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Electrical and Optical properties of ITO Films Prepared by Ion-Assisted Deposition at Ambient Substrate Temperatures

Mansour Suker Farhan - College of Engineering, Wasit University.

الخواص الكهربائية والضوئية لاغشية (ITO) المرسبة بطريقة الطلاء الايوني المعزز على ارضيات عند درجات حرارة التجربة

منصور سكر فرحان - كلية الهندسة / جامعة واسط

الخلاصـــة :

تقليدياً للحصول على أقل مقاومية وأعلى نفاذية ضوئية يتم ترسيب الاغشية الرقيقة لمركب أوكسيد الانديوم قصدير (ITO) على أرضيات بدرجة حرارة عالية بحدود 400^oC ، أو بترسيبها على ارضيات بدرجة حرارة التجربة ومن ثم تعامل حرارياً بدرجات حرارة عالية ولفترات طويلة. في هذا البحث تم الحصول على المواصفات المطلوبة لاغشية (ITO) التي رسبت بطريقة الطلاء ألايوني المعزز على أرضيات بدرجة حرارة التجربة. الخواص الكهربائية والضوئية تم دراستها لهذه الاغشية كدالة لمعدل سريان الاوكسجين ومعدل الترسيب بالاضافة الى سمك الغشاء. تم حساب النفاذية الضوئية وطاقة الفجوة الضوئية لهذه الاغشية باستخدام المطياف "Spectrophotometer" أما مقاومة السطح فقد حسبت باستخدام المجس رباعي النقاط . حيث لوحظ لدى معدل سريان الاوكسجين (25 Sccm) ومعدل ترسيب (0.4 nm/sec) وعند سمك غشاء مقداره (140 nm) أدت ألى تحسين خواص النفاذية الضوئية و فجوة الطاقة والمقاومية بقيم (92% و4.2 eV و $175x10^{-4}$ Ω-cm) على الترتيب . بينما عند زيادة محتوى الاوكسجين إلى (30 Sccm) ستقل النفاذية وفجوة الطاقة.

ABSTRACT

Traditionally, to achieve low resistivity and high transmission indium-tin oxide (ITO) films were deposited at elevated substrate temperatures about 400^o C. In some cases, films deposited at low substrate temperatures can then annealed at higher temperature to achieve lower resistivity. In this paper thin films of ITO with various oxygen flow rates were prepared by ion-assisted electron beam evaporation at ambient substrate temperature. The electrical and optical properties of ITO thin films have been investigated as a function of oxygen flow rate, rate of deposition and the layer thickness. The transmittance and optical band-gap energy were measured by spectrophotometer, whereas the sheet resistance was measured using four-point probe method. It has been found that at 25 sccm oxygen flow, 0.4 nm/sec rate of deposition and 140 nm layer thickness were suitable for improving the properties of ITO films. The optical transmittance, optical band-gap and the resistivity were 92%, 4.2 eV and $175x10^{-4}\Omega$-cm, respectively.

INTRODUCTION

A special class of transparent oxide films comprises those that are electrically conducting. While most oxides are good insulators, some are wide band-gap semiconductors. Usually Indium tin oxide (ITO) thin films are widely utilizes in numerous industrial applications due to the unique combined properties of transparency to visible light and electrical conductivity [1]. ITO films are highly degenerate n-type semiconductors, low electrical resistivity ($10^{-4}\Omega$-cm), and high carrier concentration. Furthermore, ITO has a wide band-gap (E_g>4.1 eV), high transmittance (>85%) in the visible range [2]. This unique combination of electrical and optical properties has led numerous researchers to a thorough investigation of the growth and characterization of ITO films. It has potential applications in many devices, such as flat panel displays, solar cells, gas sensors, camera lenses, anti-reflection coatings, heat reflection mirrors and surface heaters for automobile windows [3]. Considerable data has been reported on the use of ion sources [4] for both substrate pre-cleaning and assisting in the deposition and growth processes of thin films over the last 22 years [6,7]. There is now a plethora of ion sources available for commercial use as well as many improvements on the older designs. IAD modifies many of the physical characteristics of thin films. Fundamentally, there is conflict between visible transmission and electrical conductivity. However, ITO is one of the better film materials available for these applications. However, as the oxygen deficient material it behaves like metal, becoming conductive, optically absorbing and highly reflective in the infrared region. ITO films has been prepared by many methods including reactive evaporation [8-10] and by sputtering; DC magnetron reactive [10,11] and RF sputtering [12]. All of these processes involve a reactive background of oxygen. The oxygen level during process being a critical component in controlling quality of the films. Traditionally, the better films (i.e. low resistivity high transmission) are deposited at elevated temperatures [9-11]. Honda, et al [13] studied the oxygen content of deposited at range of substrate temperatures from ambient room temperature to 400 ^{0}C In some cases, films that are deposited at low temperatures can then be annealed at higher temperatures to achieve lower resistivities [9,10]. Using a broad beam ion source to this is ideal since it will run in pure oxygen. ITO has a refractive index with a real part of about 2.05 [4,9,14]. All application allowed for a low index quarter-wave outer layer to increase the transmission. The higher resistivity applications had no limitations on the film structure. Therefore, the ITO could be incorporated into multi-layer anti-reflection structure. Because of this it was desirable to fully characterize the optical properties of the films.

