JOURNAL OF SOLID STATE CHEMISTRY **128,** 305–309 (1997)
ARTICLE NO. SC967174

## BRIEF COMMUNICATION

# Spray Pyrolysis Preparation and Humidity Sensing Characteristics of Spinel Zinc Stannate Thin Films

I. Stambolova, K. Konstantinov, D. Kovacheva, P. Peshev, and T. Donchev*

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; and *Institute of Electronics, Bulgarian Academy of Sciences, 1784 Sofia, Bulgaria*

Received September 23, 1996; accepted September 25, 1996

**Polycrystalline spinel $Zn_2SnO_4$ films were successfully deposited on alumina substrates by spray pyrolysis. It was found that the ratio of the two cations in the films obtained differs considerably from the ratio in the initial solutions. By optimizing the solution compositions and the deposition and heat-treatment parameters, it was possible to obtain homogeneous single phase films with good adhesion to the substrate. At room temperature the electrical resistance of the films was strongly dependent on humidity, the response and recovery times being very short (1–2 min). The humidity sensing characteristics deteriorated in the presence of a binary oxide (ZnO or $SnO_2$) impurity in the film.** © 1997 Academic Press

## INTRODUCTION

The spray pyrolysis of solutions is an inexpensive method (especially in equipment costs) for deposition of a great variety of oxide films on different substrates. In some cases this technique is used in the fabrication of gas sensor structures based on changes in the electrical characteristics of the films. It is also suitable for the preparation of thin films with interesting optical or photovoltaic performances as well as of films used as electrodes (1).

The binary oxides of zinc (ZnO) and tin ($SnO_2$) belong to the classical materials from which thin films are prepared by various routine procedures including spray pyrolysis (2–4). However, data on ternary oxides of the system ZnO–$SnO_2$ are scarce despite expectations of a wide variety of applications of zinc stannate, $Zn_2SnO_4$ (5). Hashemi *et al.* (5) have investigated the synthesis of this spinel oxide by a solid state reaction between the binary oxides at elevated temperatures. They have shown that the preparation of a single-phase product is accompanied by some difficulties due to the low reaction rates at 1000–1300 °C and the resulting evaporation of part of the ZnO, which leads to the appearance of microdomains with an inhomogeneous chemical composition.

Recent publications report the preparation of films of spinel zinc stannate. Thus, Enoki *et al.* (6) and Minami *et al.* (7) have succeeded in depositing $Zn_2SnO_4$ thin films of fused silica and glass substrates, respectively, by RF magnetron sputtering. A thick film preparation using a paste composed of $Zn_2SnO_4$ powder and a polyvinyl alcohol solution is described in a communication of Matsushima *et al.* (8). These authors have established that the films obtained have good $NO_2$ gas sensing properties.

The present paper is aimed at investigating possible preparation of $Zn_2SnO_4$ thin films by spray pyrolysis. In addition, due to increasing interest in oxide spinel films as sensors for humidity detection (9), it was worth while to see whether the films obtained might be promising in this respect.

## EXPERIMENTAL

Aqueous solutions (0.5 *M*) of $SnCl_4$ (99.9% purity) and $Zn(NO_3)_2$ were used in the investigations. The zinc nitrate solution was obtained by dissolving analytical reagent grade ZnO in nitric acid. The mixtures of the two solutions subjected to spray pyrolysis had a Zn:Sn atomic ratio that corresponded to the stoichiometric (2:1) ratio in $Zn_2SnO_4$ or to different quantities of zinc in excess to the stoichiometric amount (Zn:Sn = 3:1, 3.5:1, 3.7:1, 3.9:1, 4.1:1, and 4.2:1, respectively) because of the expected prevailing evolution of zinc during the processing.

The films were deposited on commercially available alumina substrates subjected to cleaning with high-purity ethanol and acetone followed by drying in a pure nitrogen flow prior to film deposition.

