

OPTICAL AND ELECTRICAL PROPERTIES OF REACTIVELY D.C. MAGNETRON-SPUTTERED $\text{In}_2\text{O}_3:\text{Sn}$ FILMS

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The deposition of transparent conductive indium oxide doped with tin is investigated. Characterization of the d.c. magnetron-sputtered films shows that it is possible to obtain transparent conductive films from an In–Sn alloy by sputtering in a reactive atmosphere. This deposition method in combination with an appropriate anneal results in a very low light absorption and a high electrical conductivity of the films. In this paper the two-step deposition technique and the electrical and optical properties of the deposited transparent and conductive layers are described.

1. INTRODUCTION

The first experiments with thin films which combine a good electrical conductivity with a high transmittance of visible light date from the end of the last century. Fritts¹ and Bidwell² obtained very thin metal films on photoconductive material. In spite of this long history, research involving transparent conductive material received a new start during the Second World War. During this period there was for the first time an application for this kind of material: de-icing of aircraft windows. In the meantime NESA glass was developed³. It is made from SnO_2 , an n-type degenerate semiconductor with a wide forbidden energy gap. A second semiconducting transparent oxide, In_2O_3 , was first studied around 1950⁴. In particular, the possibility of doping In_2O_3 with tin has made this material popular for transparent conductive thin film applications.

Their high transmittance of visible light, high electrical conductivity, mechanical hardness and chemical stability made the semiconducting oxides attractive in such applications as defrosting of windows, antistatic coatings on instruments, electrodes for electroluminescent lamps and displays, electrodes for imagers and ferroelectric memories^{5–7}.

In this paper the technology of In_2O_3 doped with tin ($\text{In}_2\text{O}_3:\text{Sn}$, indium tin oxide or ITO) is described. In particular, the light transmittance in the blue spectrum, which is technology dependent, is optimized. A low light absorption is

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combined with a high electrical conductivity. $\text{In}_2\text{O}_3:\text{Sn}$ is chosen in preference to SnO_2 because of its superior electrical characteristics and in preference to CdSnO_4 because of its superior light transmittance. The application of the technology described in this paper is in the field of solid state image sensors where ITO is used as transparent conducting material above the photosensitive pixels of the device.

2. EXPERIMENTS

All films are deposited by means of a d.c. magnetron system, type BAS450PM from Balzers. The starting material is an alloy of the metals indium and tin with a concentration of 90 wt.% In and 10 wt.% Sn. To convert this metal target into an oxide film (indium oxide doped with tin) the deposition is carried out in a reactive atmosphere which is a combination of argon and oxygen. There is no substrate heater available before or during the deposition.

As substrates quartz plates or silicon wafers are used depending on the measurement which has to be done. The former are used for optical purposes, such as reflectance and transmittance measurements, while the latter are used for the characterization of the refractive index and the electrical properties. The thickness of the deposited layer and its refractive index (at one fixed wavelength $\lambda = 628 \text{ nm}$) are determined by means of an ellipsometer. The electrical resistivity is characterized with a four-point probe, while a spectrophotometer is applied to measure the reflectance and transmittance of a specimen as a function of the wavelength of the incident light. Other parameters, such as the refractive index $n(\lambda)$ and the absorption coefficient $\alpha(\lambda)$ can be calculated from the measured data: the refractive index from the maxima and the minima in the measured spectra of reflectance $R_M(\lambda)$ and transmittance $T_M(\lambda)$. The absorption coefficient can be deduced from the calculated absorbed light energy A by

$$A(\lambda) = 1 - R_M(\lambda) - T_M(\lambda) = \exp\{-\alpha(\lambda)d\} \quad (1)$$

or

$$\alpha(\lambda) = -\frac{1}{d} \ln\{1 - R_M(\lambda) - T_M(\lambda)\} \quad (2)$$

where d is the thickness of the ITO film. In this way $\alpha(\lambda)$ can be analysed without a knowledge of the refractive indices of the film and the substrate.