In this study, thin films of ITO were deposited at ambient substrate temperature using ion-assisted electron-beam evaporation. The effects of oxygen flow rate, deposition rate and layer thickness on the electrical and optical properties of deposited ITO films were investigated.

EXPERMENTAL TECHNIQUES

This study was conducted in fully automated turbo-pumped coating chamber equipped with resistive sources, 6-pocket 270^0, 14 kW electron beam gun (E-gun) with the deposition pocket centered in the chamber. A quartz crystal rate/thickness controller and 3 kW quartz lamp heater. Internal fixturing consists of domed calotte and ion source (Denton Vacuum CC-105) 8 inches off-center position. The "Kaufman" ion source was characterized by putting Faraday probe into the tooling around the outer radius. The general equipment is shown in figure 1. The evaporation source material was ITO 10% tin oxide and 90% indium oxide. The pressure during the evaporating process was about $<5x10^{-6}$ mbar and was started at ambient temperatures ($\sim 27\ ^0C$). The thickness of the films and the evaporation rate were monitored for all films using quartz-crystal monitor. During deposition, the ion current and the ion energy were maintained at 2 A and 600 eV, respectively, whereas, the temperature would rise slightly due to thermal energy from E-gun and the ion source. Typically rise during deposition of a half wave at 560 nm was $10\ ^0C$.

