

## Transparent Conducting Films of Antimony Doped Tin Oxide on Glass

A. R. Peaker and B. Horsley

Citation: [Review of Scientific Instruments](#) **42**, 1825 (1971); doi: 10.1063/1.1685015

View online: <http://dx.doi.org/10.1063/1.1685015>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/rsi/42/12?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Fluorine doped tin oxide \(FTO\) thin film as transparent conductive oxide \(TCO\) for photovoltaic applications](#)  
AIP Conf. Proc. **1512**, 710 (2013); 10.1063/1.4791235

[Deposition of transparent, conductive tin oxide films on glass using a radio-frequency induction heater](#)  
Rev. Sci. Instrum. **80**, 126105 (2009); 10.1063/1.3270256

[Structural, electrical, and optical properties of antimony-doped tin oxide films prepared at room temperature by radio frequency magnetron sputtering for transparent electrodes](#)  
J. Vac. Sci. Technol. A **27**, 996 (2009); 10.1116/1.3139891

[Electrical Transport in Transparent Conducting Tindoped Indium Oxide Films](#)  
AIP Conf. Proc. **850**, 1548 (2006); 10.1063/1.2355295

[Physical properties of antimonydoped tin oxide thick films](#)  
J. Appl. Phys. **53**, 3629 (1982); 10.1063/1.331144

---

An advertisement for Asylum Research Cypher AFMs. The background is dark blue with a film strip graphic on the left. The text is in orange and white. The Oxford Instruments logo is in the bottom right corner.

**Not all AFMs are created equal**  
**Asylum Research Cypher™ AFMs**  
**There's no other AFM like Cypher**

[www.AsylumResearch.com/NoOtherAFMLikeIt](http://www.AsylumResearch.com/NoOtherAFMLikeIt)

**OXFORD**  
INSTRUMENTS  
*The Business of Science®*

## Transparent Conducting Films of Antimony Doped Tin Oxide on Glass

A. R. PEAKER\* AND B. HORSLEY

*University of Manchester Institute of Science and Technology, Manchester, M60 1QD, United Kingdom*

(Received 19 July 1971; and in final form, 23 August 1971)

A simple laboratory technique for the routine preparation of transparent conducting films on soda and borosilicate glasses is described. The process uses the surface hydrolysis of stannic chloride at a temperature approaching the softening point of the glass. High electrical conductivity ( $50 \Omega/\text{sq}$ ) and good optical transmission (80%) have been obtained by the addition of small quantities of antimony and the optimization of deposition conditions. The technique has been found to give uniform and consistent results.

### INTRODUCTION

Tin oxide in its pure state has a high resistivity of the order of  $10^8 \Omega \cdot \text{cm}$ . If it is to be used to form a conducting film it must be deposited in a nonstoichiometric form or suitable dopants must be added. It has been known for some time that thin films of tin oxide could be deposited on glass in a conducting form by allowing a tin halide to react with water at the glass surface.<sup>1,2</sup> Thermal probe and Hall measurements made in our laboratories on films produced in this way show the tin oxide to be *n* type as has been observed previously.<sup>3,4</sup> In layers in which no intentionally added dopants are present the free electron population has been attributed to oxygen vacancies or interstitial tin ions.<sup>5</sup> Aitchison<sup>5</sup> and Spence<sup>6</sup> have examined tin oxide films containing relatively large quantities (5 mole%) of antimony and of indium and found that indium increases the resistivity while antimony decreases it, a result compatible with the impurity atoms substituting for tin in the oxide lattice and producing free electrons. Consequently antimony has been used as a dopant in the films produced by the technique described in this paper because it was considered that the added impurity concentration would be easier to control than the degree of deviation from stoichiometry, and would therefore more easily fulfill the requirements of obtaining uniformity and reproducibility.