3. RESULTS AND DISCUSSION

3.1. As-deposited $\text{In}_2\text{O}_3:\text{Sn}$ films

The deposition rate of the ITO films is dependent on the various sputtering parameters: the total sputter pressure p_{tot} , the partial oxygen pressure p_{O_2} and the sputter power P . This dependence is also reflected in the characteristics of the films, as can be seen in Fig. 1. Here the deposition rate, the electrical resistivity and the light transmittance of the ITO film for blue light ($\lambda = 400 \text{ nm}$) are plotted *versus* the partial oxygen pressure. The light transmittance is here defined as

$$T = 1 - \exp\{-\alpha(\lambda)d\} \quad (3)$$

and is dependent only on the absorption characteristics of the film and not on the

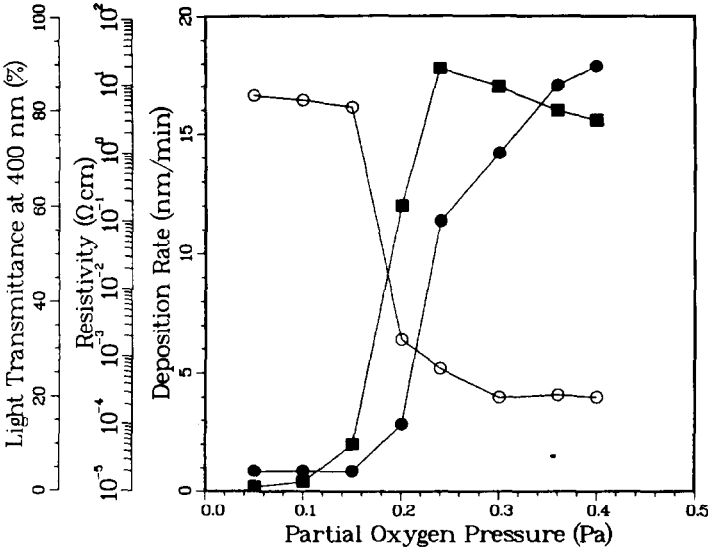


Fig. 1. Deposition rate (○), resistivity (●) and light transmittance (■) of an ITO film prepared by d.c. magnetron sputtering as a function of the partial oxygen pressure p_{O_2} during the deposition ($p_{\text{tot}} = 0.6 \text{ Pa}$; $P = 750 \text{ W}$; $t = 60 \text{ min}$).

refractive index of the ITO layer or the optical parameters of the substrate. This implies that in Fig. 1 (and others) the light transmittance T of an ITO film is plotted as though the film were surrounded by two ideal antireflective coatings.

The same three parameters as depicted in Fig. 1 are illustrated in Figs. 2 and 3 but *versus* the total sputter pressure and the sputter power respectively.

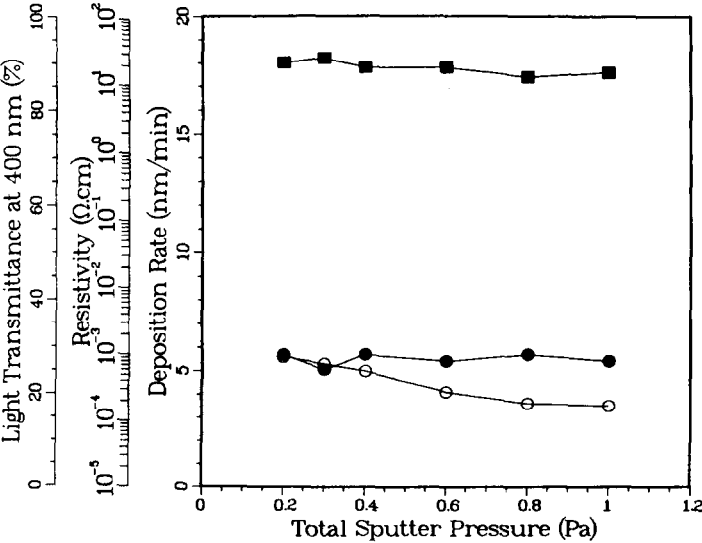


Fig. 2. Deposition rate (○), resistivity (●) and light transmittance (■) of an ITO film prepared by d.c. magnetron sputtering as a function of the total sputter pressure p_{tot} ($p_{\text{O}_2} = p_{\text{Ar}}$; $P = 750 \text{ W}$; $t = 60 \text{ min}$).