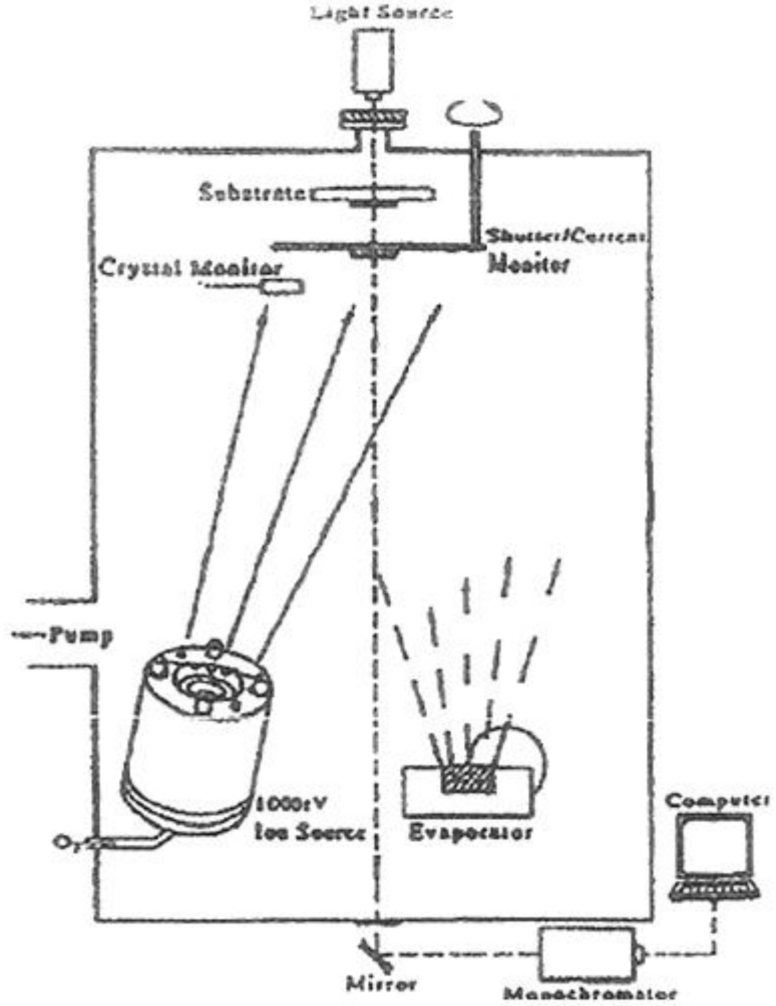

Figure 1.. Schematic diagram of the deposition system.

The oxygen flow rate was regarded as variable parameter, and hence configured at 20, 25 and 25sccm flow rate monitored by mass flow controller (MKS). The sheet resistance of the ITO films were measured by a four-point probe method (Jendel). The transmittance spectra measurement was made using UV-NIR spectrophotometer (Perkin-Elmer Lambda 900) in double-beam configuration. Before loading the glass substrates, they were cleaned by ultrasonic washer with acetone, alcohol, and de-ionized water to remove organic contamination and blew in dry nitrogen gas.

RESULTS & DISCUSSION

ITO thin films with oxygen flow rate between 20 and 30 sccm were prepared onto glass substrates. Sheet resistance of the ITO thin films deposited by varying the oxygen flow rates are shown in Table 1. The sheet resistance showed a maximum value at 20 Sccm oxygen flow rat. The increase of oxygen flow rate, caused the increase of oxygen incorporation into the oxygen-deficient ITO films, which increased the sheet resistance of the films by compensating oxygen vacancies in the evaporated ITO films. However, the increase of oxygen flow rate higher than 20 sccm resulted in decreased the sheet resistance of the films. The sheet resistance (R_s) measurements were performed using a four-probe method. By assuming that the thickness of the films was uniform, the film resistivity (ρ) was determined using the simple relation ρ = R.d, where d is the film thickness. The resistivity of ITO thin films increases from 75x$10^{-4}\Omega$-cm to 400x10^{-4} Ω-cm because the carrier concentration increases. The oxygen flow rate can change the carrier concentration due to oxygen vacancies.

Table 1. Properties of ITO thin films at different oxygen flow rates.

Oxygen flow rate (Sccm)	Sheet resistance (Ω/□)	Resistivity ($10^{-4}\Omega$.cm)	Transmittance (%)	Energy band-gap (eV)
20	800	75	85	4.15
25	600	165	92	4.20
30	250	400	87	4.17

The transmittance with increasing oxygen flow rate up to 25 Sccm and further increase of oxygen rate decreased the transmittance. The optical transmittance can be increased with reasonable increase in the oxygen flow rate. When the oxygen flow rate is up to 25 sccm, the optical transmittance of ITO thin films with 140 nm thickness shows the highest value. If the oxygen flow rate above 25 Sccm, the optical transmittance will begin to decrease. The results can be explained as following: when the oxygen flow rate is lower, the particles evaporated from the target cannot be oxidized enough so the prepared ITO thin films are anoxic and sub-oxides such as InO_x and SnO_x. The transmittance oxidated with an increasing oxygen flow rate. However, when the oxygen flow rate is over a maximum, the redundant oxygen can be absorbed in the defects such as grain boundaries and micro-cracks. Furthermore, the optical band-gap values of these films were calculated from the transmittance spectra. In the strong region absorption coefficient (α) can be calculated from Lambert's formula [15,16]

$$\alpha = d^{-1} \ln (1/T) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

where T and d are the transmittance and film thickness, respectively. The absorption has its minimum at low energy and increases with optical energy in a manner similar to the absorption edge of the semiconductors. The absorption coefficient for directly allowed transition for simple parabolic scheme can be ascribed as a function of incident photon energy as

$$\alpha h\nu=(h\nu-E_g)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where hν is the photon energy. The optical band–gap of ITO thin films can be determined by plotting $(\alpha h\nu)^2$ versus hν, and extrapolation method. It is observed that the optical band-gap increased from 4.15 to 4.20 eV corresponding to the increase of oxygen flow rate from 20 to 25 Sccm

