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DEPOSITION AND CHARACTERIZATION OF ZINC OXIDE THIN FILMS

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ABSTRACT

Zinc oxide thin films were intensively applied in optical devices, solar cells, sensors, and in many electronic devices as semiconductor material. The field of application depends on the morphology of the formed zinc oxide. In this work, thin films of zinc oxide were prepared by deposition of zinc oxide colloids from ethanolic solution of zinc acetate in the presence of formamide and lithium hydroxide onto glass microscope slides via sol gel technique. The transmittance of the formed films was measured in the range of 0.8 to 1.2 μm. The thermal analysis was also given and discussed. The prepared ZnO thin film can be utilized in the field of aerospace especially in manufacturing of solar cells.

INTRODUCTION

Zinc oxide is a technologically important material. It is a promising material for many different applications such as, solar cells, gas sensors, ultrasonic oscillators, transducers and in many electronic devices as semiconductor material [1]. The physical properties, the low cost and the various fabrication techniques available make zinc oxide a promising material for optoelectronic devices. Zinc oxide thin films are used extensively as piezoelectric transducer for the generation and detection of bulk and surface acoustic waves. Intensive investigations of the optical properties and applications have been carried out, but it's very important to characterize the film microstructure and to correlate it with the deposition parameters [2]. The deposited films had a sufficiently smooth surface for them to be suitable as optical films [3]. Highly conductive films of ZnO have actively investigated in recent years because of their potential applications as transparent and conductive coatings and as IR reflective coatings. The constituent elements of ZnO are abundant and the material has a low cost. If highly conductive films of ZnO with a high optical transmission can be prepared using an inexpensive thin film deposition technique, ZnO would be useful as a less expensive coating material than ITO (indium tin oxide) which used as films with a low resistivity (10^{-4} Ωcm) and with stable electrical and optical properties generally used as a transparent

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electrode for optoelectronic devices [4]. ZnO is often called a promising material for planar wave-guides. Its potentially low cost can be sputter deposited onto many types of substrates and has large electromechanical, electro-optical and elasto-optical constants. ZnO is used in fabrication of single-mode wave-guides [5].
Zinc oxide films have been prepared using several techniques such as, spray pyrolysis, sputtering, evaporation, metalorganic chemical vapor deposition [6], and sol-gel technique [7]. The characteristics of zinc oxide film obtained differ from one technique to another and also its applications. Zinc oxide films can be used as an essential component in solar cells in the field of aerospace applications.
In this work zinc oxide colloid were prepared via sol gel technique using zinc acetate as a precursor. Thin films were prepared by dip coating of glass microscope slides into zinc oxide colloidal solution. The transmittance of the formed films was measured. The morphological analyses of the formed films were studied by scanning electron microscope. The factors affecting the formation were studied (drying temperature and the use of drying control chemical additives). The higher homogeneity appears by adding formamide as drying control chemical additives.

EXPERIMENTAL SECTION

The source, origin and specification of the used chemicals are listed in the following table 1. They were used in the experimental work without further purification.

Table 1. Chemicals used and their specifications

Name	Formula	M wt. g/mole	Grade %	Source
Zinc acetate dihydrate	$Zn(CH_3COO)_2.2H_2O$	219.49	98	May & Baker, England
Ethanol	C_2H_5OH	46.07	>99	Merck Germany
Lithium hydroxide monohydrate	$LiOH.H_2O$	41.96	99	BDH, England
Formamide	$HCONH_2$	45	Pure	Prolab.

The preparation procedure followed in this study was essentially the same as that of Spanhel [7].
The procedure consists of three major steps:
(1) Preparation of precursors: -
A 0.1M ethanolic solution of zinc acetate was prepared by dissolving 0.05 mol of zinc acetate in 0.5 L of ethanol in a 1-L round-bottom flask. The flask was

fitted with condenser and calcium chloride moisture trap and refluxed while stirring (with a magnetic stirring bar) for 180 min at 80°C. The condensate was collected continuously at the end of this procedure, 0.2 L of reaction product (precursor) and 0.3L of condensate (which was discarded) were obtained.

