Morphology, Optical and Electrical Properties of Tin Oxide Thin Films Prepared by Spray Pyrolysis Method

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ABSTRACT:

Transparent conducting tin oxide thin films have been prepared by spray pyrolysis technique. Structure, optical and electrical properties of prepared films at different concentration (0.1, 0.2,0.3,0.4) mol/litter were studied at substrate temperature (550ºC) .UV-Vis spectrophotometer shows that the transmittance increases with the decrease in the concentration of SnO_2 thin films and it received 87% for the lower concentration (0.1 mol/litter). From AFM image notice that the smoothness and homogeneous of the films are decreasing with increasing the aqueous solution molarity. I-V characteristic of the SnO_2 films shows the thin film behavior was close to Ohm's law.

Keyword: Thin film, Spray Pyrolysis, Concentration, AFM.

الخصائص الشكلية ,البصرية والكهربائية لاغشية اوكسيد القصدير المحضره بتقنية الرش الكيميائي

الخلاصة

في هذا البحث تم دراسة الخصائص البصرية والكهربائية و التركيبية لأغشية ثنائي اوكسيد القصدير الموصلة الشفافة و المحضرة بطريقة الرش الكيميائي بتراكيز مختلفة (0.2,0.1, 0.3, 0.4) مول /لتر ومن خلال نتائج مطياف الاشعة المرئية-الفوق بنفسجية تم ملاحظة ان النفاذية تزداد مع نقصان تركيز اغشية SnO_2 ,حيث وصلت لنسبة 87% للاغشية المحضرة باقل تركيز (0.1) مولاري. من خلال الصور الطبوغرافية للأغشية المحضره بتراكيز مختلفة و التي تم قياسها بمجهر القوى الذري لوحظ ان نعومة وانتظامية السطح تقل مع زيادة المولارية للمحلول المائي , اضافة لذلك اظهرت خصائص تيار- فولتية السلوك الاومي لاغشية SnO_2.

INTRODUCTION

Tin Oxide thin films are n-type semiconductors with high transparency and very good electrical conductivity. It is used as a window layer in solar cells [1-2] , heat reflectors in solar cells [3], various gas sensors [4],liquid crystal displays etc… Tin oxide thin films have been prepared by several methods: Reactive sputtering [5], evaporation [6], chemical vapour deposition [7], dip coating [8], and spray pyrolysis [9,10].Of these methods the spray pyrolysis represent the less expensive alternative, since it can produce large area, high-quality and low cost thin films (11).In this method the substrate temperature and flow rate control the most desirable optical, structural and electrical properties of tin oxide films. Tin oxide can exist in two structures belonging to direct and indirect optical transitions, with different band gaps; a direct band gap that ranges from 3.6 to 4.6eV [11] at room temperature and indirect band gap of about 2.6 eV[12].An important property of tin oxide is that it is the most chemically stable in atmospheric ambient [13] amongst the other metal oxides. This technique involves a simple technology in which anionic solution (containing the constituent element of a compound in the form of soluble salts) is sprayed over heated substrates. Though a number of tin salts are available for this purpose, the most suitable is one whose decomposition temperature is not very high the decomposition reaction leading to the formation of SnO_2 is thermodynamically feasible, and no residue of the reactants is left behind in the deposited material [14]. When the substrate temperature is below 250ºc, the spray falling on the substrate will undergo in complete thermal decomposition (oxidation) giving rise to a foggy film whose transparency as well as electrical conductivity will be very poor. If the substrate temperature is too high the spray gets vaporized before reaching the substrate and the film become almost powdery [15]. Whereas at substrate temperature in the range (550ºC) the spray reaches the substrate surface in the semi vapour state and complete oxidation will take place to give clear SnO_2 film as a final product as observed in our experiments .Keeping these in view we have used an aqueous solution of $SnCl_4.5H_2O$ as the precursor solution for spray pyrolysis in the present investigation. The aim of this work is to studies the electrical, optical properties and morphology of the thin films of Sno_2 prepared by spray pyrolysis and notices the effect of the different concentration of these properties.

Experimental part

System of chemical spray

The scheme of chemical spray set up consists of simple parts shown in fig (1) and the various process parameters in the film deposition are listed in Table 1:

Table (1): Process parameters for the spray deposition of the films.