Initial thin films were made in a half-wave optical thickness (~130 nm) in the visible region. Low deposition rates parameters and oxygen flows yielding pressures in the $2x10^{-4}$ mbar range. The deposition rate and pressure were similar to what had been used for high temperature depositions. The first film was optically good (i.e. clear and non-absorbing) but not a conductor. Increasing the deposition rate, reducing the oxygen flow and increasing the deposition rate resulted in a significant reduction in the resistivities while maintain fairly good transparency in the visible. Although several parameters were varied, the resistivities were dropping significantly with the increasing deposition rate while the transmission at the half-wave optical thickness remained fairly high. The resistivity vs. deposition rate is plotted in Fig. 2.

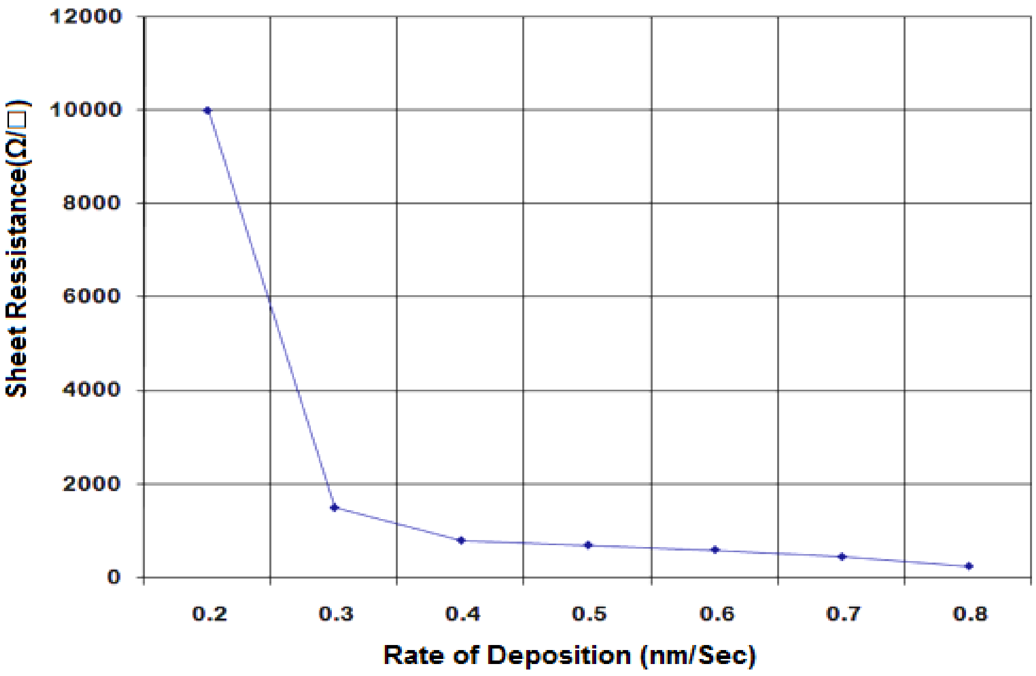

Figure 2. Sheet resistivity vs. deposition rate

These parameters (oxygen flow was increased slightly to 25 Sccm to make more transparent films) were then used to deposit three films of increasing thickness $\lambda/2$, λ.3$\lambda/2$ in the visible. The resulting films were 87Ω/cm^2 and 40Ω /cm^2 and 30Ω /cm^2 increased 132 nm, 250 nm and 420 nm thick, respectively as shown in Fig. 3. The 132 nm film is too thin to obtain dispersion data and is represented only by the index at the quarter-wave optical thickness. Only minimal absorption data could be extracted by this method since it required using spectral data from multiple half-wave thick wavelengths.

