IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Electrical properties of undoped In_2O_3 films prepared by reactive evaporation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1980 J. Phys. D: Appl. Phys. 13 1129

(http://iopscience.iop.org/0022-3727/13/6/023)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.234.252.65
The article was downloaded on 16/02/2011 at 08:56

Please note that terms and conditions apply.

J. Phys. D: Appl. Phys., 13 (1980) 1129–33. Printed in Great Britain

Electrical properties of undoped In_2O_3 films prepared by reactive evaporation

S Noguchi and H Sakata
Research Laboratory, Asahi Glass Co. Ltd., Hazawa-cho, Kanagawa-ku, Yokohama 222, Japan

Received 31 July 1979

Abstract. Electrical properties of reactively evaporated In_2O_3 films are studied in relation to evaporation conditions and the carrier scattering mechanism is discussed. The films are made on heated glass substrates by evaporation of In metal in oxygen at about 1×10^{-3} Torr. The films become polycrystalline above substrate temperature 200 °C, showing 75% transparency at 550 nm. Electrical resistivity of the films, $\rho = 2\text{–}3 \times 10^{-3}$ Ω cm is obtained for substrate temperatures 200–400 °C. Hall coefficient measurements show the film to be a n-type conductor and have relatively high mobility, 25–60 $cm^2\ V^{-1}\ s^{-1}$. The degeneracy of free carriers in the film is established by the high carrier concentration (above $3{\cdot}5 \times 10^{19}\ cm^{-3}$) and absence of temperature dependence of electrical properties. Discussion of the mobility-carrier concentration relationship from the experiments and theory leads to the conclusion that the dominant scattering process in the films is due to ionised impurity scattering centres.

1. Introduction

Indium oxide (In_2O_3) and indium–tin oxide (ITO) films are n-type semiconductors with a moderately high concentration of free carrier electrons, of the order of $10^{20}\ cm^{-3}$, low resistivity, 10^{-3}–10^{-4} Ω cm, and a sufficiently wide band gap, 2·62–3·75 eV (Weiher and Ley 1966, Müller 1968); this causes high transparency in the visible light region and high infrared reflectance for frequencies $\omega \lesssim \omega_p$, where ω_p is the plasma frequency.

With these electrical and optical characteristics, In_2O_3 and ITO films, like SnO_2 films, have found a variety of applications in electronic and optical devices: transparent electrodes for display devices, e.g. liquid crystal displays (Gläser 1977), selective transparent coatings for solar energy heat mirrors (Fan and Bachner 1976, Ohata and Yoshida 1977) and window films in n–p heterojunction solar cells (Matsunami *et al* 1975, Nagatomo and Omoto 1976).

Requirements to obtain the lowest resistivity and highest visible transparency in parallel with clarifying the physical properties for these films have led to various methods for their deposition, such as vacuum evaporation (Rupprecht 1954, Hori *et al* 1965), RF sputtering (Vossen 1971, Vossen and Poliniak 1972, Fan and Bachner 1975, Itoyama 1978, Hoffmann *et al* 1978), DC sputtering (Clarke 1977, Vainshtein *et al* 1968), RF ion-plating (Murayama 1975), spray pyrolysis (Groth 1966, Vaisfel'd *et al* 1969, Nagatomo and Omoto 1978) and CVD (Ryabova and Savitskaya 1968, Kane and Schweizer 1975).

With these sputtering techniques one can easily prepare ITO films of lower resistivity

0022-3727/80/061129+05 $01.50 © 1980 The Institute of Physics

of 2×10^{-4} Ω cm and high visible transmission ~90%. Similar results are obtained using the spray process mentioned above.

On the other hand, Katsube (1974) reported that transparent and highly conductive In_2O_3 film with a resistivity 2×10^{-4} Ω cm was obtainable by reactive evaporation of indium oxide on a heated substrate. Nevertheless, the film-forming mechanism and optical and electrical properties of these reactively evaporated films have not been well established.

We started the present work intending to make films of lower resistivity and higher transparency by reactive evaporation, and also to clarify the electrical properties as a semiconductor. This paper deals with undoped In_2O_3 films; if this is an intrinsic conductor it is expected to exhibit no conduction at room temperature; the results however show the well-prepared films to have a resistivity $\sim 2 \times 10^{-3}$ Ω cm due to degeneracy.

