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# High gas sensitivity of tin oxide ultrathin films deposited on glasses and alumina substrates

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Tin oxide ultrathin films were deposited on optically flat Pyrex glass, optically flat quartz glass and sintered alumina substrates by the ion-beam sputtering method. Films with thickness varying from about 1 to 500 nm were annealed in air at 500 °C for 50 h. The gas sensing properties of these films were investigated at 300 °C against synthetic air containing 0.5% hydrogen. A small substrate dependence of sensor behaviour was observed; however, an overwhelmingly important thickness dependence occurred in all substrates tried. Sensitivities higher than $\sim 10^4$ or $10^5$ were obtained in films in a narrow thickness range of about 3 to 20 nm, and films thicker or thinner than this were relatively insensitive.

## 1. Introduction

Ultrathin tin oxide films have been found to exhibit an extremely high sensitivity of greater than $10^4$ to 0.5% hydrogen at 300 °C [1, 2]. Achievement of such a high sensitivity was due to control of the ultrathin film thickness and also to the prolonged annealing time. Another important factor which determines the nature of the deposited films is the substrate. Thus we undertook here to study the relative sensor properties of films deposited on three different substrates: Pyrex glass, quartz glass and sintered alumina plate.

## 2. Experimental procedure

### 2.1. Sensor fabrication

Glasses were optically flat. The sintered alumina had a theoretical density of < 96%, an average grain size of 22 μm and a surface roughness of 4 μm. Substrates were finished by washing with ion-exchange water and methyl alcohol using ultrasonic waves. Films were deposited using an ion-beam sputtering apparatus [3, 4]. Deposition was carried out by sputtering a sintered $SnO_2$ target with an argon ion beam under a pressure of $1 \times 10^{-4}$ torr. The purity of sintered $SnO_2$ and argon gas were 99.99 and 99.9995%, respectively. Four substrates were set on a holder and eight holders were mounted on a rotable axis. Thus 32 films were prepared successively in a run. Control of the shutter on–off time, and thus the sputtering time, and the rotation of the axis were carried out using a microcomputer. The substrate temperature did not exceed 100 °C during sputtering and the deposition rate was $\sim 0.05\ \mathrm{nm\,s^{-1}}$. As-deposited films were annealed in air for 50 h at 500 °C. In order to perform the electrical measurements by a two-probe d.c. method, Pt electrodes of thickness ~ 150 nm were deposited on the annealed films. The surface between the electrodes was ~ 4 mm long and ~ 0.4 mm wide. The exact dimensions of each sensor were measured by a microscope for calculating the resistivity.

### 2.2. Film thickness analysis

Films of eight different thicknesses were fabricated in a run and the thickness of one of them was measured as a standard for that series of films. The standard thickness was obtained from low-angle X-ray diffraction (XRD). XRD was carried out with 30 kV–20 mA nickel-filtered Cu$K_\alpha$ radiation (Rigaku RAD-B) using a 0.5° divergence slit and a 0.15 mm receiving slit. The intensity data were collected with a scan speed of $0.2^\circ\ \mathrm{min^{-1}}$ and a step sampling of 0.002° in $2\theta$. Fig. 1 shows an example of the XRD diagram for an as-deposited and annealed film on Pyrex glass. The presence of sharp peaks indicates that the film is very flat. The film thickness was obtained in the following way. Applying the method of Kiessig [5] to the adjacent peaks from $n$th and $(n + 1)$th reflections ($n = 0, 1, 2, 3, 4 \ldots$), the thickness $d$ is given from the relation

$$d = \frac{\lambda}{2}\left(\frac{2n + 2}{\sin^2\theta_{n+1} - \sin^2\theta_n}\right)^{1/2} \qquad (1)$$

where $\lambda$ is the wavelength of the X-rays (0.154 nm) and $\theta_n$ is the angle of incidence from the $n$th reflection. Here it is supposed that a phase change of $\pi$ occurs at the interface tin oxide–Pyrex glass. Fig. 2 shows the angle dependence of thickness calculated from Equation 1 assuming that the first peak ($2\theta \sim 1.4^\circ$) in Fig. 1a corresponds to either $n = 1, 2, 3, 4$ or 5. Evidently, a correct plot should give a constant value independent of $\theta$. Thus we see that the $n = 3$ line is correct and that the thicknesses of the as-deposited and annealed films are $26.3 \pm 0.3$ and $23.7 \pm 0.1$ nm, respectively. Because the sputtering time was 502 s,