Conventional spray pyrolysis equipment similar to that described in the literature (1) was used for the preparation of



0022-4596/97 $25.00

**TABLE 1**
**Spraying Conditions for Deposition of $Zn_2SnO_4$ Films**

| $T_{sub}$(°C) | Carrier gas | Nozzle–substrate distance (cm) | Flow rate (ml/s) |
|---|---|---|---|
| 450–480 | Ar | 10–12 | 0.2–0.3 |

the films. The solutions were sprayed intermittently onto the substrate for 10 s at regular time intervals of 20 s. The optimum spraying conditions for deposition of the films are shown in Table 1.

The deposits obtained were subjected to thermal treatment in air at 1000°C for 8–10 h. Films with a thickness of 1–3 μm were prepared.

The phase composition of the films obtained was studied by X-ray diffraction (XRD) and their morphology was established on the basis of scanning electron microscopy (SEM) observations. Energy dispersive X-ray (EDX) analysis was used to determine the zinc and tin content in the films.

To prepare sensor elements, two silver painted electrodes were deposited on the films, the distance between them being 0.5 mm. The elements were placed in a test chamber where, by introducing different steam amounts into the dry air at 25°C, the conditions needed for attaining different relative humidities (rh) were achieved. The rh values were found using a conventional hygrometer with an accuracy of $\pm$ 4%. The value of the electrical resistance $R$ of the films was determined for each rh value and the $R = f(\text{rh})$ dependencies were plotted. The response and recovery times were evaluated by the change in resistance with the relative humidity varying from 94% to 50% and vice versa.

## RESULTS AND DISCUSSION

The determination of the zinc and tin content in the films after the final thermal treatment showed that the Zn/Sn atomic ratio differed drastically from that in the initial solutions. As it appears from the data in Fig. 1, obtaining a single phase film with a cation ratio that corresponds to the stoichiometric value (2:1) under our experimental conditions requires a ratio in the initial solution of 4.1:1. The results from the EDX determinations of the basis of which the curve in Fig. 1 has been plotted are in excellent agreement with the XRD patterns of the films. Fig. 2 shows, as an example, the XRD pattern of the single-phase film where all lines agree with the data available in the literature concerning $Zn_2SnO_4$ (10).

As is mentioned above, the formation rate of the spinel phase $Zn_2SnO_4$ during the solid phase reaction between the binary oxides is low; as a consequence, after spray pyrolysis, the films obtained should be submitted to a relatively long

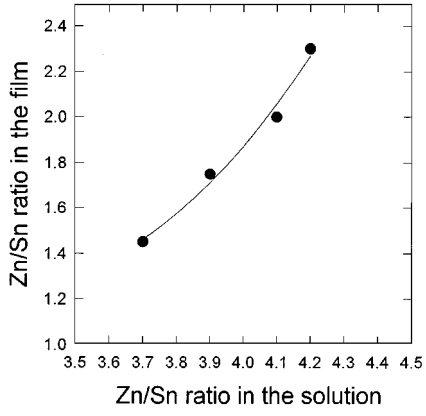


**FIG. 1.** Relationship between the Zn/Sn atomic ratios in the initial solutions and in the thin films obtained after heat treatment.

thermal treatment. It has been established that 10 h heating in air at 1000°C is the optimum annealing time for the preparation of a single $Zn_2SnO_4$ phase with good crystallinity. This duration of treatment eventually allows removing from the film a small ZnO excess by evaporation.

If the Zn:Sn atomic ratio in the initial solution has a value differing from the optimum (4.1:1), a second phase ($SnO_2$ or ZnO) is present in the film. It has been established that this impurity phase affects the film morphology, as shown by the SEM photographs of films obtained in solutions with a Zn:Sn ratio differing from the optimum. Thus, if the film contains ZnO as an impurity phase, it has a dense structure with large agglomerates on the surface (Fig. 3a). The structure is more inhomogeneous, with specific "flower-like" regions, if $SnO_2$ is present in the film (Fig. 3b). A large

