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A novel method of producing dicadmium stannate in thin film form

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The possibility of dicadmium stannate thin film production using a vacuum evaporation technique has been investigated. Thin films produced by this method have been characterized using X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS), electron diffractometry and analytical scanning electron microscopy (SEM).

1. Introduction

Dicadmium stannate is of special interest for a number of technological applications including solar energy conversion [1], heat mirrors [2], and transparent photoanodes [3]. More recently, the use of dicadmium stannate as an electroactive material for secondary battery applications has been suggested [4]. Preparation of dicadmium stannate thin films has been traditionally carried out by sputtering techniques [5–7], although attempts have been made to produce Cd_2SnO_4 thin films by means of spray pyrolysis of $CdCl_2$ and $SnCl_4$ [8], plasma spraying [9], and electroless deposition from organometallic compounds [10].

As far as we are aware, no work has been done on the potential use of simple vacuum deposition techniques for the preparation of Cd_2SnO_4 thin films, despite the apparent fact that this technique is easier to handle, more versatile and also cheaper. The technique may seem handicapped at a first glance because of the well-known problem of the evaporation of CdO. The problem can be solved, however, by elimination of the CdO evaporation, using metallic cadmium instead. Our detailed studies of the dicadmium stannate system have shown that dicadmium stannate can exist as Cd_2SnO_4, Cd_2SnO_3 and/or Cd_2SnO_2. These species can be produced directly from suitable rectants and are easily converted to each other upon subsequent treatment. It thus follows that a thin film of cadmium stannate can be produced by vacuum evaporation using SnO_2 and Cd, each being evaporated from its own boat. With proper control of stoichiometry, Cd_2SnO_4 can be produced by subsequent annealing of this product in air.

In this communication we report for the first time the possibility of cadmium stannate film production using the vacuum evaporation technique. Characterization of the films was carried out by means of XRD, XPS, and SEM techniques.

2. Experimental details

Analar grade tin dioxide and cadmium powder were obtained from BDH Ltd (Poole, Dorset, UK) and Aldrich Chemical Co. (Gillingham, Dorset, UK), respectively. Cadmium stannate films were prepared by the technique of co-evaporation described by Hogarth and Wright [11], using a Balzers BA 510 vacuum coating unit. Molybdenum boats were used for evaporation of both SnO_2 and Cd. The thickness of the film was controlled by means of a crystal monitor. Films for transmission electron microscopy were deposited on carbon-coated mica while the substrates used for other measurements were Corning 7059 glass. The substrates were held at room temperature during the deposition processes. A JEM 7 instrument was used for transmission electron microscopy and electron diffraction measurements. For obtaining scanning electron micrographs together with elemental analyses a Jeol 840 SEM was employed.

3. Results and discussion

X-ray diffraction examination of reasonably thick Cd_2SnO_4 films (of order 5 μm) prepared by the co-evaporation of SnO_2 and Cd and subsequent air annealing proved to be identical to those patterns reported previously [12] either obtained from bulk samples or thin films. In some instances, small quantities of CdO, SnO_2 and/or $CdSnO_3$ could also be identified. By careful control of the stoichiometric ratios during the co-evaporation of the reactants, however, it was possible to grow films virtually free from other impurities. The resultant product had the familiar colour of yellow, typical of cadmium stannates with divalent cadmium and with tin in the tetravalent state. All films produced this way were highly conductive and transparent. XRD examination of the as-deposited films on substrates held at room temperature prior to any heat treatment, revealed an amorphous structure, judging by the absence of any sharp peak in the diffraction pattern. Because the XRD technique yields essentially only average information about the crystallinity of the compound under investigation, electron diffraction patterns were obtained using transmission electron microscopy in order to check the individual points. Fig. 1 shows a typical electron diffraction pattern of an as-deposited film prior to heat treatment. The diffused rings in this figure are typical of an amorphous material. Fig. 2 shows a typical pattern of a sample which had undergone annealing in air. The diffused rings in Fig. 1, have been replaced with sharp and clear rings together with the appearance of spots, typical of crystalline materials.

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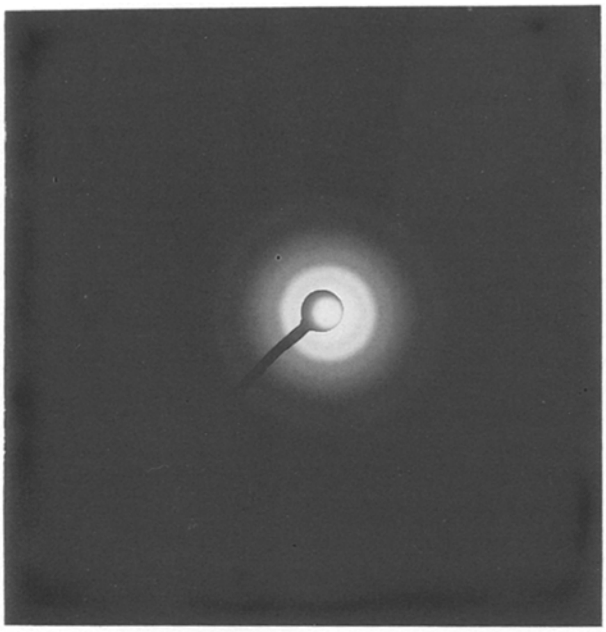

Figure 1 Electron diffraction pattern of the as-deposited Cd/SnO_2 film prior to heat treatment.