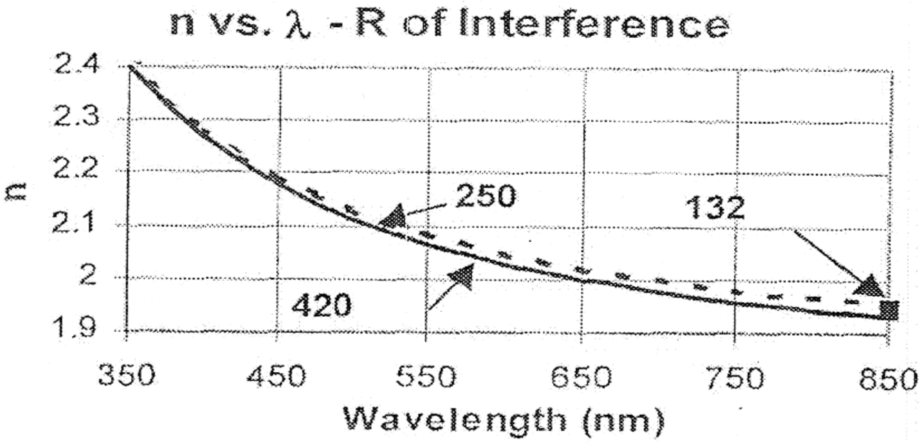

Figure 3 Refractive index of 3 different film thicknesses as a function of wavelength using an interference calculation.

The refractive index data was not as good as desired, obviously deviating from the real values near wavelengths where the film was $3\lambda/8$, $5\lambda/8.7\lambda/8$, etc thick. However, the extinction coefficient data looked good over most of the measured spectrum. If the obvious good data is selected from the output, then the index results for the three films are shown in Fig. 4.

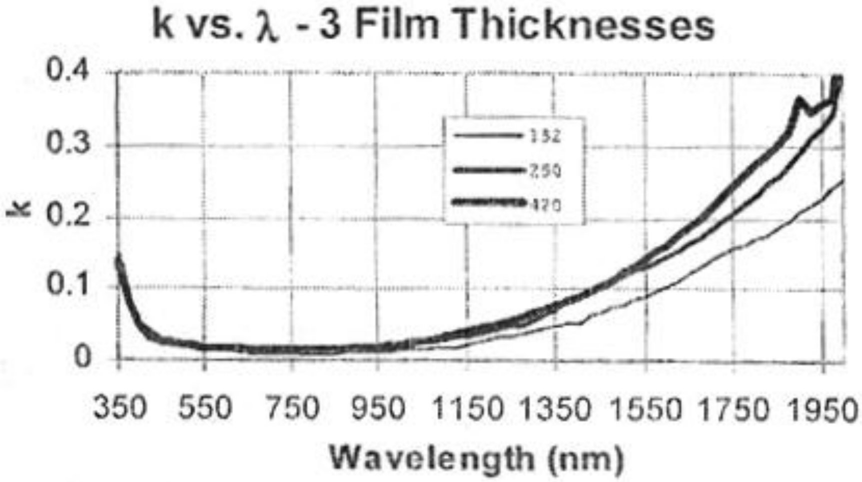

Figure 4. Extinction coefficient of 3 different film thickness as a function of wavelength

Over the visible spectrum, these results are similar to what was obtained by simple interference method (see Fig. 3). The extinction coefficient (K) data for the three films is shown in Fig. 5.