At this point, the synthesis, the precursor, likely contains a zinc ethoxide-type compound (and the reaction by products such as acetic acid derivatives), although we did not determine their structures [7,8].

(2) Hydrolysis of the precursor to form the colloid: -

The 0.2L of precursor was diluted back to the original volume of 0.5 L with absolute ethanol. Then, 0.07 mol of lithium hydroxide powder ($LiOH.H_2O$) was added to this precursor to give a final lithium concentration of 0.14 M.

The mixture was then hydrolyzed in an ultrasonic bath to accelerate the reaction. This hydrolysis reaction was continued at room temperature until lithium hydroxide powder no longer visibly present (about 1h).

The ZnO colloidal suspension was filtered to remove any undissolved lithium hydroxide that might remain.

(3) Concentrating the colloid to form the final sol: -

This colloid was then concentrated by evaporation from 0.1 M to 0.5 M (with respect to zinc concentration) by heating at 80°C with stirring, the product is a colorless liquid, and if it remains in open atmosphere more than 3 days, the white bulk of ZnO will appear.

Preparation of zinc oxide thin film: -

Zinc oxide thin films were prepared by two methods: -

(1) By immersing two glass substrates adhered to each other (previously washed with ethanol and dried in closed oven to 100°C) in zinc oxide colloidal solution, then the substrate was elevated slowly from the bath.

(2) By pouring the solution on the glass substrate. A plastic syringe was used as tool to pour the solution on the glass surface.

The thin films prepared were dried at atmospheric conditions in open atmosphere for 3 days dried in closed oven at 50,100,120 and150°C. Transmittance and thickness were measured for the thin films formed. The thin films prepared by pouring were dried at 200, 300, 400°C and at 500, 600, 700°C. The thickness and transmittance were measured for thin film formed.

Formamid was added as a drying control chemical additive to ZnO colloidal with different concentrations in the range of 30,35 and, 40% (volume percentage). These samples were then used to form a thin film by dip coating of a glass substrate in colloid solution to 20 sec and elevated slowly. The thin films formed calcined to 600 °C. The thickness and scanning electron microscope were measured for the thin films formed.

RESULTS AND DISCUSSION

Transmittance of zinc oxide thin films: -

The formed films which formed at room temperature 25°C and which dried at 50,100,120,150°C can be removed by thumbnail, they are not homogeneous

distribution. Figure 1 shows the average transmittance of the formed films in a region 900 to 1200nm. The thickness of the formed films is ranged from 2-8μm. The transmittance of thin films decreases as the drying temperature increased. From the thermal analysis as will be shown later in thermogravemetric analysis, we found that the weight loss of 44.2% was observed at 450°C get off. The samples were thermally treated putting the thin films formed in an oven at room temperature and the temperature was elevated gradually by 1°C/sec. up to 500,600 and 700°C. It was noted that the rate of heating had an effect on the formed film. It was noted that the rate of heating had an effect on the formed film. If the samples were heated spontaneously or started to be heated above 60°C the thin film was burned and black color of burning residual organic compounds appeared. Figure 2, shows the transmittance of the formed films at 500°C. The thin films formed were characterized by good adhesion and the transmittance decreased as the thickness increased. The thickness of the formed films was ranged from 1-18μm. Figures 3 and 4 show the transmittance of the formed films at 600 and 700°C respectively. The transmittance of thin films decreased as the drying temperature increased. From figures 1,2,3 and 4, we can conclude that the minimum transmittance can be obtained at higher temperature (700°C), but the substrate (soda glass) starts to melt at about 643°C.
So the suitable temperature for calcination will be kept in our study at 600°C.
Zinc oxide thin film with higher transmittance can be obtained at low preparing temperature, but from the physical properties of zinc oxide, it absorb humidity from the atmosphere below 39°C and form zinc hydroxide. Above 39°C ZnO is a stable form, so the stable condition of thin films at low drying temperature must be kept in a temperature above 39°C [9,10] or thermally treated as shown at a higher temperature. That's explained the poor adhesion of the thin film formed at lower temperature. The Zinc oxide thin films formed at higher temperature has a stable form and with no weight loss and can't be affected by humidity.
In figure 5 a comparison between thin films with the same thickness formed at different temperatures and their transmittances. From figure 1 and 5 we can observe that as the drying temperature increased the transmittance of thin film decreased, the deferent behavior observed at 700°C, may be due to the deformation of the glass substrate at high temperature. There was no noticeable dependence on the film thickness. We added a formamide as drying control chemical additives DCCAs, with different volume percentage in order to obtain more uniform surface, it affect the rate of drying as it contribute with different evaporation rate [11]. Figure 6 shows the change of transmittance of different samples prepared with different formamide concentrations thermally treatment at 600°C. The transmittance of thin films decreased as the percentage of formamide increased up to 40%.