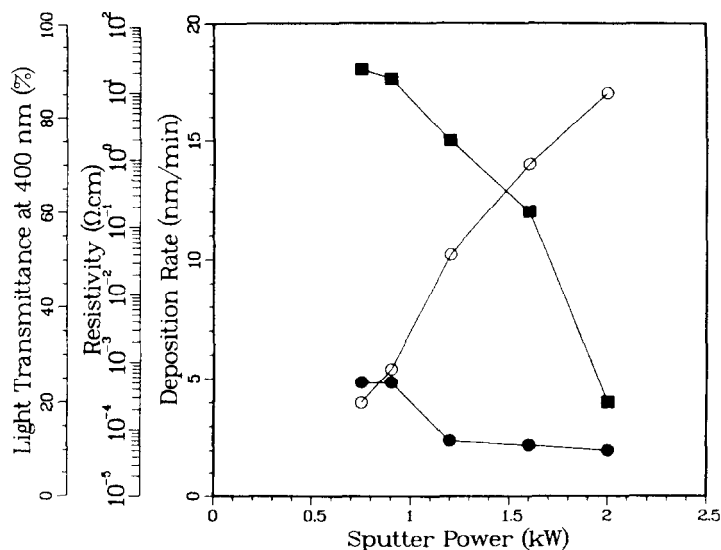


Fig. 3. Deposition rate (○), resistivity (●) and light transmittance (■) of an ITO film prepared by d.c. magnetron sputtering as a function of the sputter power P ($p_{O_2} = 0.15$ Pa; $p_{Ar} = 0.15$ Pa; $t = 10$ min).

The behaviour shown in Fig. 1 can be explained by means of a combination of three different processes which take place on the sputter target, in the sputter chamber and on the substrate⁸: (1) the chemical reaction of the reactive gas with the sputtered atoms and with the film already deposited onto the substrate, (2) the oxidation of the target surface and (3) the sputtering of the target. If the curve of the deposition rate *versus* the partial oxygen pressure is divided into three parts, then in each part the deposition rate will be determined by one of these three processes.

3.1.1. High p_{O_2} (more than 0.23 Pa in Fig. 1)

The partial pressure in the sputter chamber is sufficiently high to keep the target surface continuously in an oxidized state. As a consequence, an oxide has to be sputtered with its characteristic low deposition rate. Further chemical reactions between the sputtered particles and the reactive atmosphere are excluded because the oxide is almost stoichiometric. The deposited film shows quite a low light absorption but also a very low electrical conductivity, which are two characteristics typical of stoichiometric $In_2O_3:Sn$.

3.1.2. Low p_{O_2} (less than 0.16 Pa in Fig. 1)

The oxidation of the target is almost impossible because all the oxygen atoms are consumed in the oxidation of the sputtered metal atoms. For these low partial pressures of oxygen the highest deposition rates can be assigned to the sputtering of the metal atoms, which oxidize partially during their transport to the substrate. The deposited films are non-stoichiometric. The metallic nature of the layers is also reflected in a low value for the electrical resistivity and a very high light absorption.

3.1.3. Intermediate p_{O_2} (0.23 Pa $> p_{O_2} > 0.16$ Pa in Fig. 1)

If the partial pressure of oxygen is less than 0.23 Pa (p_{tot} is kept constant to 0.6 Pa), a competition exists between the oxidation and the sputtering of the atomic layers of the target surface. This includes the sputtering of a non-stoichiometric oxide of which the degree of non-stoichiometry is dependent on the oxygen partial

pressure. A higher value of p_{O_2} leads to more oxidation, whereas a lower p_{O_2} value results in more metallic films. Further oxidation of the sputtered species can take place during their transport from the target to the substrate or on the substrate itself.

Optically transparent and electrically conductive films can be deposited in this transition region between films with high deposition rates, low resistivities and low light transmittances and films with low deposition rates, high resistivities and high light transmittances. However, the useful window of oxygen partial pressures is very small ($0.16 \text{ Pa} < p_{\text{O}_2} < 0.23 \text{ Pa}$) and the various film characteristics are very steep functions of p_{O_2} . This is translated into a very critical deposition technique which results in quite unreproducible ITO films.

Figure 2 shows that the deposition rate, the electrical resistivity and the light transmittance ($\lambda = 400 \text{ nm}$) are nearly insensitive to the total sputter pressure. This behaviour is not surprising because the total sputter pressure p_{tot} is of secondary importance for d.c. magnetron sputtering processes. The plasma intensity is primarily determined by the electromagnetic fields in the system. Hence the deposition rate does not change with variations in the total sputter pressure.

