

Gas Sensitization of Tin Oxide Film by Resistance

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Gas sensitizations of tin oxide film were investigated by measuring the change of film resistance in various gas atmospheres such as N_2 , O_2 , H_2 , and H_2O . The main test sample, polycrystalline SnO_2 film containing small Sb as a dopant was prepared by a sputtering technique and showed a long term stability in base resistance and thus, in gas sensitivity. The adsorption of oxygen on the film surface as a type of $(O_{ads})^-$ at the temperature of around $300^\circ C$ played important roles in sensor operating mechanism. The roles were i) the increase of base resistance in ambient air, which consequently lead to high sensitivity and ii) the promotion of fast recovery. The reaction of hydrogen gas with the already adsorbed $(O_{ads})^-$ ions was considered as a decisive sensitization mechanism of tin oxide film. However, the dissociation of hydrogen molecules on film surface, followed by direct donation of electron to film also took a major part in the sensitization. The effect of humidity on gas sensitization was found to be negligible at the sensor operating temperature of around $300^\circ C$.

Key words : Tin Oxides film, Gas sensitization, Humidity effect, Sensor resistance

I. Introduction

Tin oxide films have been widely investigated on their electrical and optical properties for many practical applications.¹⁻⁴ The films were also exploited to fabricate high-performance gas sensor miniaturized on a silicon chip with the development of solid state electronics.⁵ The thin films are fairly suitable for gas sensing, because they have a large surface to volume ratio and fast adsorption-desorption processes on their surface.⁶

Tin oxide has an n-type semiconductor property due to its nonstoichiometric composition.⁶ In case of film, the conductivity of undoped tin oxide is ranged from semiconductor to insulator, depended on the composition of as-deposited film, and do not have long term stability in its base resistance because the film nonstoichiometry gradually varies through the reaction between film and ambient air.⁷ The conductivity of tin oxide films is also largely affected by the adsorption and desorption of ambient gases on the surface at moderate temperature. Even if the sensor operating mechanism of tin oxide is based on the change of base resistance in ambient air before and after exposing to detecting gas, the film resistance at various atmospheres were scantily investigated.⁸⁻¹⁰ The sensing mechanism of tin oxide film was not clearly established as well. In addition, it is important to stabilize the base resistance of the film in order to fabricate a gas sensor having a long-term reliability.

The purpose of our present work is to improve the stability in resistance of tin oxide film and to clarify the sensitizations of tin oxide film to O_2 , N_2 , H_2 and H_2O gases.

II. Experimental Procedures

1. Sample preparation

Undoped and Sb-doped tin oxide films were prepared on Corning 7059 glass by a reactive rf-magnetron sputtering technique. The films were obtained by sputtering metal targets of Sn and Sb-Sn in the gas mixture of argon and oxygen. The detailed method for the preparation of tin oxide films was described in the previous work.¹¹ The films prepared at $400^\circ C$ were chosen as samples because those films were basically SnO_2 polycrystalline, consisted of microcrystals of around 100 \AA in size, and showed excellent gas sensing behaviors. On the other hand, the film prepared at low temperature, e. g., room temperature were nearly amorphous and was insensible to reducing gases.

2. Sample resistance measurement

The platinum electrodes were fabricated on the surface of tin oxide film by sputtering technique and annealed at $400^\circ C$ in nitrogen atmosphere for 30 minutes. Platinum wire was used to connect the sample to a multi-meter or an electric circuit for measurement of the film resistance. A small assembly for measurement of sample resistance was placed in a quartz tube (30 mm in diameter and 500 mm in length) which was located in a resistance furnace, and connected to vacuum pump for purging the chamber. The whole system was protected from outer atmosphere. Schematic diagram of the measuring system was depicted in Fig. 1. High-purity gases of O_2 , N_2 and H_2 above 99.9993% were used to synthesize various atmospheres, and humidity in the chamber was artificially controlled