Thermal analysis of zinc oxide particles: -
Figure 7 shows the result of thermal gravimetric analysis studies of the product formed. The sample weight was observed to decrease gradually up to 60°C and decreased sharply between 60°C and 130°C (at 122.3 °C) with

about 23.4%. The weight decreased slowly up to 335°C, and decreased sharply between 335°Cand 400°C (at 393.2°C) with about 15.4, the weight was observed to level off at a constant value at 440°C, about 44.2% of the initial weight. This result suggests that the sample contained quite large amount of organic materials. The weight loss observed at temperature lower than 130°C is considered to be due to the evaporation of loosely bound organic materials remaining in the sample as ethanol, water, and acetic acid, which turned out to be byproducts produced in the colloid preparation processes, mainly acetic acid. The smell of acetic acid is observed during the drying of the sample at 120°C. The more remarkable decrease in weight between 335°C and 400°C is probably due to the thermal degradation of the more strongly adsorbed organic molecules in the form of bonded acetate or alkoxide groups [7]. The weight of these materials accounted for about 18.1 % of the initial weight.

Morphology analysis: -

The morphology analysis of the formed films shown in figures 8,9,10 and 11. Figure 8 shows the thin film of the sample calcined at 500°C where the surface of the sample has some irregularities, which may be induced during thermal treatment. On raising the calcination temperature up to 600°C the SEM of the formed films shown in figure 9 gives smoother surface and more regular. Figure 10 shows the thin film calcined at 700°C for which the SEM has the optimum surface regularities as a uniform thin film is obtained but the glass substrate starts its deformation at 643°C.

Figure 11 shows the SEM of sample prepared with different formamide concentration calcined to 600°C, in order to achieve the same properties as at 700°C. The uniformity increased as the percentage of formamide decreased, the optimum was shown to be at 30 % by volume.

CONCLUSION

Zinc oxide thin films were successfully prepared via the sol-gel technique using zinc acetate dihydrate starting material hydrolysed under basic conditions using lithium hydroxide. The thin film was deposited from the colloidal solution obtained under ultrasonic effect on microscopic glass slides. The transmittance measurement in the near infrared region from 900 to 1200 nm showed a decreased with the increased in calcination temperature. There is no remarkable effect of the thin film thickness within the examined range.

The more uniform film formed at higher calcination temperature at about 700°C. The calcination at 600°C with the addition of about 30% by volume of formamide as a drying control chemical additive improved the surface regularity of the formed thin film at related lower calcination temperature than 700°C.