### I. APPARATUS

The apparatus consisted basically of a means of spraying a fine mist of stannic chloride solution onto a glass substrate held at a temperature of about  $500^\circ\text{C}$ . A method of pre-heating the mist was also provided so that when it impinged on the substrate, only small changes in temperature occurred at the glass surface; this was particularly important if a good surface finish was to be obtained.

The stannic chloride solution was sprayed from a Pyrex glass atomizer similar to the type employed in chromatography but in this case a continuous gas flow was used. The atomizer was designed so that at a pressure of  $0.4 \text{ kg} \cdot \text{cm}^{-2}$  it delivered  $2 \text{ ml} \cdot \text{min}^{-1}$ . Previous results with a stainless steel spray gun were unsatisfactory because it was found that corrosion occurred and this resulted in the tin oxide film containing up to 100 ppm of iron. Although this did not affect the transmission or resistivity of the coating significantly it was unacceptable because the conducting glass was to be used in studies of electroluminescent films of zinc sulfide, and these are particularly susceptible to contamination by elements of the iron group.

The oven used for depositing the tin oxide films is shown in Fig. 1, the width of the chamber being 30 cm. The side walls were constructed from alumina bricks and the base and top from asbestos sheet. The oven was heated by three

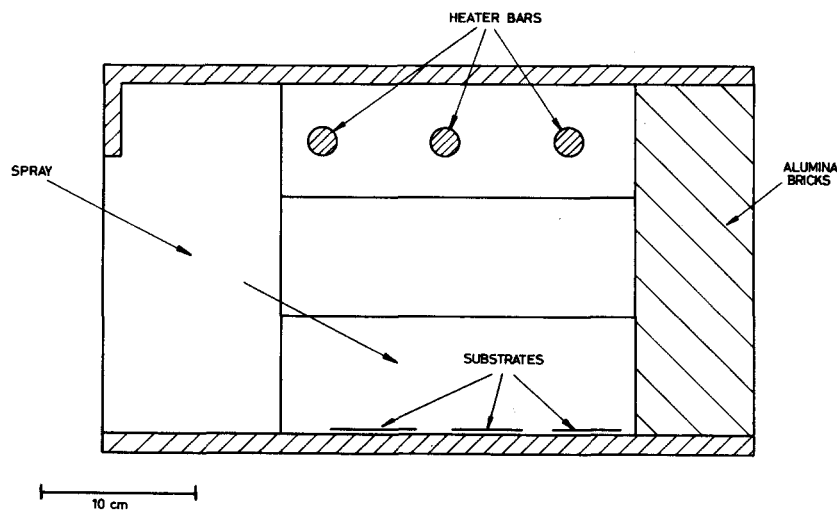


FIG. 1. Section through the spraying oven.

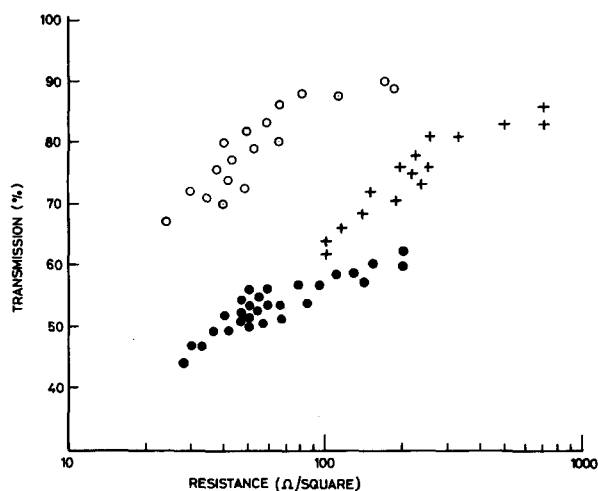
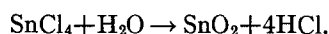


FIG. 2. Variation of optical transmission with film resistance for various doping conditions: +—no antimony, O—0.4 mole% antimony, ●—2 mole% antimony.