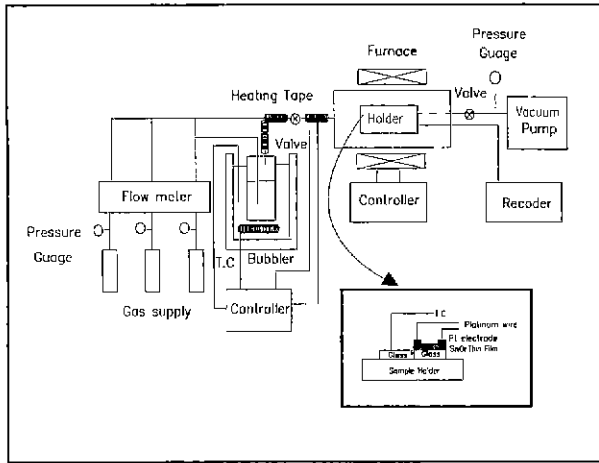


Fig. 1. Schematic diagram of sensor element and experimental apparatus for resistance measurement.

by introducing relevant amount of water gas, which was obtained from bubbling deionized water. The resistance change of sample was measured by a precise multi-meter.

III. Results and discussion

1. Long-term stability in base resistance of tin oxide films

The sensor operating mechanism of tin oxide is based on the change of the base resistance in ambient air before and after exposing to detecting gas. It is, therefore, important to stabilize the base resistance of sensor in ambient air for a long time in order to improve the sensor reliability. Fig. 2 shows the changes of base resistance for a pure SnO_2 film and $\text{Sb}(7.53 \text{ wt}\%)$ -doped SnO_2 film with the holding time in air, respectively. The films were maintained at 300°C , typical sensor operating temperature of tin oxide. The base resistance of the pure SnO_2 film was found to be very unstable in long term and gradually increase. It was also found from our experiments that heat-treatments of the pure tin oxide in air increased the resistance of pure tin oxide eventually to a very large value at which the sensor can not operate in the electrically pre-designed circuit. The unstability in base resistance of tin oxide film arise from its conduction mechanism, where the electrical conduction is dominated by nonstoichiometry associated with oxygen vacancies as follows.



The oxygen vacancies react with an ambient oxygen gas, and thus, the vacancy concentration of tin oxide varies toward an equilibrium as follows.



As the equilibrium concentration of oxygen vacancies depends on the ambient oxygen partial pressure and the

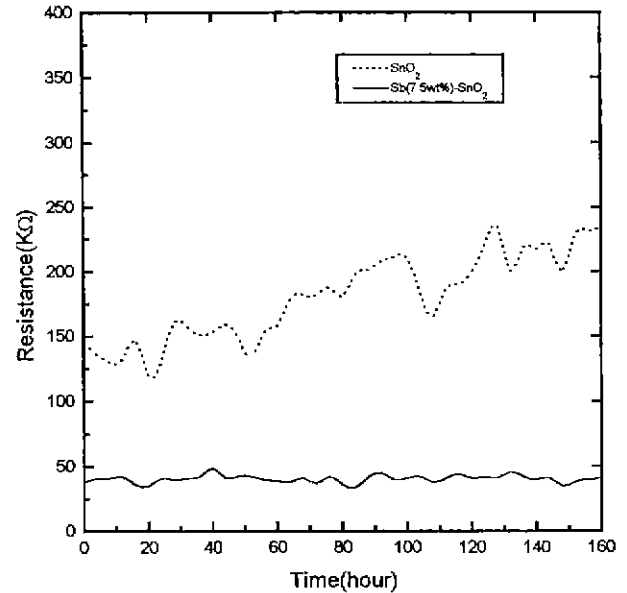


Fig. 2. Change of film resistance as a function of operating time in air (operating temperature, 300°C).

temperature, as-deposited tin oxide film is fundamentally unstable in its base resistance.

On the other hand, $\text{Sb}(7.53 \text{ wt}\%)$ -doped SnO_2 film had a long-term stability of the base resistance as shown in Fig. 2. The conduction mechanism of Sb -doped SnO_2 film was adequately explained by controlled valency mechanism as follows.⁶⁾



This means that the conductivity of Sb -doped SnO_2 film is dominated by antimony dose instead of nonstoichiometry. Because the film conductivity depends mainly on the antimony dose, the change of oxygen vacancy concentration by an ambient condition has little influence on the film resistance. Consequently, Sb -doped SnO_2 film has a long-term stability in the base resistance, and thus, in gas sensitivity.