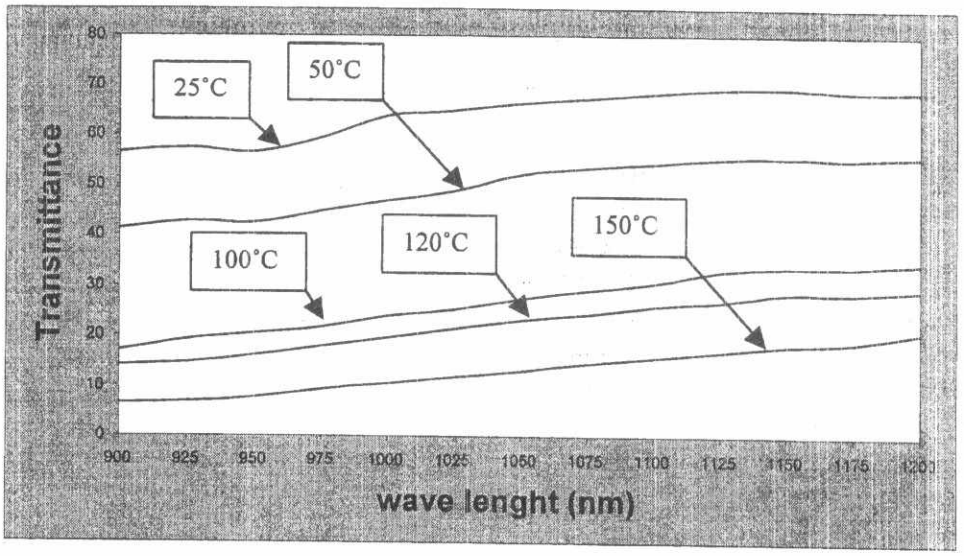


Fig.1. The change of transmittance of thin films prepared at different temperatures.

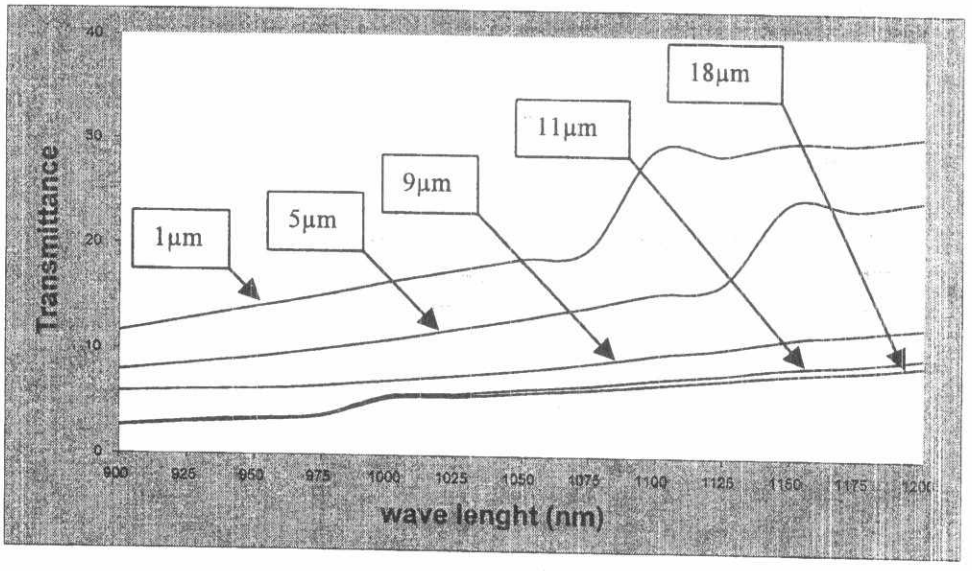


Fig.2. The change of transmittance of thin films has different thickness formed at 500°C.

