JOURNAL OF MATERIALS SCIENCE 29 (1994) 281–284

Humidity-sensitive characteristics of SnO_2–Fe_2O_3 thin films prepared by spray pyrolysis

T. M. RACHEVA, I. D. STAMBOLOVA
Higher Institute of Chemical Technology, Department of Semiconductors, 8 kl. Ohridski Blvd., 1156 Sofia, Bulgaria
T. DONCHEV
Institute of Electronics, 72 Tsarigradsko Chausse, 1184 Sofia, Bulgaria

The humidity sensitivity of mixed iron oxide–tin oxide films has been investigated. The films were deposited by spraying alcohol solution of $SnCl_4$ and $Fe(NH_4)\,(SO_4)_2$ or $Fe_2(C_2O_4)_3$ on to quartz substrates heated at 480 °C with subsequent annealing in various ambients – oxygen or humid air. The films were investigated by Auger electron spectroscopy (AES) and scanning electron microscopy (SEM). The humidity-sensitivity characteristics are plotted in the range 0%–93% RH. It was established that the humidity sensitivity, the response and the recovery time depend on the type of solution used for deposition, the type of thermal treatment, and the film thickness. It was found that the nature of the iron salt, used for the preparation of the spraying solution, and its concentration are of great importance for the humidity-sensitive properties of the films. The $SnCl_4$ and $Fe_2(C_2O_4)_3$ films, treated thermally in humid air at 900 °C for 1 h, possessed a short response time and high sensitivity to moisture.

1. Introduction

Humidity measurement and control is very important for a number of manufacturing and technological processes [1]. Therefore, the production and investigation of humidity sensors is of great theoretical and practical value. Conductivity sensors on the basis of semiconductor metal oxides in the form of porous ceramics have been intensively studied [2, 3]. The data in the literature on the utilization of thin metal-oxide films for the same purpose are quite scarce [4]. Interest is drawn to thin films of SnO_2, that are widely used as active sensor material for toxic gas detection [5] and various other applications [6]. SnO_2 films are highly resistant to aggressive environments and are readily prepared by various methods [7, 8]. Good opportunities for the production of pure and doped SnO_2 films are offered by the method of spray pyrolysis [9].

It is known that water vapour increases the conductivity of semiconductor gas sensors [10]. The water molecules, however, have a weak effect on the conductivity of SnO_2 [11]. In addition, the films of pure SnO_2 have the disadvantage of exhibiting poor stability of their humidity characteristics with time. That is why they are unsuitable for the fabrication of reliable humidity sensors with reproducible characteristics.

It is also known that the electrical conductivity of α-Fe_2O_3 (porous ceramics) increases sharply in the presence of water molecules [12]. Therefore, if Fe_2O_3 is added to the SnO_2 films, considerable improvement of their humidity-sensitivity characteristics can be expected.

The present work is devoted to the experimental results obtained after preparation of mixed SnO_2–Fe_2O_3 films by spray pyrolysis, and to the investigations of their humidity-sensitivity properties. The work also contributes to the clarification of the influence of the technological factors (nature and concentration of the iron salt in the spray solution, type of thermal treatment and film thickness) on the humidity sensitivity of the films.

2. Experimental procedure

The spray solutions were prepared by mixing certain quantities of 0.2 M $SnCl_4$ in C_2H_5OH and 0.2 M $Fe(NH_4)(SO_4)_2$ or $Fe_2(C_2O_4)_3$ in $C_2H_5OH + H_2O$. The molar ratio Sn:Fe in these solutions was 19:1, 9:1, 6:1, 4:1, 1:1 and 1:4.

The solutions were sprayed on to a substrate heated to 480 °C intermittantly at regular time intervals of 10 s. The substrates were quartz plates, oxidized silicon wafers and quartz tubes with a diameter of 6 mm and length 10 mm. In order to evaluate the relationship between the humidity sensitivity and the film thickness, films with two different thicknesses were deposited – about 250 and 100 nm.

After deposition, some of the films were thermally treated in an oxygen medium at 900 °C for 30 min, and others in humid air at 900 °C for 1 h. In all cases of thermal treatment, the samples were rapidly cooled to room temperature.

The films deposited on quartz tubes were used for the fabrication of sensor elements. The construction of the sensor element is the same as in our previous work [13]. The two electrodes on the film were made of silver and were placed 1 mm apart.