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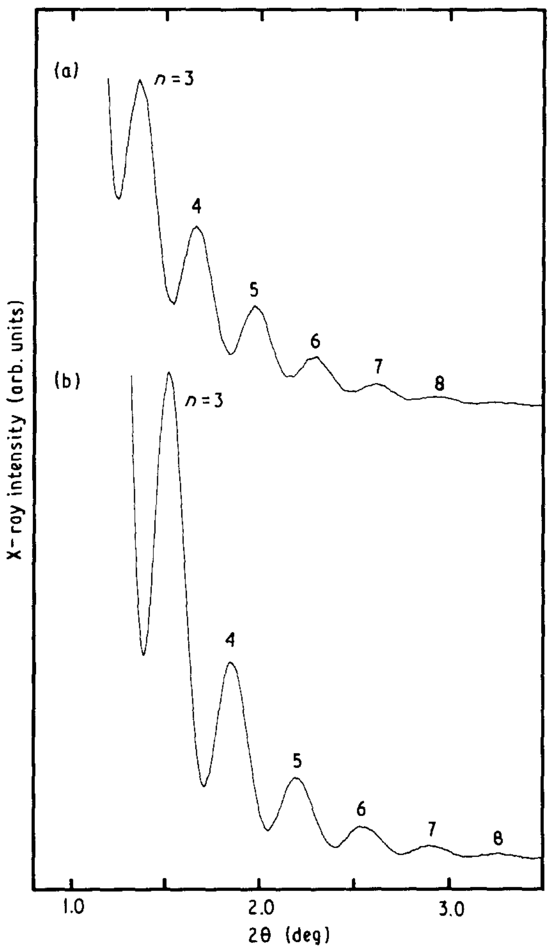

*Figure 1* X-ray intensity of *n*th order reflected from air–tin oxide–glass interface at small angles of incidence, θ: (a) as-deposited film, (b) film annealed at 500 °C for 50 h.

the deposition rate becomes 0.052 nm $s^{-1}$. Contraction along the thickness was 9.9%. Using the deposition rate and contraction thus obtained, the thicknesses of other films in the same run were determined. It is to be noted that the sharp peaks in Fig. 1 indicate a flat and very smooth surface of the film.

## 2.3. Measurement of sensor property

Gas sensing properties were measured at 300 °C by exposing the film alternately to synthetic air ($O_2$ 20.7%, $CO_2 < 0.1\%$, $CH_4 < 0.1$ p.p.m., $N_2$ balance) and to synthetic air containing 0.5% hydrogen. The flow rate of the gases was 50 ml $min^{-1}$. The chamber consisted of an alumina tube 25 mm in diameter and 400 mm in length inserted in an electric furnace whose heater was wound non-inductively. The film, standard resistance and generator were connected in series for the electrical measurement. The film resistance $R$ was obtained through the recorded potential difference $V_x$ between the standard resistance $R_x$ under an applied d.c. voltage of $V_A$ using the relationship $R = (V_A/V_x - 1)R_x$. The sensitivity was defined as the ratio of the film resistance in synthetic air ($R_o$) to that in 0.5% hydrogen gas ($R_g$). The response behaviour was measured three times. Details of the experimental procedure have been published elsewhere [1, 6].

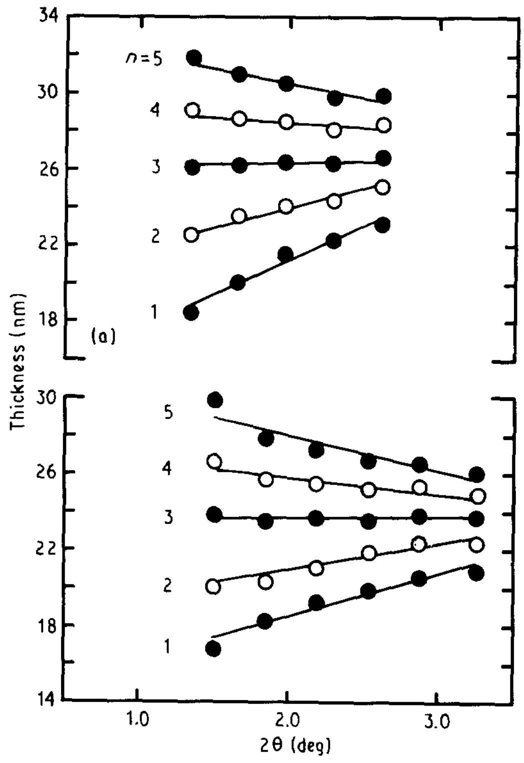

*Figure 2* An example for determining the order of reflection *n*. The plot indicates that $n = 3$ is right. (a) As-deposited film of thickness 26.3 ± 0.3 nm, (b) annealed film, 23.7 ± 0.1 nm.