2. Experimental details

The evacuating system was a commercially available one. Indium metal of 'five nines' purity was evaporated in vacuum at a pressure 1×10^{-3} Torr from a beryllia crucible by the resistance heating method. The substrates were commercial glass plates 3 mm thick, which were heated during the deposition.

After the ultimate vacuum pressure had been reached (1×10^{-6} Torr by ion and sublimation pumps), we switched pumping to only one diffusion pump and passed O_2 gas into the chamber. We kept the total gas pressure during evaporation to 1×10^{-3} Torr to facilitate oxidation of the film, the background pressure being about 1×10^{-5} Torr.

The glass substrate was heated in vacuum by an electric heater up to about 500 °C. The source–substrate distance was constant, at 35 cm, in the present experiments. Film thickness in the specimens for measurements was fixed to 700–900 Å. The monitored deposition rate was about 3 Å s^{-1}.

We determined the specific resistivity ρ of the films by the four-terminal method, where film thickness was measured by use of a 'Talystep' profile tester (Taylor Hobson Co., London). From measurement of the Hall coefficient R_H by a conventional technique, we determined Hall mobility μ_H and carrier concentration N for the films, using the well-known relationships adaptable to degenerate state, $\mu_H = R_H/\rho$ and $N = 1/|eR_H|$ where e is electron charge.

Structure and surface texture of the films were examined by x-ray diffraction and transmission electron microscopy respectively using the carbon-replica technique. Optical transmission and reflection were also measured to investigate optical properties and oxidation behaviour of the evaporated In_2O_3 films.

3. Results and discussion

We have found throughout the experiments that all the In_2O_3 films formed by this reactive evaporation are n-type semiconductors. In figure 1 are shown resistivity, Hall mobility and carrier concentration for undoped indium oxide films in relation to substrate temperature T_S. The carrier electron concentration decreases from $1{\cdot}3 \times 10^{20}$ to $3{\cdot}7 \times 10^{19}$ cm^{-3} as substrate temperature increases from 200 to 440 °C while the mobility rises from 26 to 59 cm^2 V^{-1} s^{-1} in this temperature range. As a result, the resistivity gradually increases as function of the temperature. We obtained for instance an In_2O_3

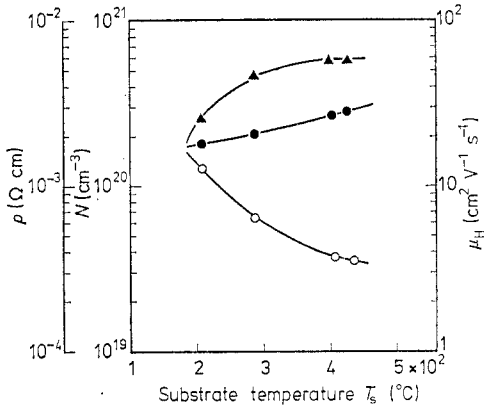

Figure 1. Effect of substrate temperature on electrical properties of evaporated In_2O_3 films at room temperature. ▲, μ_H; ●, ρ; ○, N.

film with $\rho = 2{\cdot}7 \times 10^{-3}\ \Omega$ cm, $N = 4{\cdot}1 \times 10^{19}$ cm^{-3}, and $\mu_H = 56$ cm^2 V^{-1} s^{-1} when deposited at $T_s = 390$ °C.

The decrease in carrier density is evidence of oxidation of the deposited In and/or InO_x film, since higher temperatures of the substrate accelerate the oxidation in vacuum. When we compare optical transmission and reflection at $\lambda = 550$ nm of the films shown in figure 2 in relation to substrate temperature, this oxidation seems to accomplish an optical change at temperatures above $T_s \simeq 200$ °C, giving a high transparency of 75%. The higher carrier concentration of an In_2O_3 film with $N = 3{\cdot}7 \times 10^{19}$ cm^{-3} almost completely oxidised at $T_s = 440$ °C is attributable to the continued existence of structural imperfections in the film, oxygen vacancies and/or excess In atoms acting as charged donor centres.