Relative humidities from 0%–93% were obtained in a set of glass flasks, containing saturated water solutions of salts that maintain a certain humidity [14]. They were placed in a chamber thermostatted at 20 °C. The relationships $R = f(\mathrm{RH})$ were measured by sealing the sensor element in the flask with a definite humidity. The electrical resistance of the sensor in dry air was measured in the same way using a flask with a drier. The electrical resistance was measured with a conventional multimeter.

The response and recovery times were evaluated by the electrical resistance change on increasing the humidity from 0%–93% and on decreasing it from 93% to 0%, respectively.

The chemical composition of the films and the concentration profiles of tin, iron and oxygen in the depth of the film were evaluated by Auger electron spectroscopy. The morphology of the surface and the microstructure of the films were investigated by scanning electron microscopy (SEM).

3. Results and discussion

The analysis of the experimental data shows that the humidity characteristics of the samples are strongly affected by the film thickness, the conditions of thermal treatment and the nature of the iron salt, introduced in the spray solutions. The $SnCl_4$ and $Fe_2(C_2O_4)_3$ films, treated thermally in oxygen, possess a very high electrical resistance at 20 °C ($> 10^9\ \Omega$). The curve illustrating the electrical resistance dependence on the relative humidity has a step-wise section in the range 65% – 85% RH (Fig. 1). The sensors, based on the same films, but treated thermally in humid air, have lower electrical resistance and higher sensitivity to humidity (Fig. 1). Their curves $R = f(\mathrm{RH})$ are smoother, displaying just a hinted step around 40% RH (Fig. 1).

As is evident from Fig. 1, the highest activity with respect to moisture is exhibited by the sensors based on films deposited from solutions of $SnCl_4$ and $Fe_2(C_2O_4)_3$ in a molar ratio Sn:Fe = 1:1, annealed in humid air at 900 °C for 1 h. Their electrical resistance changes approximately by four orders of magnitude when the relative humidity varies from 0% – 93% RH.

The analysis of the experimental data shows that thinner films have higher electrical resistance and lower humidity sensitivity. The electrical resistance of these films diminishes almost exponentially with about two orders of magnitude when the moisture contents increase (Fig. 1).

The nature of the iron salt introduced into the spray solutions was found to influence the humidity sensitivity of the samples. Films obtained from a solution of $SnCl_4$ and $Fe(NH_4)(SO_4)_2$ possess lower electrical resistance and lower humidity sensitivity. The curve $R = f(\mathrm{RH})$ (Fig. 1) has a clearly marked step-wise section in the range 40% – 70% RH.