2. Gas sensitizations of tin oxide film

Because the small Sb -doped SnO_2 film showed a long-term stability of base resistance in air, the Sb -doped SnO_2 film was investigated on its sensitizations. Fig. 3 shows the resistance changes of the tin oxide film with heating temperature in pure oxygen atmosphere. During the first heat-treatment up to 500°C , the sample showed gradual increase of resistance in spite of its semiconductor property. The gradual increase of sample resistance was considered to be due to oxygen adsorption on many vacant sites which were produced by the precedent heat-treatment in nitrogen atmosphere for the preparation of electrode. After several cyclic heat-treatments in oxygen atmosphere, the sample showed a reproducible shape of resistance vs. temperature, that is, a sigmoid variation. The sigmoid variation, characterized by

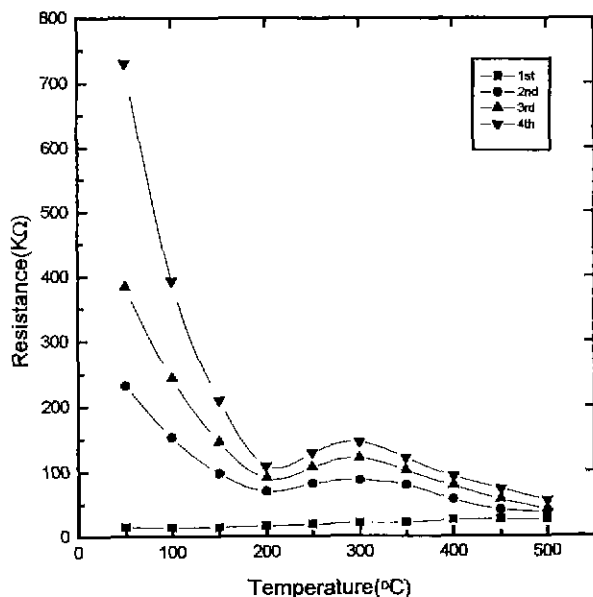


Fig. 3. Change of sample resistance as a function of operating temperature in oxygen atmosphere.

the increase of resistance over a certain temperature range against the semiconductor property of tin oxide, was thought to be related with the reaction between the adsorbed oxygen species on the film surface. It was reported that $(O_{2ads})^-$ species generally covered on the film surface at room temperature, but $(O_{ads})^-$ ions were found as the prevailing species above approximately 450 K⁽²⁾ by following reaction taken place with increasing temperature.



The transition causes an increase of surface charge density with the resultant increase of sample resistance. Our thin films showed the increase of the resistance above ~200°C, which was well consistent with the report mentioned above. The sigmoid variation characteristics of resistance with temperature had been previously reported.^(13,14) The peak resistance in the sigmoid variation of Fig. 3 is considered to appear at a saturated adsorption of $(O_{ads})^-$ ions and the decrease in resistance at higher temperature after maximum is considered due to the characteristics of a degenerated semiconductor. The present sample was switched to pure nitrogen atmosphere. Fig. 4 shows the resistance changes of the tin oxide film with heating temperature in pure nitrogen atmosphere. The resistance variations with temperature in nitrogen atmosphere were somewhat different compared with those in pure oxygen atmosphere. The base resistance of the sample exponentially decreased with increased temperature for the first heat-treatment. The drastical decrease of sample resistance with temperature was attributed to not only the semiconductor characteristics of tin oxide, but also the desorption of the already adsorbed oxygen on the film surface in oxygen at-

mosphere. In the second heat-treatment, the sample showed a gradual decrease of base resistance with increased temperature, due mainly to its semiconductor behavior.

It was concluded from our experimental results of Figs. 3 and 4 that the adsorption of oxygen on the surface of tin oxide film had critical influence on the base resistance of sample, depending on environmental gas atmosphere and the operating temperature. In addition, $(O_{ads})^-$ ions were concluded to become prevailing species on film surface at around 300°C, referred to as sensor operation temperature of tin oxide.