1 kW radiant bars close to the top of the enclosure; these were arranged to be some distance from the stream of vapor. The glass to be coated was placed on the floor of the oven and the spray was directed through an opening at the front which was the full width of the chamber. The geometry of the system ensured adequate preheating of the vapor could take place. The temperature of the glass substrate was monitored by a thermocouple in contact with the underface of the glass. The temperatures quoted in this paper are those measured by the thermocouple and are a few degrees lower than the actual surface temperature of the glass.

## II. PROCEDURE

The basic reaction used to produce the film is



This is a simplification of the conditions because deviations from stoichiometry occur as has already been discussed. It is also probable that side reactions with the glass surface take place during the initial stages of deposition and this may be responsible for the very high abrasion resistance of the films.

In order to ensure that hydrolysis takes place principally at the surface of the glass it was found necessary to dilute the solution with a carrier (industrial ethanol) and to add an excess of hydrochloric acid. Care was taken that the spray did not impinge on the brick surface and was not heated to above 400°C before striking the glass, because decomposition took place under both these circumstances, resulting in a crystalline film with an opalescent appearance. A similar effect also occurred if prolonged spraying took place at a substrate temperature less than 430°C.

A satisfactory composition for the spraying solution is given below, the weight of antimony corresponding to the 0.4 mole% data in Fig. 2:

hydrochloric acid (conc)	10 ml
stannic chloride (anh)	75 ml
ethanol (industrial)	50 ml
water	50 ml
antimony trichloride	0.6 g.

The constituents were slowly mixed in the order given in an ice bath.

The solution was sprayed at a pressure of 0.4 kg·cm<sup>-2</sup> for approximately 15 sec, the actual time depending on the thickness and resistance required. It was found that either nitrogen or argon gave slightly better results than compressed air when used as the carrier gas in the spray. The spraying process was carried out in an extracted chamber because of the toxicity of the antimony compounds and the presence of the hydrogen chloride fumes. The optimum glass temperature, that is, the temperature at which maximum transmission was obtained for a given resistance, varied from 520°C (borosilicate) to 480°C (soda glass) although the change in transmission for a 20°C change in temperature was found to be less than 10%.

## III. RESULTS

Figure 2 shows the relationship between transmission and resistance of films deposited on Chance CMD glass with different concentrations of antimony, the range of resistances being obtained by varying the film thickness. This can be adjusted by changing the spraying time, the range used to produce the values shown being from 5 to 25 sec for each value of antimony concentration.

The figure given for transmission is that for white light with a color temperature of 3200 K, only the visible wavelengths being monitored. Apart from interference effects on some of the films no absorption peaks were present over the range 400–700 nm.

The use of antimony to increase the conductivity enables a much greater degree of reproducibility to be obtained, particularly at the lower resistance values. For a given resistance the antimony doped films are thinner than the undoped ones, so that the light gray appearance of the thicker undoped films is avoided with a consequent increase in transmission. At the highest doping level shown in Fig. 2 the film is darkened by free carrier absorption. The antimony concentration of 0.4 mole% was found to give the optimum results with a good surface finish. There were no texture or crystallites observable in the optical microscope and flaws on the surface were very few provided

the oven and spraying area were free from dust and loose particles.

### ACKNOWLEDGMENTS

We would like to thank Professor C. Adamson for providing the facilities to do this work and Dr. R. S. Millman for his advice and assistance.

\* Now at Ferranti Ltd., Chadderton, Oldham, Lancashire, U.K.

<sup>1</sup> R. Gomer, *Rev. Sci. Instrum.* **24**, 993 (1953).

<sup>2</sup> H. A. McMaster, *Brit. Patent* 632256 (1942).

<sup>3</sup> Von R. Groth, E. Kauer, and P. C. v. d. Linden, *Z. Naturforsch.* **17a**, 789 (1962).

<sup>4</sup> K. Ishiguro, T. Sasaki, T. Arai, and I. Inai, *J. Phys. Soc. Japan* **13**, 296 (1958).