The dependence of the deposition rate and of the film characteristics on the sputter power P is shown in Fig. 3. These curves can be explained as follows: for $P < 900 \text{ W}$, the target surface is non-stoichiometrically oxidized. The sputtered particles can oxidize further during their transport or during the growth of the film. If the power P is increased the number of sputtered species also increases. This effect is translated into a higher consumption of oxygen atoms needed to oxidize the target surface and the sputtered atoms. With increasing power P the number of oxygen atoms available to oxidize the target decreases and the surface of the target becomes more metallic. The composition of the deposited film deviates more and more from the ideal oxide stoichiometry. The electrical resistivity of the film and the light transmittance both decrease.

3.2. Annealed films

As is known from the literature^{6,7} and from our previous work⁹, the nature of the films and also their optical and electrical characteristics are steep functions of the oxygen content in the film. This behaviour is also reflected in the aforementioned figures and can be explained by the relationship between the free-charge-carrier density and the presence of oxygen atoms in the ITO matrix. Two different theories are used to describe the role of the oxygen in the conduction mechanism; these theories can be summarized as follows.

(a) The number of oxygen vacancies determines the number of free carriers¹⁰. For each missing oxygen atom in the stoichiometric $\text{In}_2\text{O}_3:\text{Sn}$ film, an oxygen vacancy is introduced into the matrix. However, in addition to this vacancy, a free electron is left behind, which is associated with a reduced indium atom and which can move through the $\text{In}_2\text{O}_3:\text{Sn}$ layer. In this way the film becomes electrically conductive.

(b) The number of oxygen atoms present determines the number of trapped electrons¹¹. In this case, the substitutional tin atoms are responsible for the free charge carriers, but these electrons can be trapped by an interstitial and unbonded oxygen atom. The trapped electrons then no longer contribute to the electrical conductivity.

Irrespective of the conduction mechanism, too many oxygen atoms incorporated into the film increase the electrical resistivity and too few oxygen atoms make the film more metallic (the conductivity increases but the light absorption also increases). For this reason it is necessary to obtain an optimum oxygen concentration to combine good electrical conductivity with good optical light transmission. This optimum number of oxygen atoms can be obtained during the deposition itself. However, with this technology the deposition method becomes very critical and unreproducible, as already shown.

Another way to optimize the stoichiometry of the film is the removal of some of the oxygen atoms from a film which has a high oxygen concentration. In other words, annealing of a transparent and (almost) insulating ITO film in a reducing atmosphere lowers the oxygen content of the film in such a way that the layer, although still transparent, also becomes conducting. The consequences of this annealing process are shown in Fig. 4. The films, whose original characteristics are presented in Fig. 1, are annealed in forming gas (10% H_2 -90% N_2) for 30 min at 485 °C. As can be seen from a comparison between Figs. 1 and 4 the anneal in the reducing atmosphere has a strong effect on the film characteristics. For films which originally have too much oxygen incorporated ($p_{O_2} > 0.23$ Pa), part of the oxygen is removed and the films become more conducting. Films which originally have less than the optimum amount of oxygen are unaltered after the reducing anneal. They remain of low resistivity but opaque.

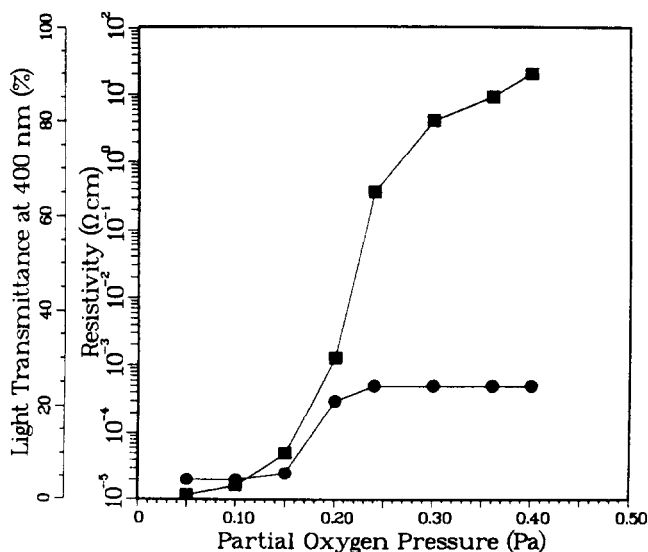


Fig. 4. Resistivity (●) and light transmittance (■) of the samples of Fig. 1 after a subsequent anneal in forming gas (485 °C; 30 min).