As to gas sensitization of tin oxide for explosive gases, e. g., hydrogen, following mechanism can be considered. The main reactions of this mechanism are: i) adsorption of oxygen on tin oxide surface at elevated temperature, along with the consumption of conduction band electrons, which leads to a increase in sensor resistance and followed by ii) reaction of a reducing gas, such as hydrogen, with the $(O_{ads})^-$ species and subsequent desorption of the product accompanied by the release of electrons which causes the sensor resistance to decrease.



Reaction (6) has been conceptionally adopted as the major sensitization mechanism.^(15,16)

However, another sensitization mechanism is also possible, where hydrogen molecules are adsorbed on the film surface, followed by the dissociation into monoatoms, and hydrogen atoms directly provide donor electrons to the film surface, which leads to decrease of sensor resistance as follows.

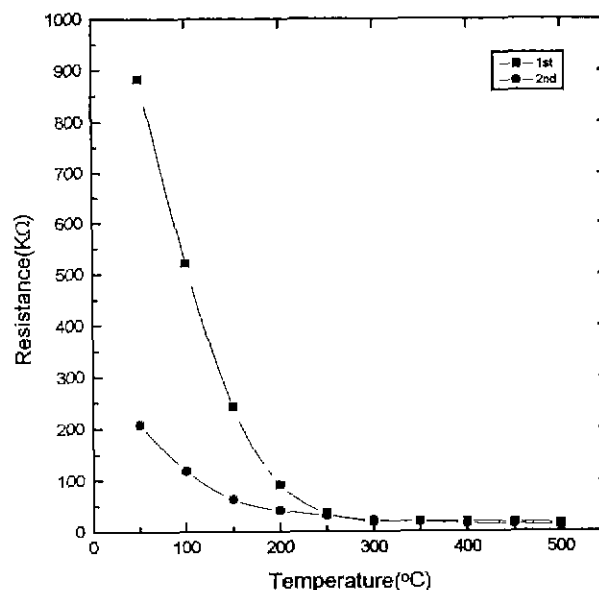


Fig. 4. Change of sample resistance as a function of operating temperature in nitrogen atmosphere.

where V and H_n denote vacant surface site and adsorbed monoatom, respectively. The assumption for the dissociation of hydrogen molecule into monoatoms is considered to be proper even though a large energy is necessary for the dissociation, because the solid surface (or Pt electrode) acts as a catalyst to reduce the dissociation energy.¹⁷⁾ This mechanism has been also suggested by R.B. Cooper *et al.*⁹⁾

To clarify the sensitization mechanism of tin oxide film to hydrogen gas, the sensing test was conducted in nitrogen and oxygen atmosphere, respectively. Fig. 5 shows the response of the sample to hydrogen gas at various temperatures in pure nitrogen atmosphere. Before test, the sample was heat-treated several times under pure nitrogen atmosphere as shown in Fig. 4 and maintained at each temperature until the sample resistance became stabilized. The sample was exposed to 50,000 ppm of hydrogen gas for 60 minutes and recovered again in pure nitrogen atmosphere. When hydrogen gas was introduced, the sample showed negligible change in resistance at 50°C, sluggish response at 100°C, however, sharp and quick drop of sample resistance at higher temperatures above 200°C. When hydrogen gas was immediately vented, the recovery of sample resistance was very retarded compared with the sample response to hydrogen gas. On the other hand, Fig. 6 shows the response of the sample to hydrogen gas at various operating temperatures in pure oxygen atmosphere. In advance of hydrogen injection, the sample was fully oxidized and showed the sigmoid variation. The base resistance of sample in oxygen atmosphere was higher than that of nitrogen atmosphere due to the adsorbed oxygen. The sample was tested with same schedule as one conducted in nitrogen atmosphere. The sample showed similar beha-