Spray parameters	Optimum value/item
Nozzle	Glass
Nozzle-substrate distance	30 cm
SnCl4·5H2O solution concentration	(0.1,0.2,0.3,0.4)mol/litter
Solvent	Distilled water
Solution flow rate	3.5 ml/min
Carrier gas	Compressed air
Substrate temperature	550ºC

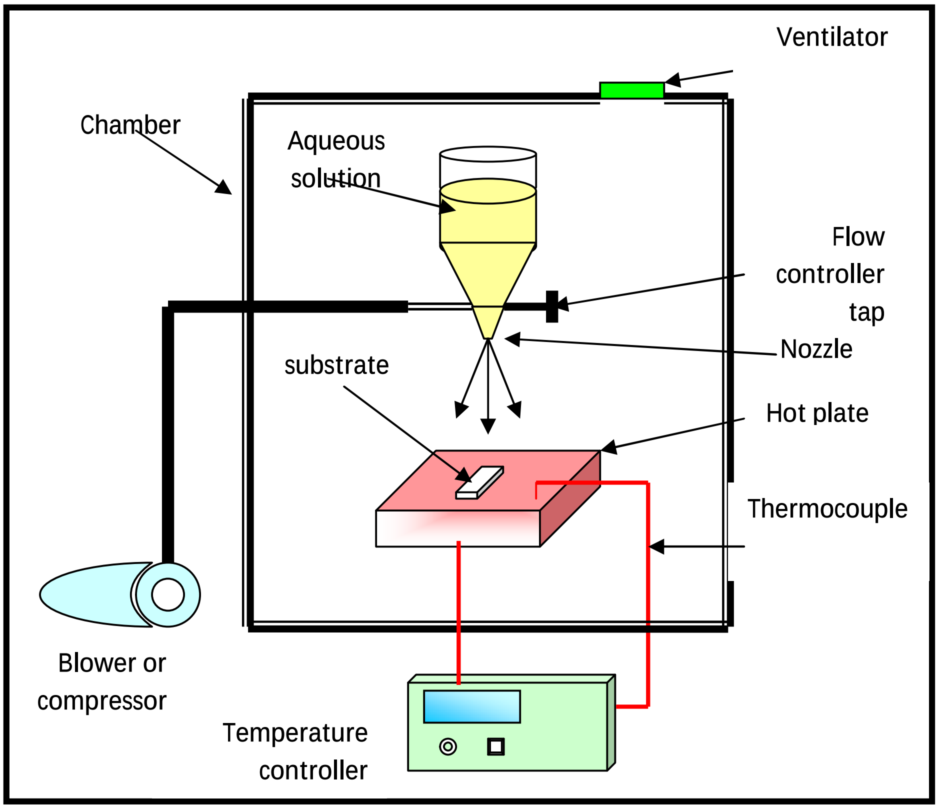


Figure (1) the scheme of the spray pyrolysis setup.

Solution preparation

Stannous chloride ($SnCl_4$)5(H_2O) was used in making the precursor solution for SnO_2 thin film. SnO_2 solution was made by dissolving white powder of($SnCl_4$)5(H_2O) of distilled water with different molarities(0.1, 0.2, 0.3, and 0.4)M .The aqueous solution was diluted in distilled water and mixed by a magnetic stirrer , and in each deposition the volume used was (50 ml) .

Substrate preparation

The substrate which are glass with dimensions ($2*2\ cm^2$) were cleaned first by dipping in distilled water to remove the dust and then they were ultrasonically cleaned in ethanol (purity 99%) for at least 15 min. And after substrate preparation the solution of SnO_2 sprayed by spray pyrolysis and the substrate temperature plays an important role in the thin film formation. The transmittance of the all films was measured by using a double beam UV-Vis spectrophotometer(CECIL C.7200 (France) and SHIMADZU)with respect to a piece of glass of the same kind of the substrate and the AFM image measurement by atomic force microscope (AFM) AA300 scanning probe microscope Angstrom Advanced Inc .I-V curves were measured with the use of a dc power supply (FARNELL E 350) in the range of (0 – 350) volt and (0 – 100) mA , and the current read out by a digital multi-meter (Tektronix (CDM250). The thickness of SnO_2 thin film is calculated using gravimetric method through weighting the substrate before and after deposition.