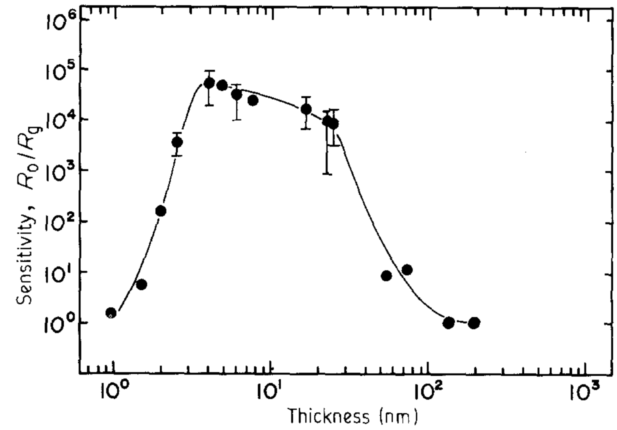

*Figure 3* Sensitivity of films on Pyrex glass at 300 °C as a function of thickness. Hydrogen gas concentration 0.5%.

## 3. Results and discussion

### 3.1. Sensitivity and resistivity

The XRD diagrams of as-deposited films thicker than about 100 nm showed only broad haloes indicating an amorphous or microcrystalline nature, while annealed ones indicated randomly oriented tetragonal structure [5]. Thinner films could not be identified because of the weak XRD intensity. A stable response behaviour was observed after several hours of transient time. Although detailed microstructural changes during the transient period are yet to be investigated, we now proceed to the stable behaviour. Fig. 3 shows the sensitivity of films deposited on Pyrex glass. Their corresponding resistivities in air and in 0.5% hydrogen gas are given in Fig. 4. Annealed films were 0.96, 1.4, 2.0, 2.5, 4.0, 4.8, 6.0, 7.5, 16.5, 22.5, 24.3, 53.8, 72.7, 135 and 197 nm thick. Similarly, Figs 5 and 6 show the sensitivity and resistivity of films on fused quartz glass, respectively. They were 0.94, 1.4, 1.8, 2.3, 3.7, 5.1, 7.4, 11.9, 17.7, 24.9, 37.7, 58.8, 99.5, 278 and 498 nm thick. Finally, the sensor properties of films on alumina substrates are given in Figs 7 and 8. Films were 1.5, 2.0, 2.8, 6.2, 8.9, 14.0, 15.6, 19.9, 27.7, 49.7, 79.5, 94.1, 132, 277 and 753 nm thick.

## 3.2. Influence of substrate

Because XRD analysis indicated no important chemical reaction between tin oxide and substrates, effects of coefficient of linear expansion and surface roughness should be considered. Coefficients of linear expansion and the surface roughness of materials used are given in Table I. Pyrex glass and tin oxide have nearly the same coefficient, while those of fused quartz and sintered alumina are about one-tenth and twice that of tin oxide, respectively. A closer look at the data shows a more gradual rise and a steeper fall of sensitivity with decreasing thickness in films deposited on quartz glass as compared with other substrates. Further, a part of the resistivity of films on alumina is about one order of magnitude greater than that on other substrates. These facts must reflect the influence of thermal expansion and the surface roughness. However, the thickness dependence of sensor properties

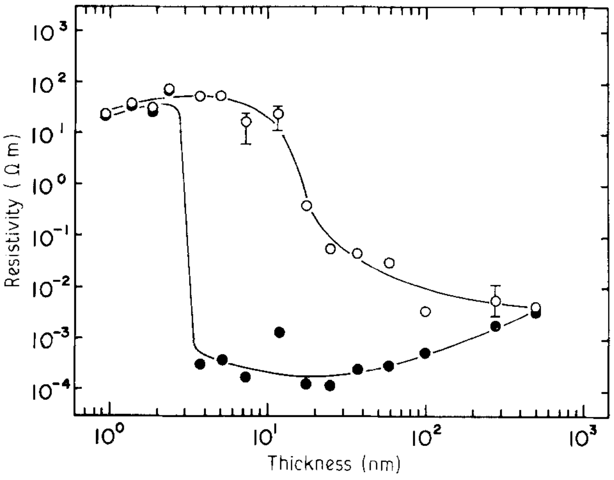

*Figure 6* Resistivity in (○) air and (●) hydrogen as a function of film thickness on fused quartz glass. The plot corresponds to that in Fig. 5.