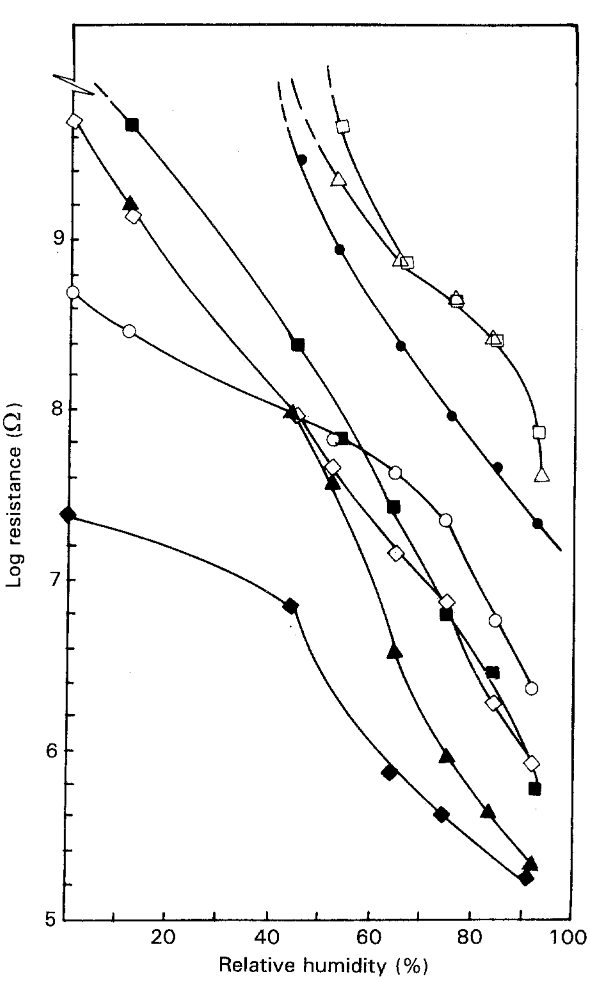

Figure 1 Humidity sensitivity at 20 °C of $SnO_2 - Fe_2O_3$ films. (△) Sn:Fe = 1:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in oxygen at 900 °C. (▲) Sn:Fe = 1:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in wet air at 900 °C. (●) Sn:Fe = 1:1 ($Fe_2(C_2O_4)_3$) in solution, 100 nm, annealed in wet air at 900 °C. (○) Sn:Fe = 1:1 ($Fe(NH_4)(SO_4)_2$) in solution, 250 nm, annealed in oxygen at 900 °C. (□) Sn:Fe = 6:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in oxygen at 900 °C. (■) Sn:Fe = 6:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in wet air at 900 °C. (◇) Sn:Fe = 19:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in oxygen at 900 °C. (◆) Sn:Fe = 19:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in wet air at 900 °C.

Fig. 2a and b show the response time and the recovery time depending on the change in the relative humidity from 0% to 93%, and vice versa. The samples with a film thickness of about 100 nm, produced from $SnCl_4$ and $Fe_2(C_2O_4)_3$ with a mole ratio Sn:Fe = 1:1, treated thermally in humid air, have a better response time. The explanation of this fact is an object of future investigations. Increasing the film thickness results in a poorer response time (Fig. 2a). On increasing the iron salt content in the spray solution, the sensor response time improves, while the humidity sensitivity does not change noticeably.

The recovery time is strongly influenced by the film thickness. The shortest recovery times are exhibited by samples about 100 nm thick, prepared from a solution of $SnCl_4$ and $Fe_2(C_2O_4)_3$ with a mole ratio Sn:Fe = 1:1, annealed in humid air (Fig. 2b).

The type of thermal treatment does not substantially affect the recovery time.

In order to explain the influence of the iron salt added to the solution on the humidity sensitivity of the films, the composition, surface morphology and film microstructure were investigated. It was discovered that the quantity of iron included in the composition of the film is much smaller than that in the spray solution. Thus, at a ratio Sn:Fe = 1:1 in the solution, regardless of the type of iron salt, the iron content in the film does not exceed 4 at %. The iron concentration on the surface and in the bulk of the film, as well as tin and oxygen, was evaluated by Auger electron spectroscopy and is shown in Fig. 3a and b for a thin and a thick film.

Despite the low iron concentration in the film, it influences strongly the response and recovery times of the sensor elements, enhancing these parameters in comparison with the pure undoped SnO_2 films.

The investigations on the microstructure of the samples showed that the use of both $Fe(NH_4)(SO_4)_2$ and $Fe_2(C_2O_4)_3$ leads to the obtainment of a strongly developed fine-grain structure in which the size of the crystalline grains is below 70 nm. This is probably one of the reasons for the good humidity-sensitivity characteristics of the samples.

The films in which iron is in the form of $Fe_2(C_2O_4)_3$ in all cases display a finer grain structure (below 50 nm).

It was found that the mole ratio Sn:Fe in the solution influences the size of the crystalline grains of the film, a decrease in this ratio resulting in a smaller