<sup>5</sup> R. E. Aitchison, *Aus. J. Appl. Sci.* **5**, 10 (1954).

<sup>6</sup> W. Spence, *J. Appl. Phys.* **38**, 3767 (1967).

## A Method for the Precision Comparison of the Densities of Small Specimens\*

A. D. FRANKLIN AND R. SPAL

*National Bureau of Standards, Washington, D. C. 20234*

(Received 28 July 1971)

The density of an unknown is compared to that of a set of several standard specimens (weighing about 40 mg each) with a standard deviation in the ratio of densities from a single determination of  $3 \times 10^{-4}$  or better. The apparatus consists of two immiscible liquids and a float in the upper, supporting the specimen in the lower by a wire that passes through the interface. The wire provides a buoyant force gradient. From the change in position of the float when the unknown is substituted for the standards, the density of the unknown relative to that of the standards can be calculated. Other contributions to the buoyant force gradient are also present; their variation during the course of the measurement established the precision of the measurement.

### INTRODUCTION

In studies of defects in crystalline solids, it is often desirable to be able to compare the densities of rather small crystals to rather high precision. The most precise measurements have involved some form of hydrostatic weighing, using beam balances<sup>1-3</sup> or a Cartesian diver<sup>4</sup> to weigh the specimen in liquid. With specimens of a few cubic centimeters volume, precision represented by errors ranging from a few parts in  $10^5$  to a few in  $10^7$  has been achieved. However, relatively large samples are required and rather special apparatus is needed.

Flotation measurements (Muller<sup>5</sup> has reviewed these and other methods) are capable also of great precision and have recently been used to<sup>6,7</sup> make measurements of relative densities to within a few parts in  $10^6$ . These methods are well adapted to very small samples indeed, but require rather elaborate temperature controls and are restricted, for results of high precision, to samples with densities below about  $4.5 \text{ g/cm}^3$ .

We describe here a new technique, suggested to us by Dr. Horace Bowman of the National Bureau of Standards, with which we have been able to compare the densities at room temperature of  $\text{CaF}_2$  crystals (density about  $3.2 \text{ g/cm}^3$ ) weighing 37 mg to within a few parts in  $10^4$ . Residual sources of error are apparent and improvements that might reduce the uncertainty considerably are discussed. The apparatus is simple to build and to operate and seems well suited for use where intermediate precision without undue complication is desired.

### APPARATUS AND TECHNIQUE

Figure 1 presents a simplified view of the apparatus. Two immiscible liquids of differing density are contained in a cylinder. From a float of suitable material in the upper liquid, a thin wire reaches down through the interface between the liquids. On a hook at the bottom of the

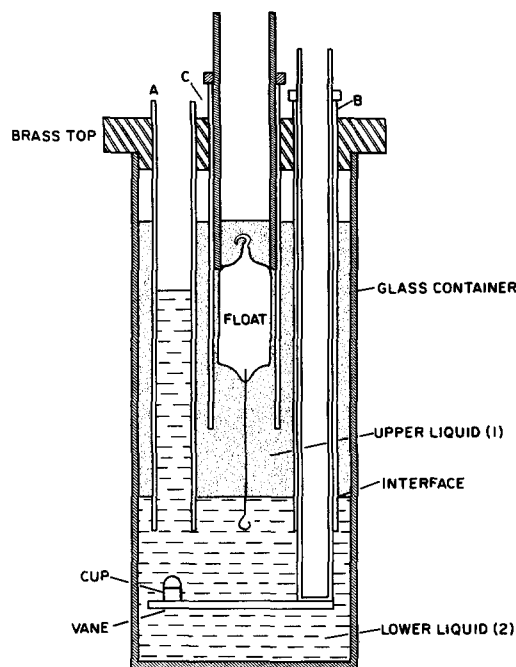


FIG. 1. Sketch of density apparatus.