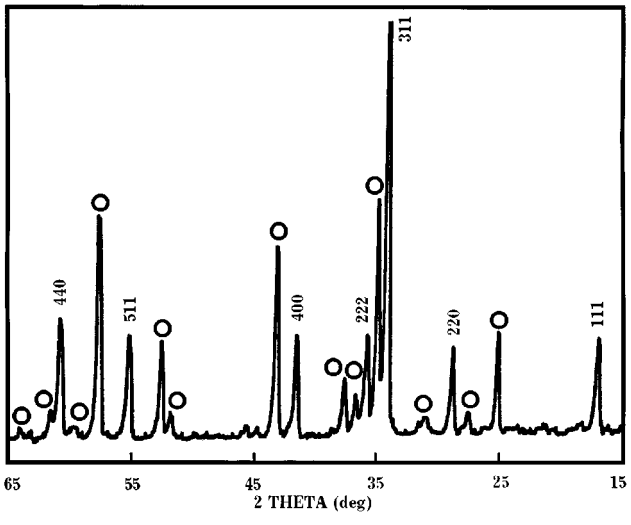


**FIG. 2.** XRD pattern of a single phase $Zn_2SnO_4$ spinel film obtained from a solution with a Zn:Sn atomic ratio of 4.1:1. (○) $Al_2O_3$ substrate.