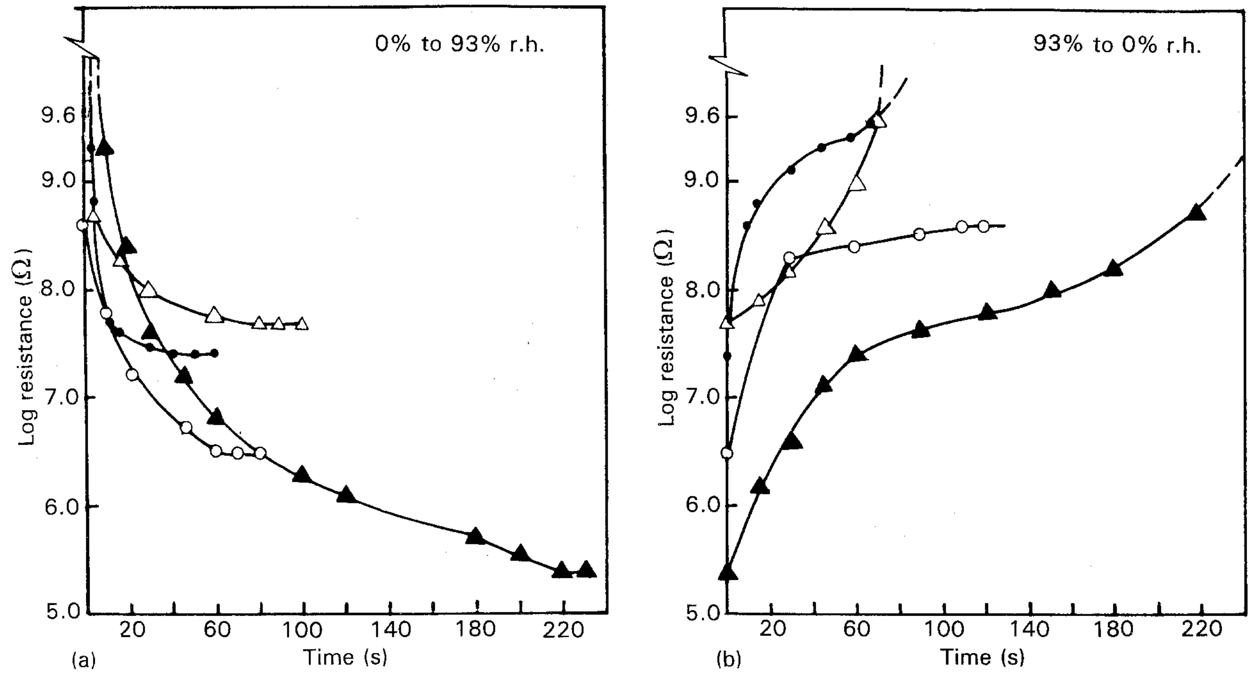

Figure 2 (a) Humidity response and (b) recovery time characteristics of $SnO_2-Fe_2O_3$ thin films at 20 °C. (△) Sn:Fe = 1:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in oxygen at 900 °C. (▲) Sn:Fe = 1:1 ($Fe_2(C_2O_4)_3$) in solution, 250 nm, annealed in wet air at 900 °C. (●) Sn:Fe = 1:1 ($Fe_2(C_2O_4)_3$) in solution, 100 nm, annealed in wet air at 900 °C. (○) Sn:Fe = 1:1 ($FeNH_4(SO_4)_2$) in solution, 250 nm, annealed in oxygen at 900 °C.