The aforementioned anneal results in almost perfect transparent conducting layers from a film which was initially transparent but highly resistive. The opposite is also true: metallic films can be converted to transparent conducting films by oxidizing them. This is shown in Fig. 5 where the characteristics of the films shown in Fig. 1 after an anneal in oxygen (at 600 °C for 30 min) are plotted. Films which were

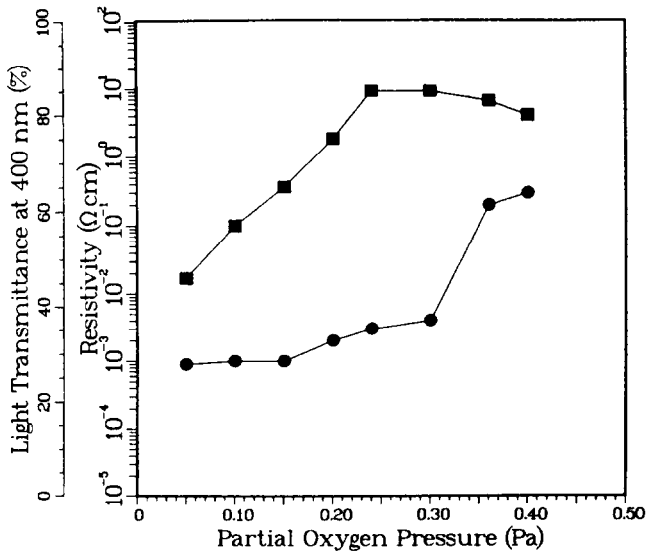


Fig. 5. Resistivity (●) and light transmittance (■) of the samples of Fig. 1 after a subsequent anneal in oxygen (600 °C; 30 min).

opaque in the as-deposited state become transparent but remain conducting. This can be explained by the oxidation of the metal-like films to the optimum non-stoichiometry to produce transparent conductive films. Films with too high an oxidation state do not change their stoichiometry during the oxidizing anneal. They remain transparent but almost insulating if the partial oxygen pressure during the deposition was higher than 0.35 Pa.

The behaviour of films which were sputtered with p_{O_2} between 0.2 and 0.28 Pa is remarkable. Originally they were transparent but had quite a high electrical resistivity, which decreases during the anneal, although because of the oxygen atmosphere the opposite would be expected. This behaviour can be explained as follows. These films lie in a transition region. Films sputtered at a lower value of p_{O_2} have too low an oxidation state and are further oxidized through the anneal. Films sputtered at a higher value of p_{O_2} have an oxygen content which is even higher than that which can be attained by the oxidation at 600 °C. Hence it can be stated that the original degree of oxidation of the films in this transition region ($0.2 \text{ Pa} < p_{\text{O}_2} < 0.28 \text{ Pa}$) is equal to the stoichiometry which can be obtained with the temperature step used. No further oxidation, nor reduction, takes place but the films reduce their resistivity through a recrystallization of the ITO. Although the oxygen concentration remains the same, the films become more conductive as a result of the growth of the individual crystals.

If the films whose characteristics are depicted in Fig. 5 are additionally annealed in forming gas (at 485 °C for 30 min), they become conductive and more or less transparent, independent of the partial oxygen pressure during the sputter deposition. This is illustrated in Fig. 6. If a comparison is made between the resistivities from Figs. 5 and 6 it might be concluded that the reducing anneal has only lowered the oxygen content of those films which were sputtered at $p_{\text{O}_2} > 0.3 \text{ Pa}$. This is not completely true, however. The concentration of oxygen in the other films