Result and Discussion

Figure (2) shows the optical transmittance spectrum of SnO_2 thin films in the wavelength range from [(300) to (900) nm]. The films are highly transparent in the visible range of the electromagnetic spectrum with the maximum value of about (87%) recorded for film with lower molarity (0.1M) , and it decreases with the increase in the concentration. Increasing molarity causes increase in the density of atoms in the aqueous solution and then causes increase in thickness of the deposition thin film that induced decreasing in the transmittance.

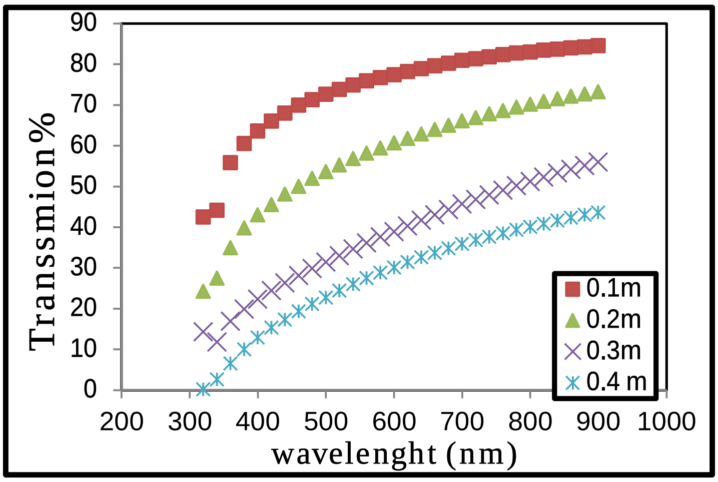
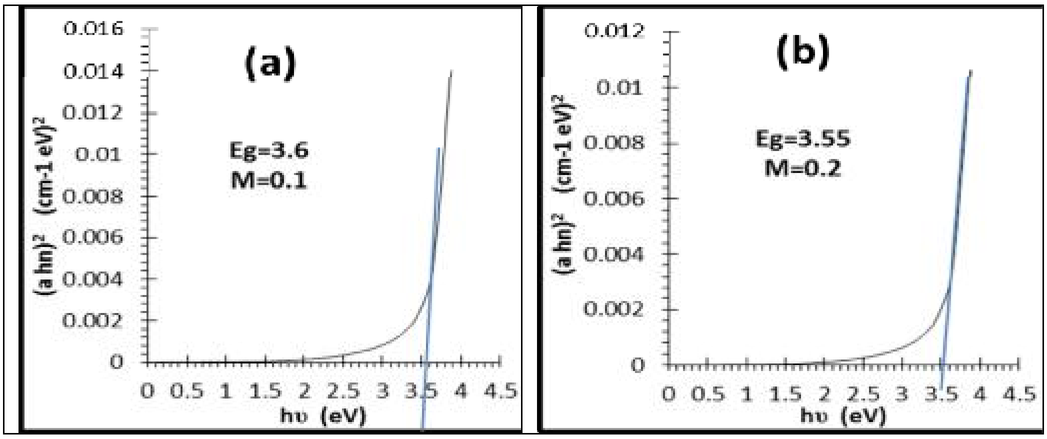


Figure (2) The transmittance spectra of SnO_2 thin films prepared with different molarities (0.1, 0.2, 0.3, and 0.4)M .

The optical energy gap was determined by using the absorption coefficient values , figure (3) shows the plot of $(\alpha h\nu)^2$ vs. hν for SnO_2 thin films with different concentration (0.1, 0.2, 0.3, 0.4) M . From figure (3) , the energy gap was narrowing with increasing molarity , and their values were (3.6 to 3.5) eV**.** Increasing molarity causes increase in the density of charge atoms and then every electron is effectively surrounded by an exchange and correlating hole that lowers the energy of the electron, and the conduction band is shifted downwards.