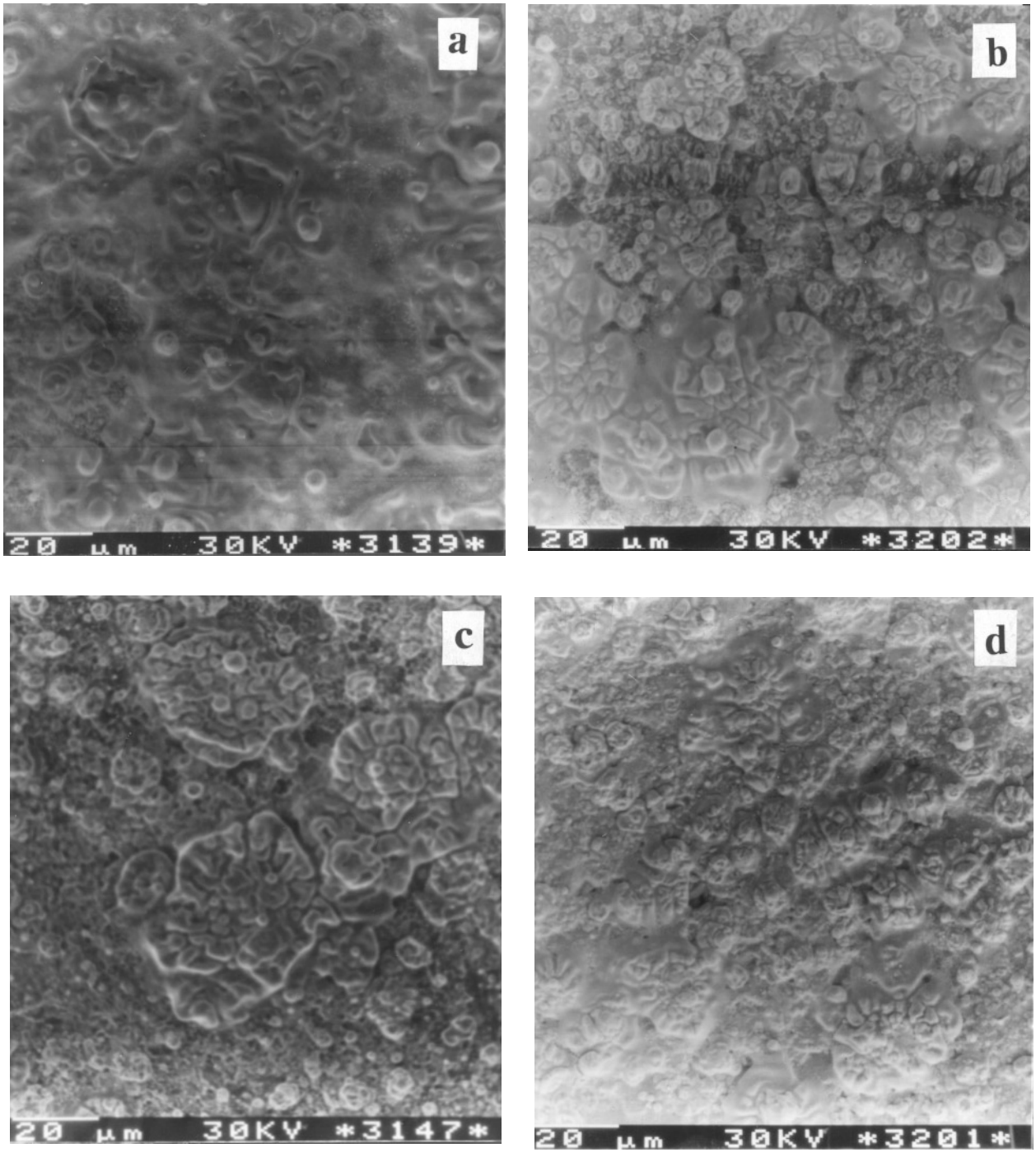


**FIG. 3.** SEM photographs of films obtained from solutions with different Zn:Sn atomic ratios: an annealed film obtained from a solution with Zn:Sn = 4.2:1 (a) and Zn:Sn = 3.9:1 (b), a sprayed film before annealing obtained from a solution with Zn:Sn = 4.1:1 (c), and an annealed film obtained from a solution with Zn:Sn = 4.1:1 (d).

similarity to Fig. 3b is exhibited by the film deposited from a solution with Zn:Sn = 4.1:1 before the thermal annealing (Fig. 3c). This is probably due to the fact that at this stage the film obtained consists of both ZnO and $SnO_2$ phases which later react completely, being transformed into a single spinel phase during the final heating at 1000°C. After such a thermal treatment the film acquires the most homogeneous structure shown on the SEM photograph in Fig. 3d.

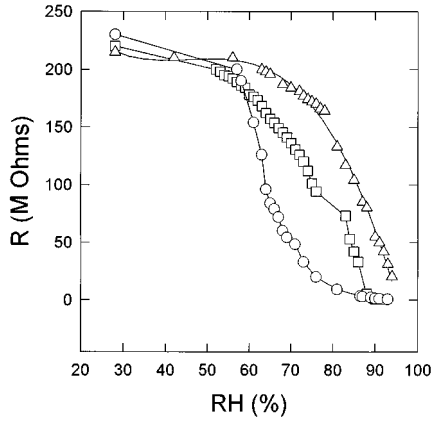


**FIG. 4.** Electrical resistance vs relative humidity dependencies at 25°C. (△) A single phase $Zn_2SnO_4$ thin film: (□) a $Zn_2SnO_4$ thin film containing ZnO as an impurity phase; (○) a $Zn_2SnO_4$ thin film containing $SnO_2$ as an impurity phase.