Grain size in the film becomes larger as the substrate temperature is higher. Results of x-ray diffraction analysis revealed that the film prepared at $T_s \leqslant 100$ °C gave no observed diffraction peaks and became polycrystalline when deposited at higher temperature; this crystalline structure was based only on the finding of one weak peak (222) corresponding to the cubic structure for In_2O_3 bulk (bixbyte). Although there was no observation of x-ray diffraction peaks with films made at substrate temperatures lower than 100 °C, the

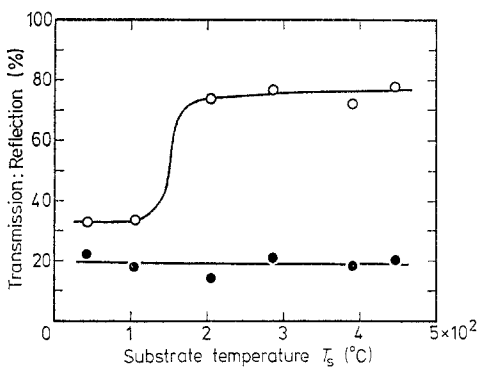

Figure 2. Transmission, ○, and reflection, ●, of In_2O_3 films as a function of substrate temperature ($\lambda = 550$ nm).

surface exhibits a granular texture. So the film would consist of fine-grained crystallites which may be incompletely oxidised indium oxide with nonstoichiometry.

Optical reflection (figure 2) also supports this interpretation since no metallic reflection is seen even in a range $T_s < 100\,^{\circ}C$, the reflection being about 20%. This means that the films obtainable at $T_s \lesssim 100\,^{\circ}C$ are not of indium metal of higher reflection but imperfectly oxidised films with nonstoichiometry.

The completely oxidised In_2O_3 films obtained at $T_s \gtrsim 200\,^{\circ}C$ have a high concentration of carrier electrons ($N = 1{\cdot}3 \times 10^{20}$–$3{\cdot}7 \times 10^{19}$ cm^{-3}) which is excited thermally from donor levels originating from the defects near the bottom of the conduction band. We evaluate the Fermi energy E_F of the film using the formula $E_F = (h^2/8m^*)\,(3N/\pi)^{2/3}$ where m^* is the reduced effective mass. With $m^* = 0{\cdot}3\,m_0$ as a mean value (Clanget 1973), and $N \simeq 4 \times 10^{19}$ cm^{-3}, we obtain $E_F \simeq 0{\cdot}14$ eV. This result means that the In_2O_3 film made by our preparation method is a degenerate semiconductor at room temperature because $E_F \gg kT$ ($\sim 0{\cdot}03$ eV).

We found that the carrier concentration and Hall mobilities of the films made at $T_s = 400\,^{\circ}C$ were scarcely dependent on temperature in a temperature range 77–300 K. If we estimate an activation energy for electrical conduction from these data using the formula $N = N_0 \exp(-U/kT)$, we have $U < 10^{-3}$ eV. This result also means that the film is in the state of complete degeneracy.

We now discuss the scattering mechanism of free carriers. The temperature dependence of mobility is related to the scattering mechanisms of free carriers. Fistul' and Vainshtein (1967) have reported that acoustical phonon scattering is a dominant mechanism in reactively sputtered polycrystalline In_2O_3 films which are strongly degenerate. The small dependence of mobility on temperature in the present films, however, suggests another dominant mechanism.

As the density of neutral impurity centres increases at very low temperatures, the scattering due to the centres could be ignored at $T > 77$ K. On the other hand, there may be a high density of ionised impurity centres in the films caused by oxygen vacancies and/or excess indium atoms, which results in a very high free carrier concentration of about 4×10^{19} cm^{-3} (figure 1). Johnson and Lark-Horovitz (1947) deduced the following form for the mobility in complete degeneracy:

$$\mu \simeq (4e/h)(\pi/3)^{1/3}\,N^{-2/3} = 9{\cdot}816 \times 10^{14} N^{-2/3}\ (\mathrm{cm^2\ V^{-1}\ s^{-1}}). \tag{3}$$

We compared the relationships between N and μ calculated from the above theory with experimental data from figure 1. Figure 3 shows the order of the mobility and its slope