Fig. 3 shows a scanning electron micrograph of a carefully prepared Cd_2SnO_4 thin film already examined by XRD to make sure of the absence of the impurities. Several X-ray point analyses of the sample showed an approximate ratio of 2Cd/1Sn, consistent with the chemistry of cadmium stannate. An X-ray image of the surface for both Sn$K\alpha$ and Cd$K\alpha$ radiation showed no singularities, indicating an even distribution of the elements present in the film. These results were compared with those for samples in which the existence of impurities had been demonstrated by means of XRD. In the latter case, there are numerous points on the surface, rich in one of the constituents of the product.

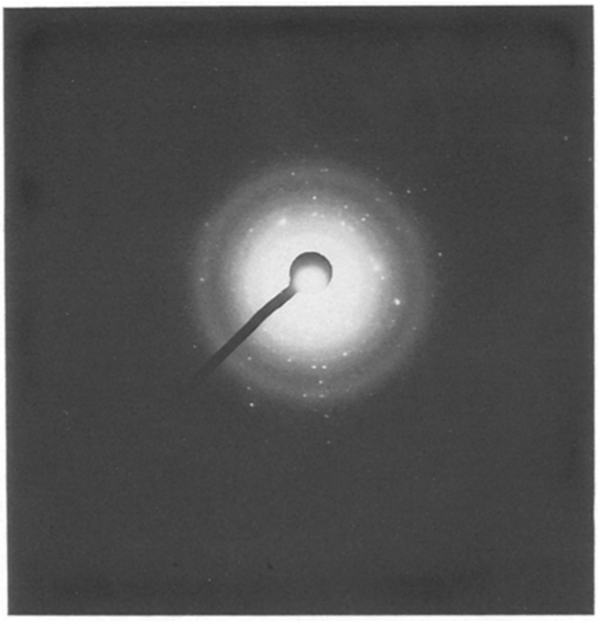

Figure 2 Electron diffraction pattern of the sample in Fig. 1 after being annealed for 30 min in air at 400° C.

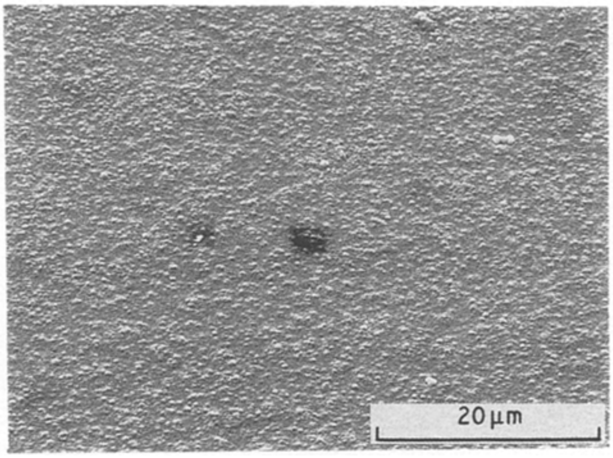

Figure 3 Scanning electron micrograph of a Cd_2SnO_4 thin film.

The chemical nature of the film before and after the process of annealing was determined using X-ray photoelectron spectroscopy (XPS). Calculation of the chemical formula of the film based on the peak heights and using the sensitivity factors revealed the formula of Cd_2SnO_3 for as-deposited and Cd_2SnO_4 for annealed films. In the first case, i.e. Cd_2SnO_3, the exact valency of cadmium or tin is not known. That is to say, if cadmium is in its monovalent state, tin remains in the tetravalent form. On the other hand, if cadmium is divalent, Sn^{4+} should have undergone a reduction to Sn^{2+} during the evaporation process. It is interesting that XPS alone can solve this problem by precise measurement of the relevant binding energies. All the binding energies obtained in the present work are given in Table I. The two different values given for CdO arise from the existence of some Cd_2O species on the top of the original oxide. The possibility of the formation of such a suboxide through a disproportionation reaction has been originally suggested by the present authors [13], and was confirmed later in the course of detailed studies of the system [14]. From these results, it is evident that although there is a chemical shift between Cd(0) and Cd(II), it is not possible to distinguish between Cd(0) and Cd(I). However, as far as the present work is concerned, this shortcoming does not preclude the validity of the results. Fig. 4 shows XPS spectra of a sample before and after heat treatment. Fig. 4a shows the spectra in the regions of $Cd3d_{5/2}$ and $Sn3d_{5/2}$ before any treatment and Fig. 4b shows the results after annealing. As stated before, there is no direct way to allocate a valency to cadmium. However, as no change has taken place in the binding energy of tin while a relatively large shift has occurred for Cd3d, it is logical to assume that the tin valency remains the same in both Cd_2SnO_3 and Cd_2SnO_4 while the change in valency occurs for cadmium. The conclusion is, therefore, that in Cd_2SnO_3, cadmium exists in a monovalent state. Finally, in some instances, traces of molybdenum were found in the evaporated films characterized by XPS