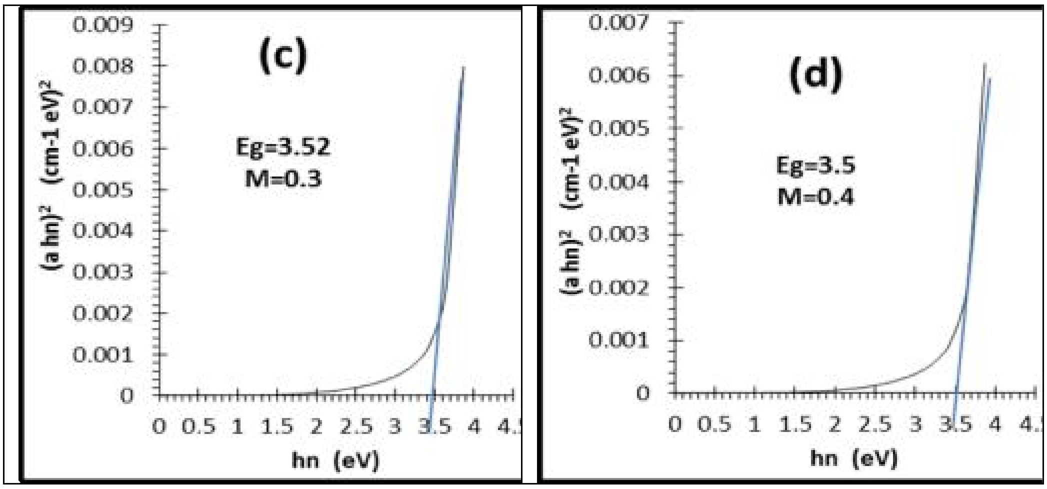
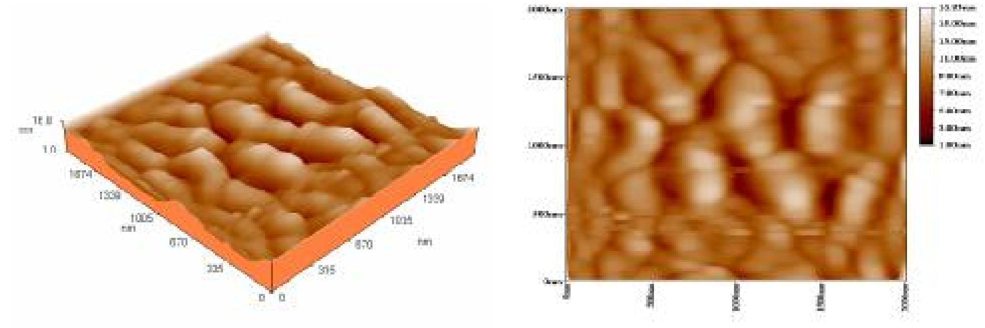


Figure (3 a,b,c,d) Energy gap of SnO_2 thin film at different molarities.

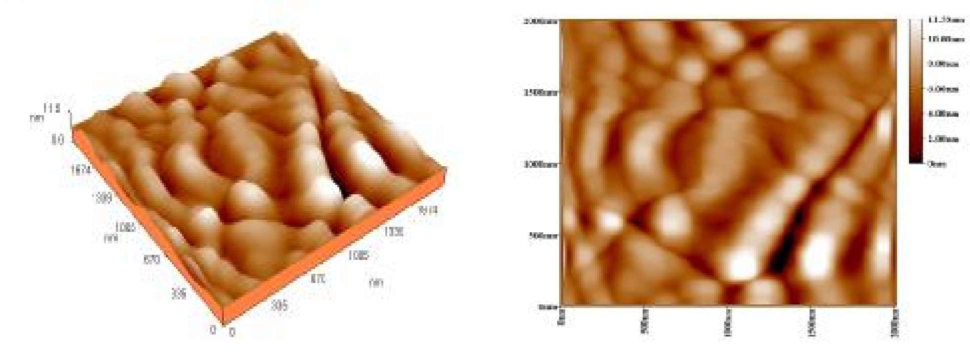
Surface topography was studied by means of atomic force microscope. Figure (4) shows the influence of solution molarity on the homogeneity and smoothness of the films. From these figures it is clear that the smoothness and homogeneous of the films are decreasing with increasing the aqueous solution molarity. That the surface roughness is increased with thickness increasing as shown below, this result is in a good agreement with those in the literature [16].

Table (2).The change in energy gab, Roughness average and Root mean square with Molarity.