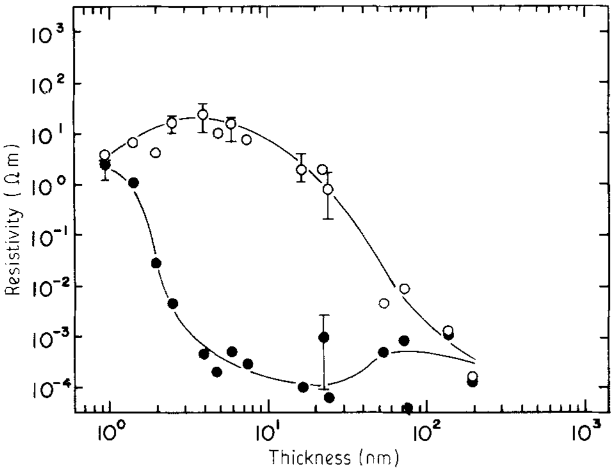

*Figure 4* Resistivity in (○) air and (●) hydrogen as a function of film thickness on Pyrex glass. The plot corresponds to that in Fig. 3.

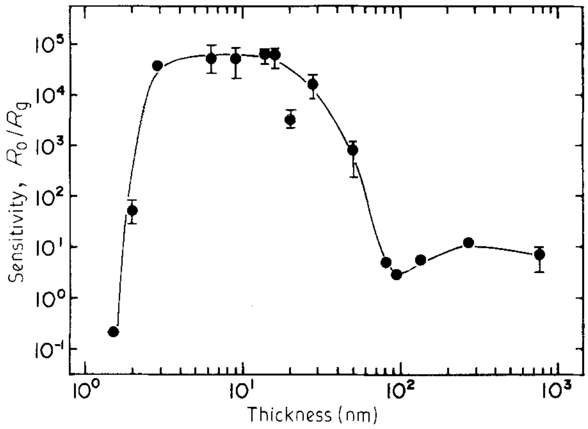

*Figure 7* Sensitivity of films on sintered alumina plate at 300 °C as a function of thickness. Hydrogen gas concentration 0.5%.

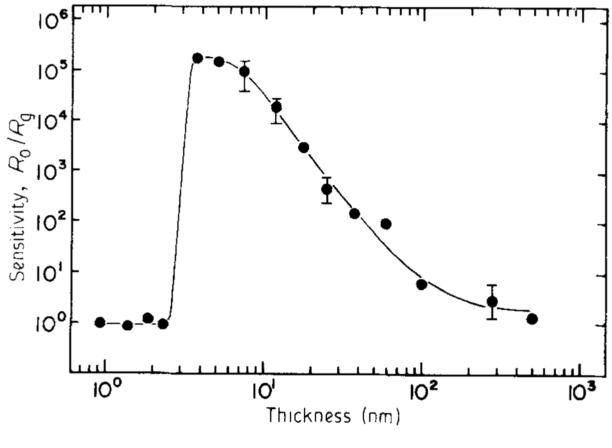

*Figure 5* Sensitivity of films on fused quartz glass at 300 °C as a function of thickness. Hydrogen gas concentration 0.5%.

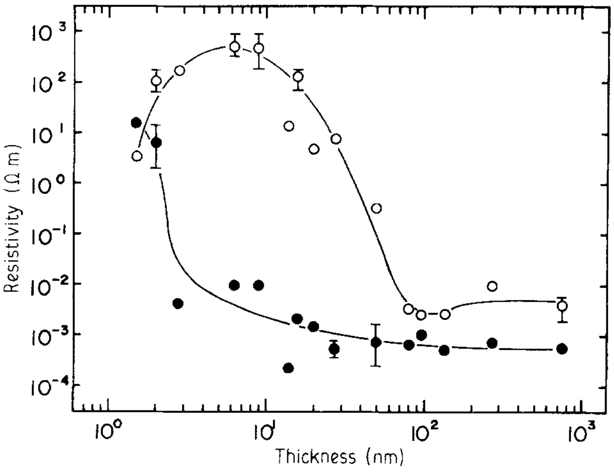

*Figure 8* Resistivity in (○) air and (●) hydrogen as a function of film thickness on sintered alumina plate. The plot corresponds to that in Fig. 7.

