fig. 5. Sensitivity as a function of operating temperature for various films.

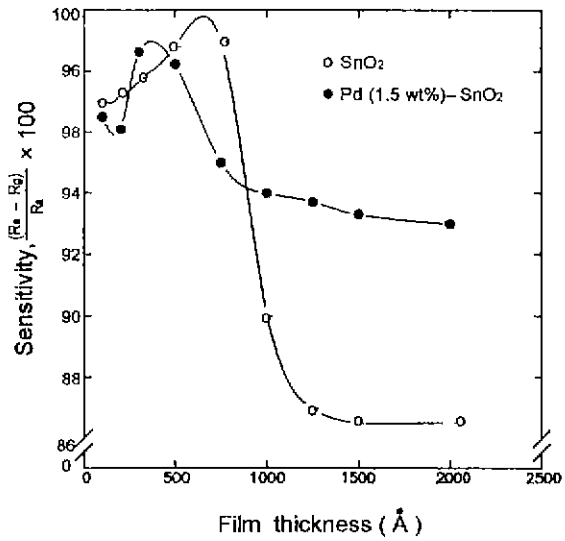

Fig. 7. Gas sensitivity as a function of film thickness for undoped and Pd-doped SnO_2 films (hydrogen concentration, 1000 ppm, sensor operating temperature, 300°C and 250°C for undoped and Pd-doped films, respectively)

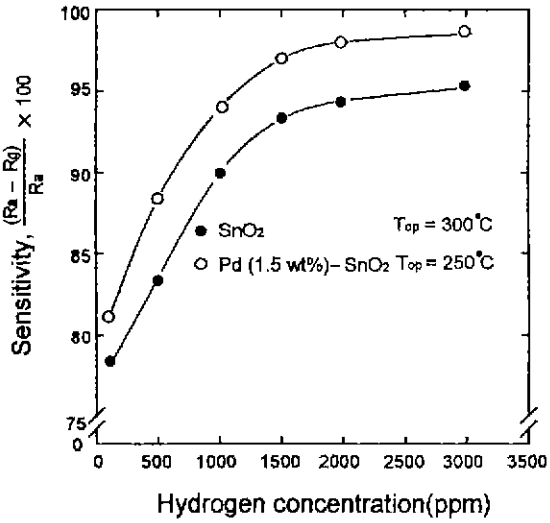

Fig. 6. Sensitivity changes with hydrogen gas concentration.

300°C and 250°C for the undoped and Pd-doped SnO_2, respectively. Figure 6 shows that the gas sensitivity improved with increasing Pd content compared with the undoped SnO_2 film. Yamazoe et al.[12] reported the significant changes in sensing response for H_2 and C_3H_8 gases by a 0.5 wt% loading of Pd into SnO_2. The sensitivity versus the operating temperature in figure 4 is similar to the results reported by Klober et al.[6] Dannetun et al.[13] reported, in study of the hydrogen sensitive Pd-MOS film, that the hydrogen molecules have a sticking coefficient of one and dissociate completely at 230°C on a Pd film. It is summarized in our experimental results that Pd doping improved the gas sensitivity and lowered the operating temperature at which the gas sensitivity became maximized. The results of figures 4, 5, and 6 are consistent with catalytic processes, induced by Pd addition,[16] where O_2 and H_2 each adsorb with considerably higher sticking coefficients and dissociation of the molecules are facilitated. The improvement of sensing characteristics can be explained by a spillover effect.[14]