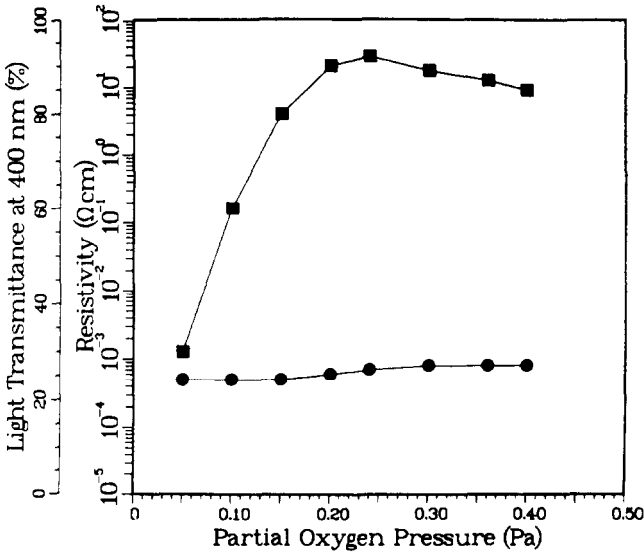


Fig. 6. Resistivity (●) and light transmittance (■) of the samples of Fig. 5 after a subsequent anneal in forming gas (485 °C; 30 min).

is also changed. This can be seen from the difference in light transmittances in Figs. 5 and 6. The absorption for blue light is enhanced through the reducing anneal because the film has become too highly metallic.

From these experiments we can draw the following conclusions. It is possible to deposit transparent conductive ITO films by a reactive d.c. magnetron sputtering technique with subsequent treatments.

(1) No further anneal is carried out if $0.16 \text{ Pa} < p_{\text{O}_2} < 0.23 \text{ Pa}$. For these conditions the film characteristics are unreproducible because of their critical dependence on p_{O_2} .

(2) An anneal in forming gas (485 °C; 30 min) is performed if $0.2 \text{ Pa} < p_{\text{O}_2}$. The films prepared under these conditions show excellent electrical properties ($\rho = 5 \times 10^{-4} \Omega \text{ cm}$) combined with a very low light absorption.

(3) An anneal is made in oxygen (600 °C; 30 min) if $p_{\text{O}_2} < 0.3 \text{ Pa}$. These films are of lower quality than the foregoing: the resistivity is higher by a factor of 2 and the light transmittance is lower by a factor of 2 for the lowest oxygen partial pressures.

(4) A combined anneal in forming gas and oxygen may be carried out. Although the characteristics are not optimum, the process is almost independent of the oxygen pressure during the sputter deposition.

These conclusions about the relation between the optical and electrical characteristics of an ITO film on the one hand and the heat treatment on the other hand can also be found in Aronson's work¹². Independent of the nature of the sputtered ITO layer, metallic or stoichiometrically oxidized, it is possible to obtain a transparent and conductive film if an appropriate heat treatment is applied to the as-deposited film.

3.3. Wavelength dependence of the optical properties

As may be expected, the optical properties of an ITO layer show a strong

dependence on the wavelength of the incident light. This is illustrated in Fig. 7 for the refractive index n and in Fig. 8 for the absorption coefficient α . In both figures it is also shown how these parameters change as a result of an anneal in a reducing atmosphere. The slight influence of the temperature step on the refractive index should be noted. This is in contrast with the work of Molzen¹³ who reports an increase of 15%–20% in n after an anneal of the film at 500 °C.

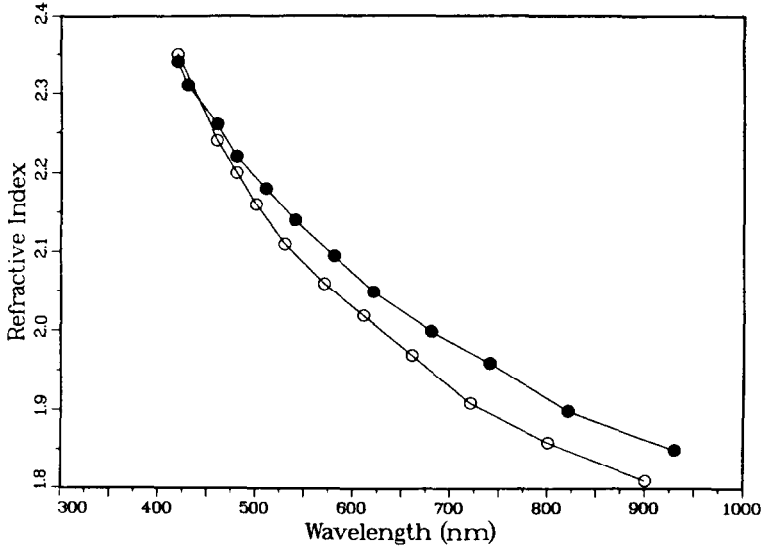


Fig. 7. The refractive index of an ITO film of thickness 400 nm prepared by d.c. magnetron sputtering as a function of the wavelength of the incident light before (●) and after (○) annealing in forming gas ($p_{\text{O}_2} = p_{\text{Ar}} = 0.15 \text{ Pa}$; $P = 750 \text{ W}$; $t = 60 \text{ min}$).