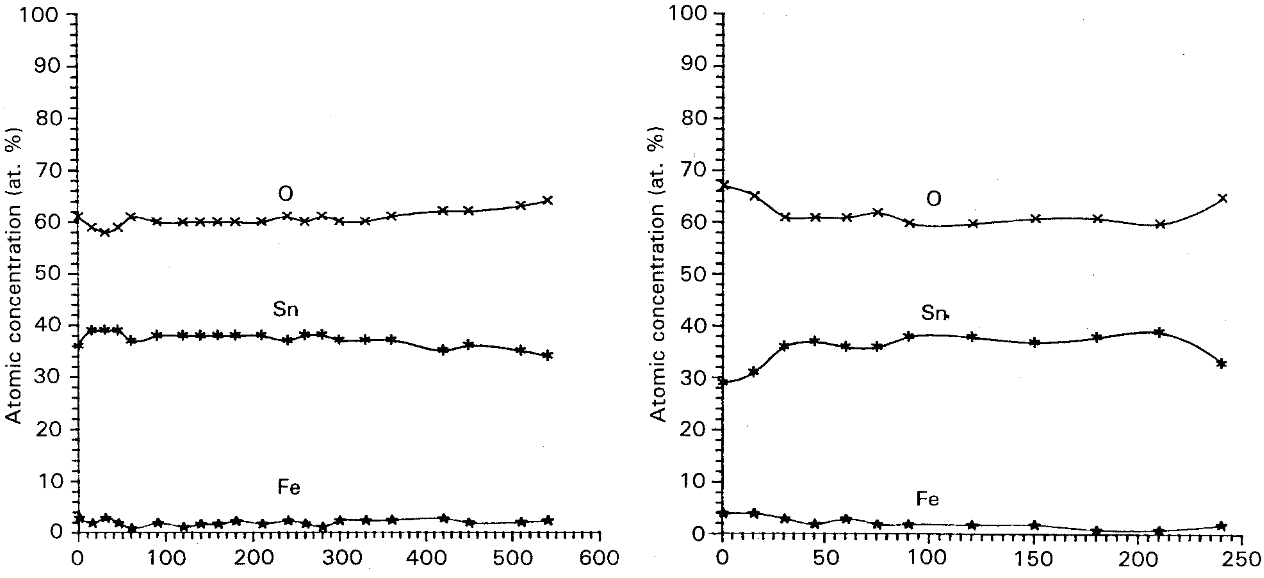

Figure 3 AES concentration profiles in the depth of a film obtained from a solution of $SnCl_4$ and $Fe_2(C_2O_4)_3$ with mole ratio Sn:Fe = 1:1 for the thickness (a) 250 nm (b) 100 nm.