Figure 7 shows the dependence of the gas sensitivity on film thickness for the undoped and Pd(1.5 wt%)-SnO_2 film sensors. The gas sensitivity increased with decreasing film thickness and was maximized at the film thickness of ~730Å for the undoped SnO_2 film. On the other hand, the sensitivity maximum appeared at the thickness of ~350Å for the Pd(1.53 wt%)-SnO_2 film. Further decreasing of the film thickness below critical thicknesses caused the sensitivity to drop again. It was reported[15] that the SnO_2 films prepared by ion beam sputtering showed a markedly high sensitivity in the thickness range of 40~600Å and that films thinner or thicker than these were relatively insensitive, at operating temperature of 300°C. Klöber et al.[6] reported that the Pd doped-SnO_2 film sensor exhibited the maximum sensitivity in the thickness range of 300~450Å for detecting H_2 gas and that the SnO_2 film thickness for maximum sensitivity was found to be dependent on the concentration of Pd additive. It is concluded from our investigations that the gas sensitivity depends largely on the film thickness. Suzuki et al.[16] suggested that the high sensitivity at a reduced film thickness was attributed to the rise of film resistivity in air(ρ_a) at the sensitivity function, $S=\rho_a/\rho_g$ (ρ_a: the resistivity in air, ρ_g: the resistivity under the detecting gas). On the other hand, Windischiman and Mark[17] suggested that the film sensor functions best when the depletion region generated by the chemisorbed oxygen is equal to the film thickness. The depletion region thickness is known to be a few

hundred Å for SnO_2. Our experimental results as to the high sensitivity at a reduced film thickness are compatible with theirs in trend and can be interpreted by their suggestions.[16,17]

IV. Discussion

When the surface of SnO_2 film is exposed to reducing gases, H_2, two processes (reaction 6, 7) can be considered for the increase of conductivity. In both cases, dissociations of hydrogen molecules are assumed to occur on the film surface.

$$2H + (O_{ads})^- \rightarrow H_2O(g) + e^- \quad (6)$$

$$H + O_{lat} \rightarrow (O_{lat}H)^+ + e^- \quad (7)$$

The hydrogen atoms react with $(O_{ads})^-$ already adsorbed on the film surface and subsequent desorption of the product. The reaction conseqently release electrons captured by $(O_{ads})^-$ ions, followed by the increase of conductivity (reaction 6). Hydrogen atoms adsorbed on the sensor surface provide donor electrons (reaction 7). It has not clearly established which reaction is mainly related to sensor operation. Pd effects on the sensing characteristics are well explained by spillover effect in the respect of dissociation of hydrogen molecules and get along with both processes. However, considering that the R_{air} vs. temperature relationships of figure 4 coincides in trend with ones of sensitivity vs. temperature of figure 5, we can presume that the former process is more relevant to sensitization mechanism. It is concluded that oxygen plays an important role in the sensitization mechanism of semiconductor gas sensors based on the surface properties of tin oxide film. Adsorption of oxygen on the film surface has a decisive influence on the surface conductivity and sensor operation. At elevated temperature for sensor operation, $(O_{ads})^-$ ions becomes prevailing species, and those are very active compared with other types of adsorbate, e. g., $(O_{2\,ads})^-$. Main reactions are adsorption of $(O_{ads})^-$ ions which act as surface acceptors, binding conduction electrons and diminishing the conductivity of the SnO_2 film, and followed by reaction (6).

In figure 7, further decrease below critical thickness caused the sensitivity to drop again. Their suggestions[16,17] are no more available to explain the sensitivity drop at further reduced film thicknesses below the critical value showing maximum sensitivity. The sensitivity drop is thought to be attributed to a substrate effect as follows. As the film begins to grow on the amorphous substrate of glass, the initial tin oxide layers become difficult to maintain a crystallinity due to lattice mismatch. This means that very thin tin oxide film loses the n-type conductivity which plays an important role in gas sensing. Thus, the film having further reduced thickness below a certain value become less sensible by losing the crystallinity. This consideration is compatable with the previous description that amorphous films were insensible to H_2 gas.

V. Conclusion

Sb-doping improved a long-term stability in the base resistance of the sensor. Resistance-temperature relationship of tin oxide film was a general semiconductor behavior in nitrogen atmosphere, whereas it showed a sigmoid variation due to oxygen adsorption in oxygen atmosphere. Main sensitization reactions were an oxygen adsorption of $(O_{ads})^-$ type on the surface of SnO_2 film at elevated temperature in air, and a followed reaction of hydrogen atom with $(O_{ads})^-$ ions. A small amount of Pd doping caused the optimum sensor operating temperature to reduce down to ~250°C and also enhanced the gas sensitivity, compared with the undoped SnO_2 film. Gas sensitivity depended largely on the film thickness. As the film thickness decreased, the sensitivity increased sharply. Further decrease of film thickness below critical values, however, caused to reduce the sensitivity again.

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