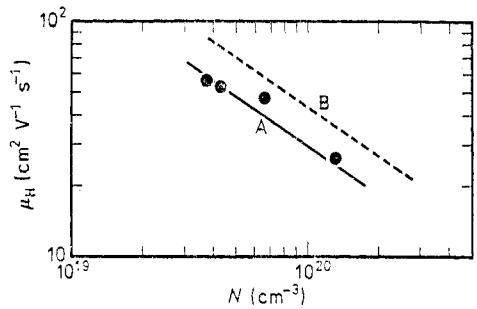

Figure 3. Mobility versus carrier concentration. A, Experimental; B, Johnson and Lark-Horovitz (1947). $\mu \propto N^{-2/3}$.

against the concentration, $\mu_H \propto N^{-2/3}$, is in good agreement with those predicted from the theory.

As for boundary scattering, the mean free path of the free carrier l is described by the following equation,

$$l=(h/2e)(3N/\pi)^{1/3}\mu. \tag{4}$$

In the present case, $l \simeq 39$ Å with $N=4{\cdot}1\times10^{19}$ cm^{-3} and $\mu_H=56$ cm^2 V^{-1} s^{-1} for the film evaporated on the substrate at $T_s=390\,^{\circ}$C. This mean free path is considerably shorter than the grain size which is observed to be about 1000 Å. Accordingly scattering due to grain boundary is not considered to be dominant.

From the above discussion, we can conclude that ionised impurity scattering is the dominant mechanism in the evaporated In_2O_3 films as well as sputtered In_2O_3 films (Hoffmann *et al* 1978) and sprayed ones (Clanget 1973). This conclusion means that the conductivity σ is uniquely determined by carrier concentration in the undoped In_2O_3 films prepared by this reactive evaporation because mobility and carrier concentration are no longer independent of each other (figure 3) but governed by a rule $\mu \propto N^{-2/3}$.

References

Clanget R 1973 *Appl. Phys.* **2** 247–256
Clarke P J 1977 *J. Vac. Sci. Technol.* **14** 141–42
Fan J C C and Bachner F J 1975 *J. Electrochem. Soc.* **122** 1719–25
—— 1976 *Appl. Opt.* **15** 1012–17
Fistul' V I and Vainshtein V M 1967 *Sov. Phys.–Solid St.* **8** 2769
Gläser H J 1977 *Glastech. Ber.* **50** 266–70
Groth R 1966 *Phys. Stat. Solidi* **14** 69–75
Hoffmann H, Pickl J and Schmidt M 1978 *Appl. Phys.* **16** 239–46
Hori Y, Doi K and Uesawa I 1965 *Oyo Buturi* **7** 507–12 (in Japanese)
Itoyama K 1978 *Japan. J. Appl. Phys.* **17** 1191–96
Johnson V A and Lark-Horovitz K 1947 *Phys. Rev.* **71** 374–75
Kane J and Schweizer H P 1975 *Thin Solid Films* **29** 155–63
Katsube Y 1974 *Proc. Japan. Soc. Appl. Phys. Spring Ann. Mtg* Vol. 2 59
Matsunami H Ook, Ito H and Tanaka T 1975 *Japan. J. Appl. Phys.* **14** 915–16
Müller H K 1968 *Phys. Stat. Solidi* **27** 723–31
Murayama Y 1975 *J. Vac. Sci. Technol.* **12** 818–20
Nagatomo T and Omoto O 1976 *Japan. J. Appl. Phys.* **15** 199–200
—— 1978 *Oyo Buturi* **47** 618–23 (in Japanese)
Ohata Y and Yoshida S 1977 *Oyo Buturi* **46** 43–50 (in Japanese)
Rupprecht G 1954 *Z. Phys.* **139** 504–17
Ryabova L A and Savitskaya Ya S 1968 *Thin Solid Films* **2** 141–48
Vainshtein V M, Gerasimova L G and Nikolaeva I N 1968 *Inorg. Mater.* **4** 298–302
Vaisfel'd M M, Sokolina V A and Fialkovskaya R P 1969 *Inorg. Mater.* **5** 1784–87
Vossen J L 1971 *RCA Rev.* **32** 289–96
Vossen J L and Poliniak E S 1972 *Thin Solid Films* **13** 281–84
Weiher R L 1962 *J. Appl. Phys.* **33** 2834–39
Weiher R L and Ley R P 1966 *J. Appl. Phys.* **37** 299–302