Molarity(mol./litter)	Thickness(nm)	Energy gab(ev)	Roughness average(nm)	Root mean square(nm)
0.1	200	3.6	1.52	1.97
0.2	210	3.55	1.48	1.98
0.3	230	3.52	1.47	1.94
0.4	300	3.5	0.803	1.13



(a)



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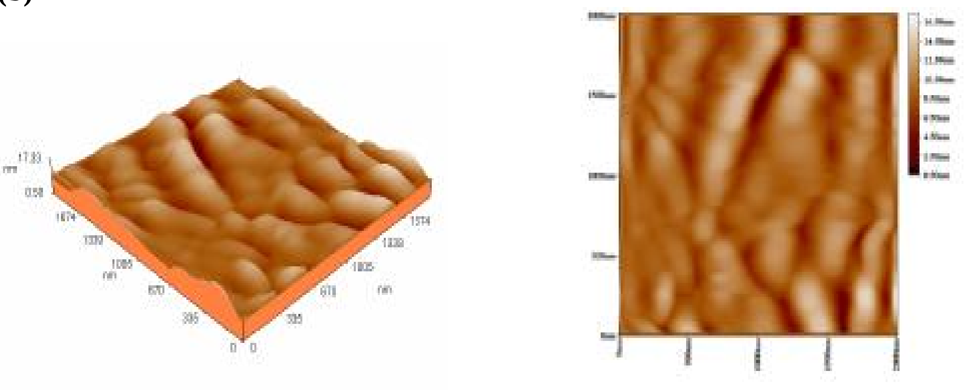
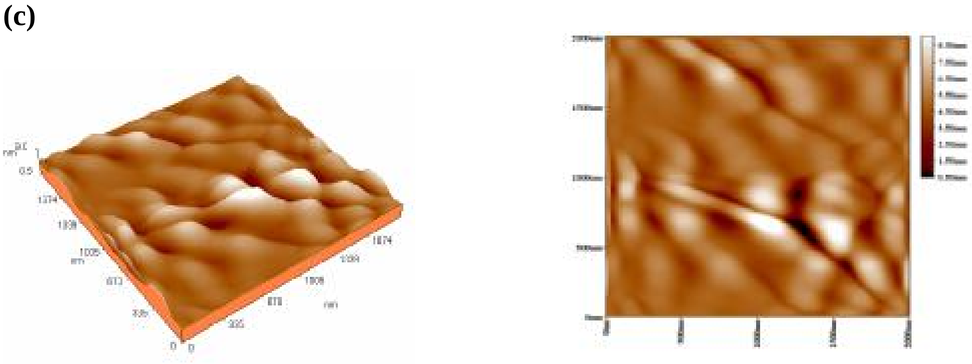


(c)



(d)

Figure (4) AFM image of the SnO_2 thin films with different concentration (mol/litter) (a) 0.1M (b) 0.2M(c) 0.3M(d) 0.4 M.

Figure (5) shows the I-V characteristics of the SnO_2 film samples deposited from solutions at different molarities. It is clear that the current increase with increased bias voltage, and with increasing the solution molarity.
The increasing of current with molarity could be attributed to the increasing average grain size which is accompanied by a decrease in the grain boundary scattering. The thin film behavior was close to Ohm's law, and the current will grow while the carriers crossing the inter atomic barrier with increasing bias voltage [17].

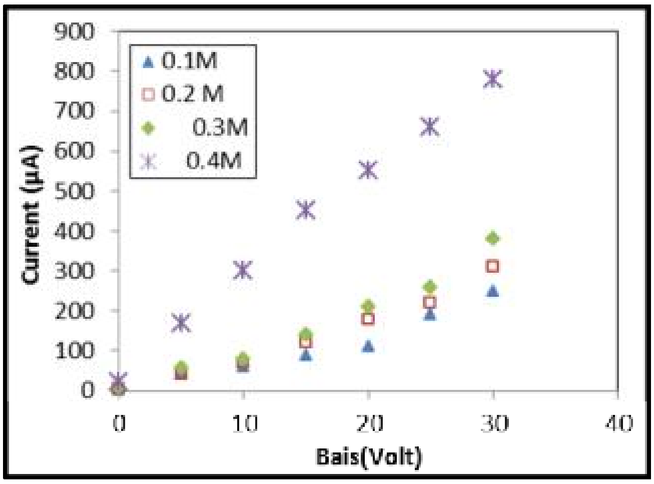


Figure (5) I-V characteristics in dark of SnO_2 films at different molarities.

CONCLUSION

Highly transparent and conductive SnO_2 films were deposited on glass substrates by using spray pyrolysis. The optical transmission of the sample deposited at a substrate temperature of 550 °C was about 87 % at lower film molarity, with optical band gap in rang (3.6-3.5) ev. The smoothness and homogeneous of the films are decreasing with increasing the aqueous solution molarity and I-V characteristics of the SnO_2 films shows the thin film behavior was close to Ohm's law.

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