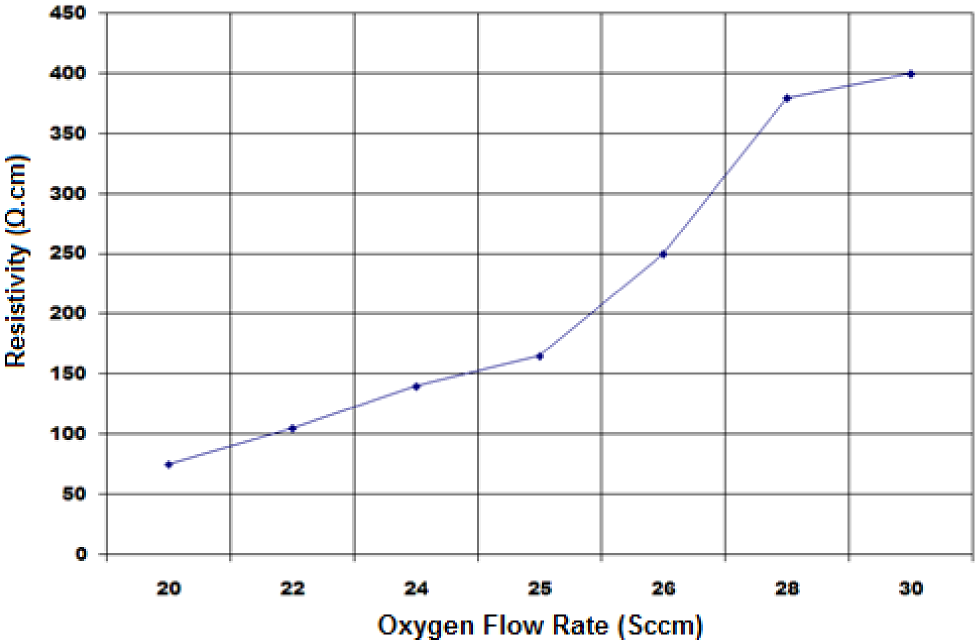

Figure 5 Resistivity of ITO films deposited at 0.4 nm/sec, 2Amp, ion current,

600 eV ion energy and various O_2 flow rates.

The UV-visible extinction coefficient did not seem to vary much for the different thickness films. In the near IR the extinction coefficient seem to increase with increasing film thickness. The transmissions of three films are shown in Fig. 6. In all examples the second surface is uncoated. The interesting feature of the many samples prepared, is that even though the thinner AR optical design may have been centered at 500 nm, the high transmission band extended out to 1000 nm. In fact, the longer wavelength AR did not even perform as well as the shorter wavelength ARs at the longer wavelengths. Thus, relatively high transmission could be achieved with one set of impedance matching thicknesses for Al_2O_3 and the SiO_2. The transmission of most of the samples averaged 92% or higher from 450 nm out 900 nm. Below 450 nm the transmission would drop significantly due to the absorption in the conductive layer.

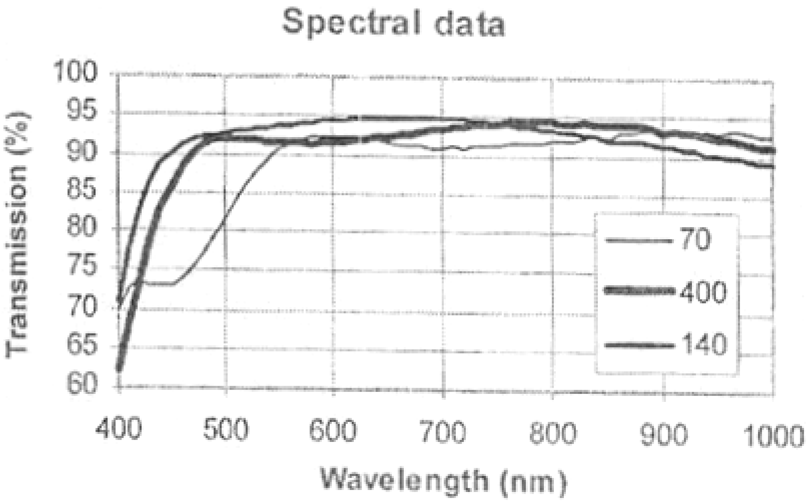

Figure 6.Transmission of 3-layers as a function of wavelength.

CONCLUSIONS

By using ion beam-assisted reactive deposition (IBAD), ITO films have been prepared by evaporating 90In-10Sn (Wt%) alloy. The electrical and optical properties of these films have been investigated as a function of oxygen flux, deposition rate and layer thickness. The films with resistivity as low as $175\mathrm{x}10^{-4}$ Ω- cm, optical band-gap of 4.2 eV, and transmittance of value 92% at 0.4 nm/sec rate of deposition, 140 nm films thickness and oxygen flow rate of 25 sccm. We have shown that IAD deposited InSnO films can be prepared at ambient substrate temperatures with resistivities in the 60 Ω/cm^2 and higher range with transmission greater than 90%. We have also determined that highly transparent film structures higher resistivities can be prepared by introducing higher oxygen levels. Lower resistivity films require thicker conductive layers which will result in lower transmission levels.

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