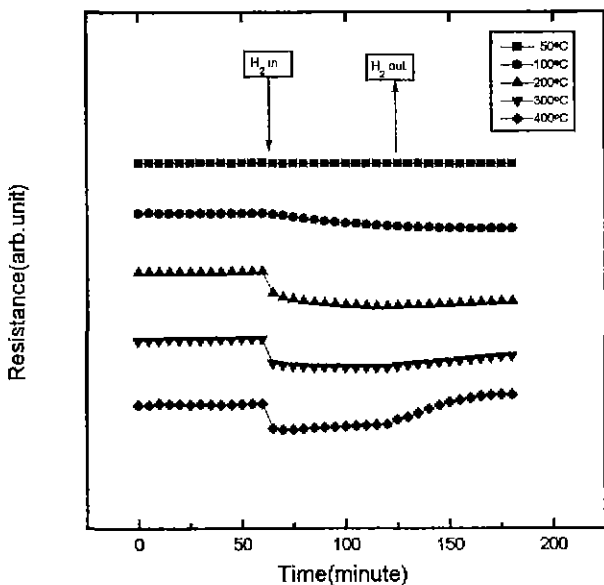


Fig. 5. H_2 -gas sensitizations and recoveries of tin oxide film at various temperatures in nitrogen atmosphere.

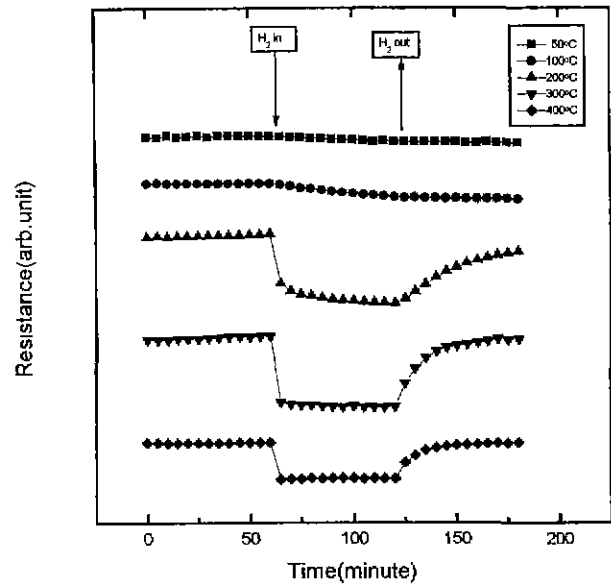


Fig. 6. H_2 -gas sensitizations and recoveries of tin oxide film at various temperatures in oxygen atmosphere.

viors to those of nitrogen atmosphere at each operating temperature. However, two different results were found compared with Fig. 5. When hydrogen gas was introduced, the degree of resistance drop was bigger than the one in nitrogen atmosphere. When the hydrogen was vented, the sample showed more rapid recovery behavior than the one in nitrogen atmosphere. Figs. 7 and 8 show the responses of sample at 300°C, typical sensor operating temperature, in each atmosphere and the two differences mentioned above are well expressed in the figures. The resistance drop (ΔR_d) in Fig. 7 is believed to be

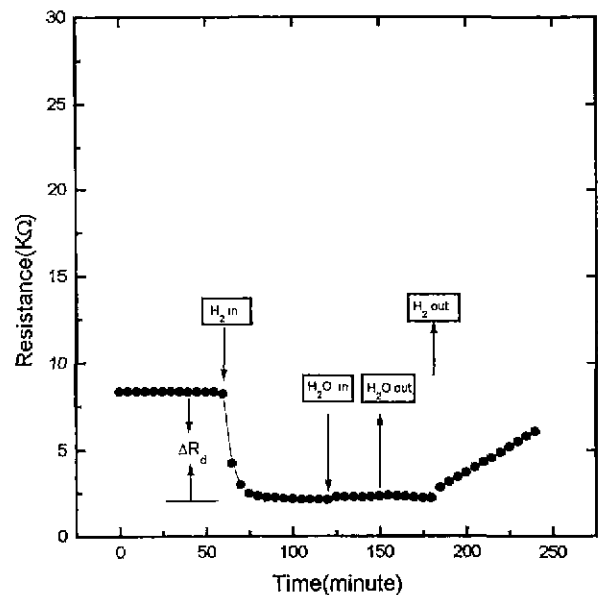


Fig. 7. Humidity effect on H_2 -gas sensitization of tin oxide film at operating temperature of 300°C in nitrogen atmosphere.