TABLE I The values of binding energies are based on the C1s level at 285.0 eV.

	$Cd3d_{5/2}$	$Sn3d_{5/2}$
Cd	405.5	–
CdO	404.8, 405.7	–
SnO_2	–	486.4
Cd_2SnO_3	405.6	486.5
Cd_2SnO_4	404.8	486.4

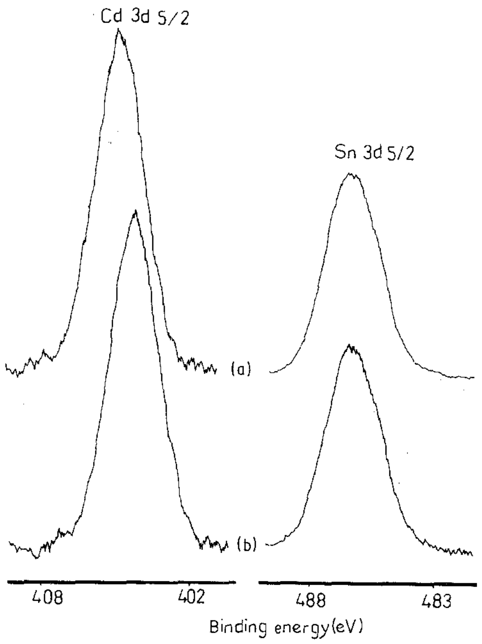

Figure 4 X-ray photoelectron spectra of the sample in the regions of $Cd3d_{5/2}$ and $Sn3d_{5/2}$, (a) before heat treatment, (b) after heat treatment.

which was due to the use of molybdenum boats for evaporation.

4. Conclusion

In this work the deposition of the films of dicadmium stannate by means of vacuum co-evaporation of metallic cadmium and SnO_2 proved to be successful. Deposited films on substrates held at room temperature are shown to be amorphous. Subsequent heat treatment in air yielded polycrystalline products. The chemical nature of the films before and after annealing proved to be Cd_2SnO_3 and Cd_2SnO_4, respectively. In these compounds the valency of tin remains unchanged, while cadmium changes from the monovalent to the divalent state during the heat treatment.

References

1. L. C. BURTON, T. HENCH, G. STORTI and G. HAACK, *J. Electrochem. Soc.* **123** (1976) 1741.
2. G. HAACK, *Appl. Phys. Lett.* **30** (1977) 380.
3. K. J. D. MACKENZIE, W. A. GERRARD and F. GOLESTANI-FARD, *J. Mater. Sci. Lett.* **14** (1976) 2509.
4. T. HASHEMI, F. GOLESTANI-FORD and J. AVANESSIAN, *J. Electrochem. Soc.* **134** (1987) 1591.
5. N. MYATA, K. MYAKE, K. KOGA and T. FUKUSHIMA, *ibid.* **127** (1980) 918.
6. R. P. HOWSON, M. I. RIDGE and C. A. BISHOP, *Thin Solid Films* **80** (1981) 137.
7. E. LEJA, T. STAPINSKY and K. MARSZALEK, *ibid.* **125** (1985) 119.
8. R. A. ORTIZ, *J. Vac. Sci. Technol.* **20** (1982) 7.
9. E. BUEDKE, G. BEISTER, H. C. HECHT, S. SCHNEIDER and W. SIEBER, Ger. (East) DD 205 (1983) 193.
10. D. RAVIENDRA and J. K. SHARMA, *J. Appl. Phys.* **58** (1985) 838.
11. C. A. HOGARTH and L. A. WRIGHT, Proceedings IX International Conference on the Physics of Semiconductors, Moscow 1968, Vol. 2, 12d (Akad. Nauk, SSSR, 1968) p. 1274.
12. F. T. J. SMITH and S. L. LYU, *J. Electrochem. Soc.* **128** (1981) 1083.
13. F. GOLESTANI-FARD, T. HASHEMI, K. J. D. MACKENZIE and C. A. HOGARTH, *J. Mater. Sci.* **18** (1983) 3679.
14. T. HASHEMI, C. A. HOGARTH and F. GOLESTANI-FARD, *ibid.* **23** (1988) 2645.

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