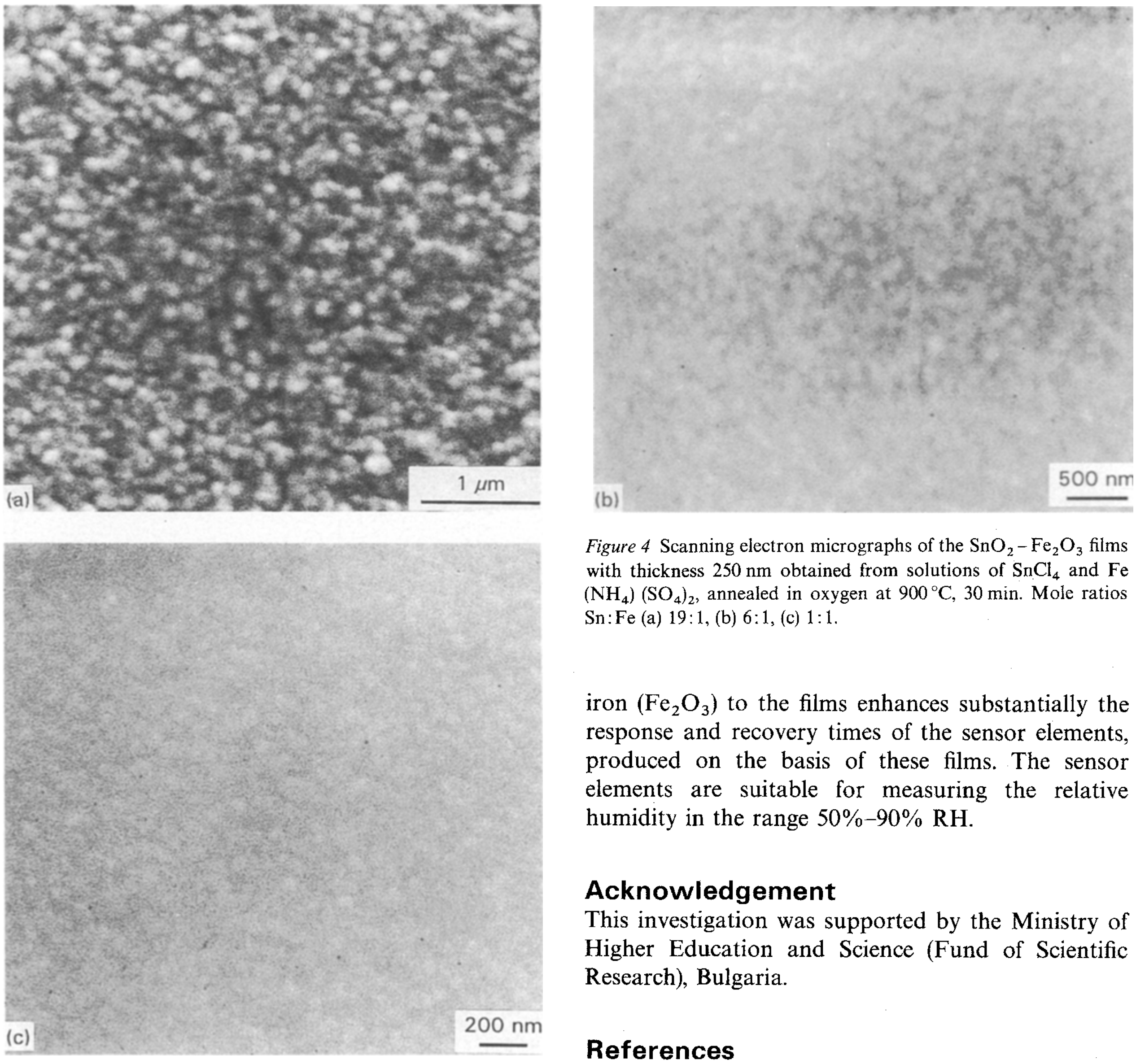

Figure 4 Scanning electron micrographs of the $SnO_2-Fe_2O_3$ films with thickness 250 nm obtained from solutions of $SnCl_4$ and Fe (NH_4) $(SO_4)_2$, annealed in oxygen at 900 °C, 30 min. Mole ratios Sn:Fe (a) 19:1, (b) 6:1, (c) 1:1.

grain size. This is demonstrated in Fig. 4a–c for the films deposited from a solution of $SnCl_4$ and $Fe(NH_4)(SO_4)_2$ at different proportions Sn:Fe in the solution. The highest humidity sensitivity is observed in sensor elements made of solutions in which Sn:Fe = 1:1. On further decreasing the Sn:Fe ratio in the solution, the film structure becomes discontinuous (islands type) and the humidity sensitivity of the samples is lost.

The better humidity-sensitive parameters of the samples, obtained from iron oxalate, are probably due to the higher porosity of the structure (larger area) of the films, because during the oxalate pyrolysis many more gaseous products of the reaction are liberated.

4. Conclusions

SnO_2–Fe_2O_3 films, deposited by spraying alcohol solutions of $SnCl_4$ and iron salt (sulphate or oxalate) on to heated substrates with subsequent thermal treatment in oxygen or humid air, possess clearly expressed humidity-sensitive properties. Their humidity-sensitive parameters are strongly influenced by the conditions of preparation and thickness. The addition of iron (Fe_2O_3) to the films enhances substantially the response and recovery times of the sensor elements, produced on the basis of these films. The sensor elements are suitable for measuring the relative humidity in the range 50%–90% RH.

Acknowledgement

This investigation was supported by the Ministry of Higher Education and Science (Fund of Scientific Research), Bulgaria.

References

1. N. YAMAZOE and Y. SHIMIZU, *Sens. Actuators* **10** (1986) 379.
2. T. NITTA, Z. TERADA and Sh. NAYAKAWA, *J. Am. Ceram. Soc.* **63** (1980) 295.
3. Y. SHIMIZU, H. ARAI and T. SEYAMA, *Sens. Actuators* **7** (1985) 11.
4. Zh. CHEN, M.-Ch. JIN and Ch. ZHEN, *ibid.* **B2** (1990) 167.
5. W. MOKWA, D. KOHL and G. HEILAND, *ibid.* **8** (1985) 101.
6. G. BLANDENET, M. COURT and Y. LAGARGE, *Thin Solid Films* **77** (1981) 81.
7. Kw. KIM and Ch. PARK, *J. Electrochem. Soc.* **138** (1991) 2408.
8. T. SUZUKI, T. YAMAZAKI, H. YOSHIOKA and K. HIKICHI, *J. Mater. Sci.* **23** (1988) 145.
9. K. NOMURA, Y. UJIHIRA, S. S. SHARMA, A. FUEDA and T. MURAKAMI, *ibid.* **24** (1989) 937.
10. K. KATYAMA, H. HASEGAWA, T. NODA and T. AKIBA, *Sens. Actuators* **B2** (1990) 143.
11. N. YAMAZOE, J. FUCHIGAMI, M. KICHIKAWA and T. SEYAMA, *Surf. Sci.* **86** (1979) 335.
12. C. CANTALINI and M. PELINO, *J. Am. Ceram. Soc.* **75** (1992) 546.
13. T. RATCHEVA, I. STAMBOLOVA and K. KONSTANTINOV, *Thin Solid Films* **217** (1992) 187.
14. V. V. KLIUEV (ed.), "*Ispitatelnaia technika*", (Mashinostroenie, Moscow, 1982) Ch. 2, p. 488.

Received 5 January
and accepted 20 April 1993