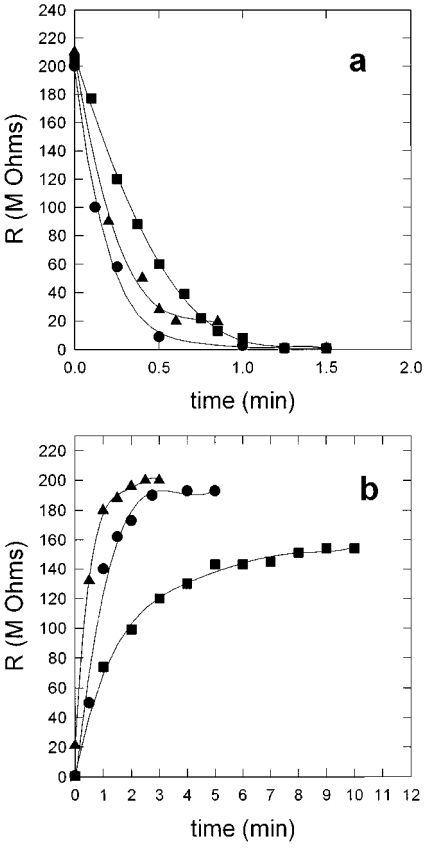


**FIG. 5.** The response (a) and recovery (b) times at 25°C when rh ranges from 50 to 94% and vice versa: (▲) a single phase $Zn_2SnO_4$ thin film; (■) a $Zn_2SnO_4$ thin film containing ZnO as an impurity phase; (●) a $Zn_2SnO_4$ thin film containing $SnO_2$ as an impurity phase.

The relationships established between the electrical resistance of films with different phase compositions and the relative humidity in the measuring chamber are shown in Fig. 4. Obviously, the single phase film displays a strong $R = f(\text{rh})$ dependence for rh values in the range 60–94%. ZnO impurities are present in the film, an additional step is observed in the range of 70–85% rh values and for rh > 85% the dependence becomes weak. When $SnO_2$ is detected as a second phase, the $R = f(\text{rh})$ dependence exhibits two distinct regions. The first corresponds to rh values in the 60–75% range where an obvious correlation is observed with $R$ while for rh > 75% the relationship is weaker. For all films a small and almost linear resistance change is observed with rh values below 50%.

The measured response times of the films under investigation are given in Fig. 5a. Obviously, in the presence of humidity the $Zn_2SnO_4$ single phase film reacts faster than the films containing ZnO or $SnO_2$ impurities. The single phase film also exhibits the shortest recovery time: it is about 2 min when the rh value changes from 94 to 50% (Fig. 5b). The longest recovery time (more than 10 min) corresponds to the film with ZnO impurities. On the basis of the results presented in Figs. 4 and 5, it can be concluded that films consisting of a single $Zn_2SnO_4$ phase have better humidity sensing characteristics than films containing ZnO or $SnO_2$ as an impurity phase.

## CONCLUSION

As a result of the present investigation it has been shown that single phase spinel zinc stannate thin films can be prepared by spray pyrolysis of aqueous solutions containing zinc nitrate and tin tetrachloride followed by prolonged annealing at 1000°C. These films have remarkable sensing characteristics which make them a promising material especially for very fast detection of relative humidity values above 50%.

## ACKNOWLEDGMENTS

The financial support of the Ministry of Education, Science and Technology of Bulgaria (National Fund of Scientific Investigations) under Contract X-566/1995 is gratefully acknowledged. Thanks are also due to Mrs. I. Khristova for technical assistance.

## REFERENCES

1. D. S. Albin and S. H. Risbud, *Adv. Ceram. Mater.* **2,** 243 (1987).
2. S. Pizzini, N. Butta, D. Narducci, and M. Palladino, *J. Electrochem. Soc.* **136,** 1945 (1989).
3. N. Butta, M. Melli, and S. Pizzini, *Sens. Actuators B* **2,** 151 (1990).
4. I. Stambolova and K. Konstantinov, *J. Mater. Sci.* in press.

5. T. Hashemi, H. M. Al-Allak, J. Illingsworth, A. W. Brinkman, and J. Woods, *J. Mater. Sci. Lett.* **9,** 776 (1990).
6. H. Enoki, T. Nakayama, and J. Echigoya, *Phys. Stat. Sol. A* **129,** 181 (1992).
7. T. Minami, H. Sonohara, S. Takata, and H. Sato, *Jpn. J. Appl. Phys. A* **33,** L1693 (1994).
8. S. Matsushima, S. Kunitsugu, K. Kobayashi, and G. Okada, *J. Ceram. Soc. Jpn.* **103,** 309 (1995).
9. E. Traversa, *Sens. Actuators B* **23,** 135 (1995).
10. "Powder Diffraction File, Inorganic Phases, JCPDS," Set 24, Card 1470. International Center for Diffraction Data, Swarthmore, PA, 1974.