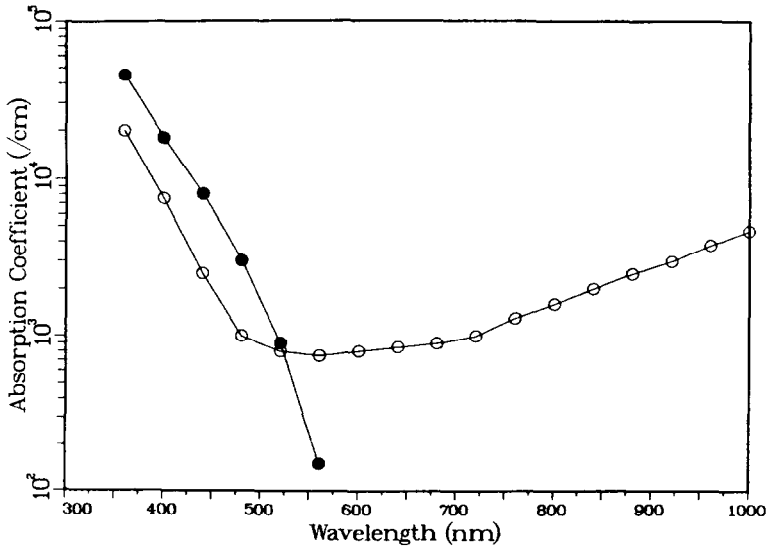


Fig. 8. The absorption coefficient of an ITO film of thickness 400 nm prepared by d.c. magnetron sputtering as a function of the wavelength of the incident light before (●) and after (○) annealing in forming gas ($p_{\text{O}_2} = p_{\text{Ar}} = 0.15 \text{ Pa}$; $P = 750 \text{ W}$; $t = 60 \text{ min}$).

The data already shown in Fig. 8 are redrawn in Fig. 9 as the light transmittance *versus* the wavelength for an ITO film of thickness 400 nm. Because this parameter is derived from the absorption coefficient α , both curves represent the same situation. As a result of the anneal, intentionally used to decrease the electrical resistivity of the almost stoichiometrically oxidized ITO film, the light transmittance changes in the following way: (1) a marked increase in the blue and near-UV spectrum; (2) almost no changes for the visible spectrum; (3) a decrease in the near-IR band.

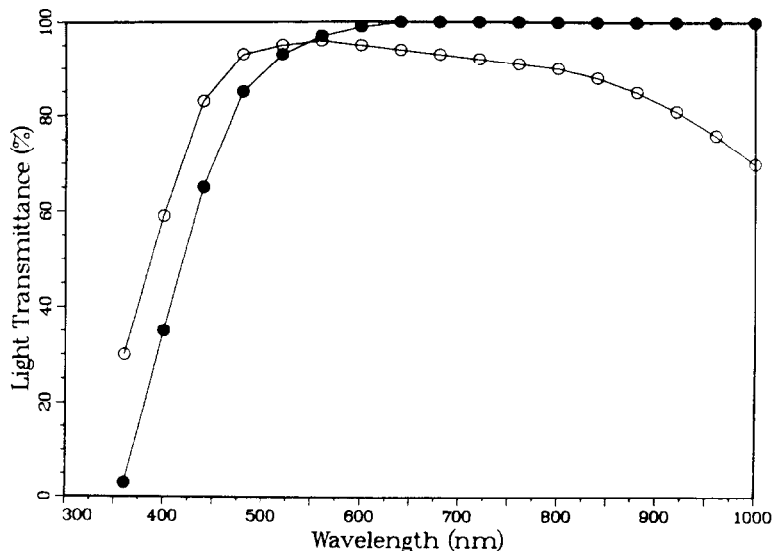


Fig. 9. The light transmittance of an ITO film of thickness 400 nm prepared by d.c. magnetron sputtering as a function of the wavelength of the incident light before (●) and after (○) annealing in forming gas ($p_{O_2} = p_{Ar} = 0.15$ Pa; $P = 750$ W; $t = 60$ min).