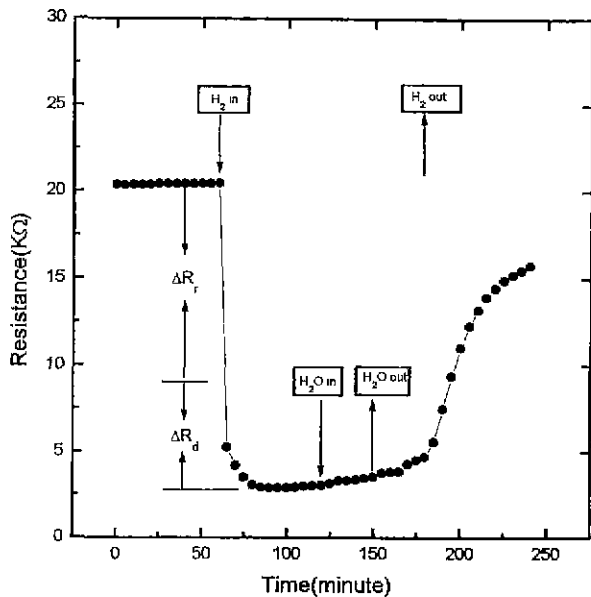


Fig. 8. Humidity effect on H_2 -gas sensitization of tin oxide film at operating temperature of 300°C in oxygen atmosphere.

attributed to the sensitization by reaction (7) because most of the adsorbed oxygen ions were eliminated as a result of heat-treatment in the nitrogen atmosphere. In Fig. 8, base resistance of the sample increased compared with one of nitrogen atmosphere. This increase (ΔR_c) was because the adsorbed oxygen ions had captured electrons from the film as already mentioned. The increased resistance due to oxygen adsorption can be reduced through the reaction (6) when the film is exposed to hydrogen gas. The large drop of the resistance in oxygen atmosphere is thought to be due to the combined effect of ΔR_r and ΔR_d .

It was concluded from our results that both reactions (6) and (7) play major roles as sensitization mechanisms, and both reactions are fast enough to sense hydrogen gas immediately at operating temperature of 300°C . However, the recovery behaviors appeared with distinct difference. While the recovery in oxygen atmosphere was fast, the one in nitrogen atmosphere was relatively retarded. The sluggish recovery in nitrogen atmosphere appeared probably because the energy barrier for the reverse reaction of reaction (7) is higher than that of forward reaction.¹⁹ On the other hand, the quick recovery in oxygen atmosphere was considered that the oxygen promoted the desorption of hydrogen and rapidly re-adsorbed the vacant surface sites.

To investigate the effect of humidity on gas sensitization, water gas was introduced during sensing test of hydrogen gas as shown in Figs. 7 and 8. The water gas corresponding to R.H.(relative humidity)70% at room temperature was introduced, and the resistance change by water gas was measured in nitrogen and oxygen atmosphere, respectively. In both atmospheres, any con-

siderable change of resistance was not found even though the injection of water gas continued for 30 minutes. H. Ogawa *et al.*¹⁴ reported that the humidity effect on sensitivity drastically decreased when the operating temperature was high. Our result is consistent with the fact that water molecules tend to desorb from the solid surface at high operating temperature.

IV. Conclusions

As the result of our work, it was revealed that the proper amount of antimony doping improved a long-term stability in base resistance of tin oxide film due to the change of its conduction mechanism from non-stoichiometry to controlled valency mechanism. In the gas sensitization of tin oxide, adsorption of oxygen, especially as a type of $(O_{ads})^-$ plays important roles in the sensor-operating mechanism of tin oxide film. The roles are i) the increase of base resistance in ambient air, which consequently lead to high sensitivity (the large change of resistance before and after test) and ii) the promotion of fast recovery. The reaction of hydrogen gas with the already adsorbed $(O_{ads})^-$ ions was considered as a decisive sensitization mechanism of tin oxide film. However, the dissociation of hydrogen molecules on film surface, followed by direct donation of electron to film also took major part in the sensitization. The effect of humidity on gas sensitization was found to be negligible at the sensor operating temperature of $\sim 300^\circ\text{C}$.