TABLE I Linear thermal expansion coefficients and surface roughness of tin oxide, Pyrex glass, fused quartz glass and sintered alumina

| Material | Expansion coefficient ($K^{-1}$) | Surface roughness | Reference |
|---|---|---|---|
| Tin oxide | $5 \times 10^{-6}$ | Very smooth | [7] |
| Pyrex | $3.25 \times 10^{-6}$ | Optically flat | [8] |
| Quartz | $5.4 \times 10^{-7}$ | Optically flat | [8] |
| Alumina | $8.1 \times 10^{-6}$ | $\sim 4\,\mu m$ | [9] |

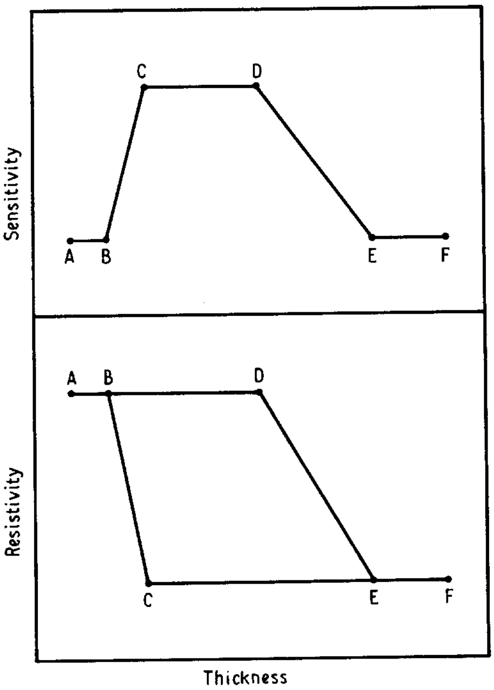

*Figure 9* Schematic diagram of sensitivity and resistivity as a function of thickness. ABDEF in the bottom figure corresponds to resistivity in air, whereas ABCEF is resistivity in 0.5% hydrogen.

for the three substrates shows that the change in the resistivity, and therefore the sensitivity, remains mostly of the same order of magnitude and thus practically independent of the substrate. This indicates that neither microstructural difference, nor probably the internal stress induced by the difference in expansion coefficients, nor the local thickness variation on the sintered alumina is important, but that the effects of thickness and the defect structure in ultrathin films are predominant.

Thus, we can neglect the influence of the substrate as a first approximation. A survey of the thickness dependence of sensitivity then gives the following general behaviour as depicted schematically in Fig. 9. The sensitivity region is divided into three parts; almost no sensitivity at < 2 nm (AB) and > 100 nm (EF), highly sensitive from 3 to 20 nm (CD) and transitional behaviour in between (BC and DE). Resistivity data show that the insensitive region corresponds to high resistivity in both air and hydrogen at the thinner side (AB) and the reverse for the thicker side (EF). The high-sensitivity plateau (CD) is due to a high resistivity in air (AD) but a low resistivity in hydrogen (CF). But why is it highly sensitive at some specified thickness region? For this, we need to analyse the potential distribution formed by negatively charged oxygen at the surface and this is under way.

## 4. Conclusions

The effects of the substrate and film thickness on the sensor behaviour of ultrathin tin oxide films were examined. Films ranging from about 1 to 500 nm were deposited on optically flat Pyrex glass, optically flat quartz glass and alumina plates. They were annealed in air at 500 °C for 50 h and the sensor properties against 0.5% hydrogen gas were measured at 300 °C. The results were as follows:

1. Annealed films contracted by about 10% along the thickness.
2. An extremely high sensitivity of $10^4$ to $10^5$ was obtained in the thickness range from 3 to 20 nm for all substrates tried.
3. Films thinner than about 2 nm and thicker than about 100 nm were almost insensitive.
4. The influences of the thermal expansion coefficient and surface roughness of substrates were far smaller compared with that of film thickness, and thus the sensor properties are mainly dependent on the latter.

## References

1. T. SUZUKI, T. YAMAZAKI and M. AZUMAYA, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi* (*J. Ceram. Soc. Jpn*) **97** (1989) 1268.
2. T. SUZUKI and T. YAMAZAKI, *J. Mater. Sci. Lett.* in press.
3. T. SUZUKI, T. YAMAZAKI, H. YOSHIOKA, K. TAKAHASHI and T. KAGEYAMA, *ibid.* **6** (1987) 437.
4. T. SUZUKI, T. YAMAZAKI, K. TAKAHASHI, T. KAGEYAMA and H. ODA, *ibid.* **7** (1988) 79.
5. V. H. KIESSIG, *Ann. Phys.* **10** (1931) 769.
6. T. SUZUKI, T. YAMAZAKI, H. YOSHIOKA and K. HIKICHI, *J. Mater. Sci.* **23** (1988) 145.
7. H. SEKI, N. ISHIZAWA, N. MIZUTANI and M. KATO, *Yogyo Kyokaishi* (*J. Ceram. Soc. Jpn*) **92** (1984) 219.
8. M. KAMIYAMA and T. TACHIBANA, "Thin Film Handbook" (Ohmsha, Tokyo, 1983) p. 4.
9. Catalogue of Nippon Kagaku Togyo Co. Ltd.

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