These effects can be explained as follows. In the visible and the near-IR spectrum, the absorption of photons takes place as an energy transfer from the incident photon to a charge carrier. For the absorption mechanism a relation exists between the absorption coefficient on the one hand and the carrier concentration n_c in the conduction band, the wavelength λ of the incident light and the mobility μ of the carriers on the other hand¹⁴:

$$\alpha = \frac{C\lambda^2 n_c}{\mu} \quad (4)$$

where C is a constant.

If it is known that because of an anneal n_c increases, it can be deduced from eqn. (4) that the same holds for α . However, the wavelength dependence of α also becomes stronger. That is why the light transmittance decreases faster with increasing wavelength (in the near-IR spectrum) after the anneal.

The so-called Moss–Burstein shift is responsible for the fact that an ITO film becomes more transparent in the near-UV and blue spectrum after the anneal¹⁵. In this spectrum the absorption of the light takes place by fundamental absorption: the energy of the photons is transferred to the electrons of the valence band, which

receive sufficient energy to travel across the forbidden gap to the conduction band. However, the concentration of free carriers after the anneal is sufficiently high to fill completely the lowest energy levels of the conduction band. This implies that the energy needed to transfer an electron is increased as a result of the anneal. As a consequence the mechanism of fundamental absorption is shifted to higher photon energies.

4. CONCLUSION

In this paper the dependence of the electrical and optical properties of ITO films prepared by reactive d.c. magnetron sputtering on the deposition parameters and on the subsequent anneal treatments is described. Too high an oxygen concentration in the ITO layer makes the film highly transparent but of low conductivity. The opposite is also true: the film becomes opaque and of low resistivity if the oxygen content is too low. The optimum oxygen concentration can be realized during the deposition of the film, but this method is rather critical and unreproducible. An appropriate anneal, the atmosphere of which depends on the oxygen partial pressure during the sputter process, can convert the deposited ITO film into a transparent conductive layer. The light absorption in such a treated film can be kept as low as 5% in the visible spectrum, for a film of thickness 400 nm, while its electrical resistivity is $5 \times 10^{-4} \Omega \text{ cm}$.

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REFERENCES

- 1 C. E. Fritts, *Proc. Am. Assoc. Adv. Sci.*, 33 (1884) 97.
- 2 S. Bidwell, *Philos. Mag.*, 20 (1885) 178.
- 3 *Br. Patent 632,256*, 1942.
- 4 *U.S. Patent 2,516,663*, 1950.
- 5 G. Haacke, *Annu. Rev. Mater. Sci.*, 7 (1977) 73.
- 6 J. L. Vossen, *Phys. Thin Films*, 9 (1977) 1.
- 7 K. L. Chopra, S. Major and D. K. Pandya, *Thin Solid Films*, 102 (1983) 1.
- 8 G. Bomchil, F. Buiguez, A. Monfret and S. Galzin, *Thin Solid Films*, 47 (1977) 235.
- 9 A. Theuwissen and G. Declerck, *Abstracts 10th Eur. Solid State Device Research Conf. and 5th Symp. on Solid State Technol.*, York, September 15–18, 1980, Vol. 4H, European Physical Society, pp. 216–217.
- 10 R. E. Aitchison, *Austr. J. Appl. Sci.*, 5 (1954) 10.
- 11 H. Hoffmann, J. Pickl, M. Schmidt, D. Krause and A. Dietrich, *Appl. Phys.*, 16 (1978) 239–246, 381–390.
- 12 A. J. Aronson, D. Chen and J. Smith, *Trans. 23rd Sputtering School, Bourg Saint Maurice, France, June 18–21, 1979*.
- 13 W. W. Molzen, *J. Vac. Sci. Technol.*, 12 (1975) 99.
- 14 R. A. Smith, in *Semiconductors*, Cambridge University Press, Cambridge, 1978, p. 294.
- 15 H. Köstlin, R. Jost and W. Lems, *Phys. Status Solidi A*, 29 (1975) 87.