References

1. N. Srinivasa Murty and S. R. Jawalekar, "Characterization of Antimony-doped Tin Oxide Films for Solar Cell Applications," *Thin Solid Films*, **108**, 277-283 (1983).
2. J. M. Jarzelski and J. P. Marton, "Physical Properties of SnO_2 Materials III. Optical Properties," *J. Electrochem. Soc.*, **123**, 333-346 (1991).
3. K. H. Kim and C.G. Park, "Electrical Properties and Gas-sensing Behavior of SnO_2 Films Prepared by Chemical Vapor Deposition," *J. Electrochem. Soc.*, **138**, 2408-2412 (1991).
4. K. H. Kim, S. W. Lee, D. W. Shin and C. G. Park, "Effect of Antimony Addition on Electrical and Optical Properties of Tin Oxide Film," *J. Am. Ceram. Soc.*, **77**, 915-921 (1994).
5. V. Demarne and A. Grisel, "An integrated Low Power Thin Film CO Gas Sensor on Silicon," *Sensors and Actuators*, **13**, 301-313 (1988).
6. Colin A. Vincent, "The Nature of Semiconductivity in Polycrystalline Tin Oxide," *J. Electrochem. Soc.*, **119**, 515-518 (1972).
7. Ya. Kuzunetsov, "Semiconducting Tin Oxide," *Fizika Tverdogo Tela*, **2**, 35-42 (1960).
8. D. Kohl, "Surface Processes in the Detection of Reducing Gases with SnO_2 -based Devices," *Sensors and Actuators*, **18**, 71-113 (1989).
9. R. B. Cooper, G. N. Advani and A. G. Jordan, "Gas Sens-

- ing Mechanism in SnO₂ Thin Films," *J. Electron Mater.*, **10**, 455-471 (1981).
10. N. Yamazoe, J. Fuchigami, M. Kishikawa and T. Seiyama, "Interactions of Tin Oxide Surface with O₂, H₂O and H₂," *Surf. Sci.*, **86**, 335-344 (1979).
 11. K. H. Cha, H. C. Park and K. H. Kim, "Effect of Palladium Doping and Film Thickness on the H₂-Gas Sensing Characteristics of SnO₂," *Sensors and Actuators B*, **21**, 91-96 (1994).
 12. S. C. Chang, "Oxygen Chemisorption on Tin Oxide: Correlation between Electrical Conductivity and EPR Measurements," *J. Vac. Sci. Technol.*, **17**, 366-369 (1980).
 13. N. Yamazoe, Y. Kurokawa and T. Seiyama, "Effects of Additives on Semiconductor gas Sensors," *Sensors and Actuators*, **4**, 283-289 (1983).
 14. H. Ogawa, A. Abe, M. Nishikawa and S. Hayakawa, "Electrical Properties of Tin Oxide Ultrafine Particle Films," *J. Electrochem. Soc.*, **128**, 2020-2025 (1981).
 15. G. Williams and G. S. V. Coles, "A Study of Tin-dioxide Gas-sensor Thermochemistry under Conditions of Varying Oxygen Partial Pressure," *Sensors and Actuators B*, **24-25**, 573-577 (1995).
 16. H. Windischmann and P. Mark, "A Model for the Operation of a Thin-film SnO₂ Conduction-modulation Carbon Monoxide Sensor," *J. Electrochem. Soc.*, **126**, 627-633 (1979).
 17. R. Sanjines, C. Coluzza, D. Rosenfeld, F. Gozzo, Ph. Almeras, F. Levy and G. Margaritondo, "Photoemission Spectromicroscopy: A new Insight in the Chemistry of SnO_x Films for gas Sensors," *J. Appl. Phys.*, **73**, 3997-4003 (1993).
 18. I. Lundström, M. S. Shivaraman and C. Svensson, "Chemical Reactions on Palladium Surfaces Studied with Pd-MOS Structures," *Surf. Sci.*, **64**, 497-519 (1977).