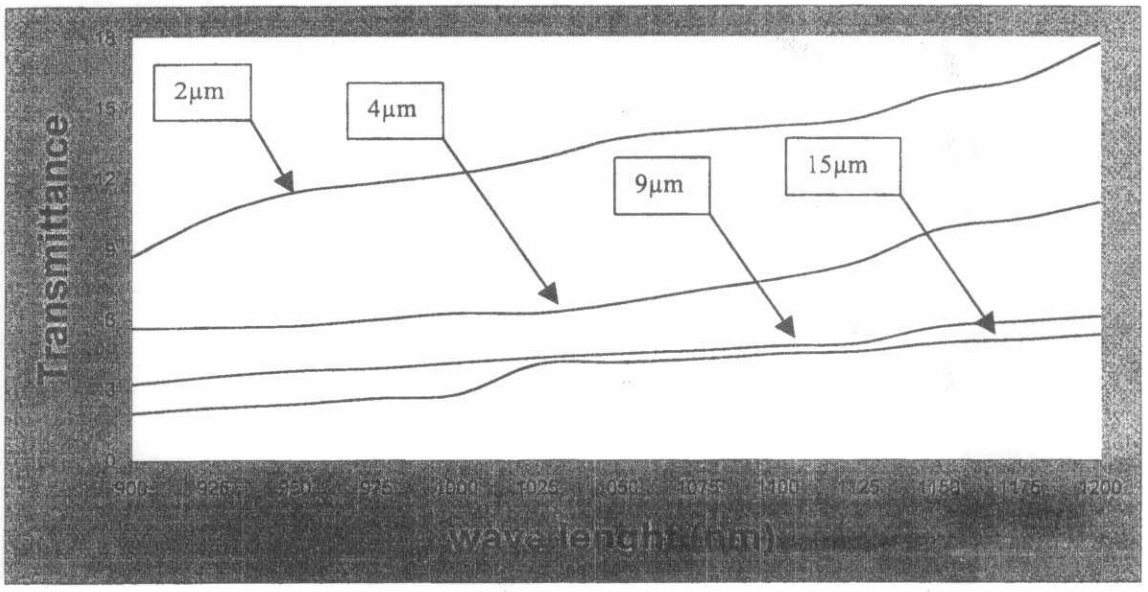


Fig.3. The change of transmittance of thin films has different thickness formed at 600°C.

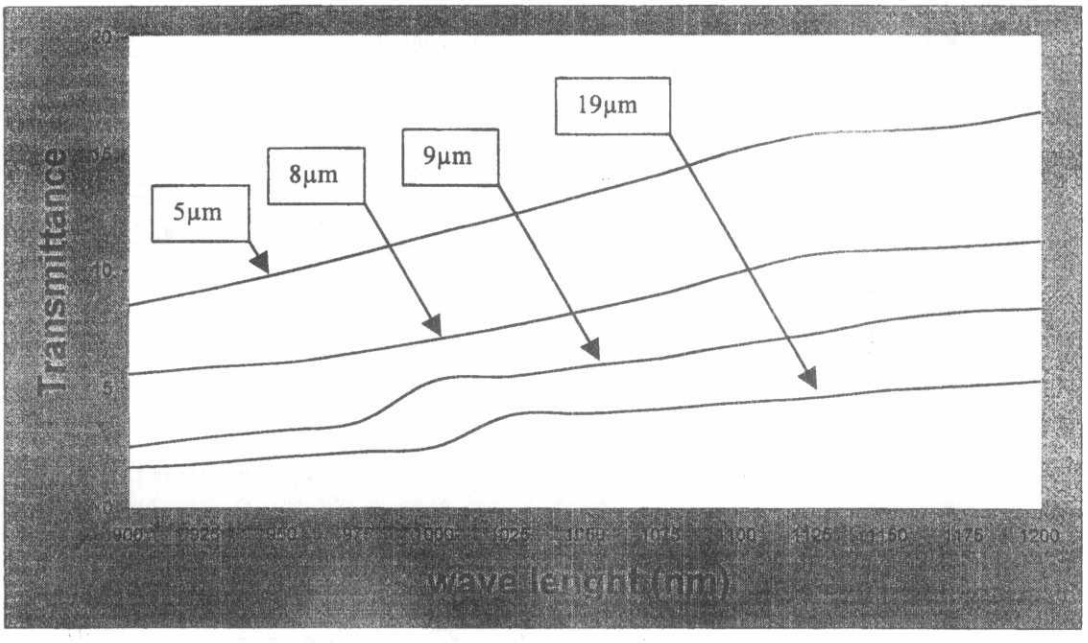


Fig.4. The change of transmittance of thin films has different thickness formed at 700°C.

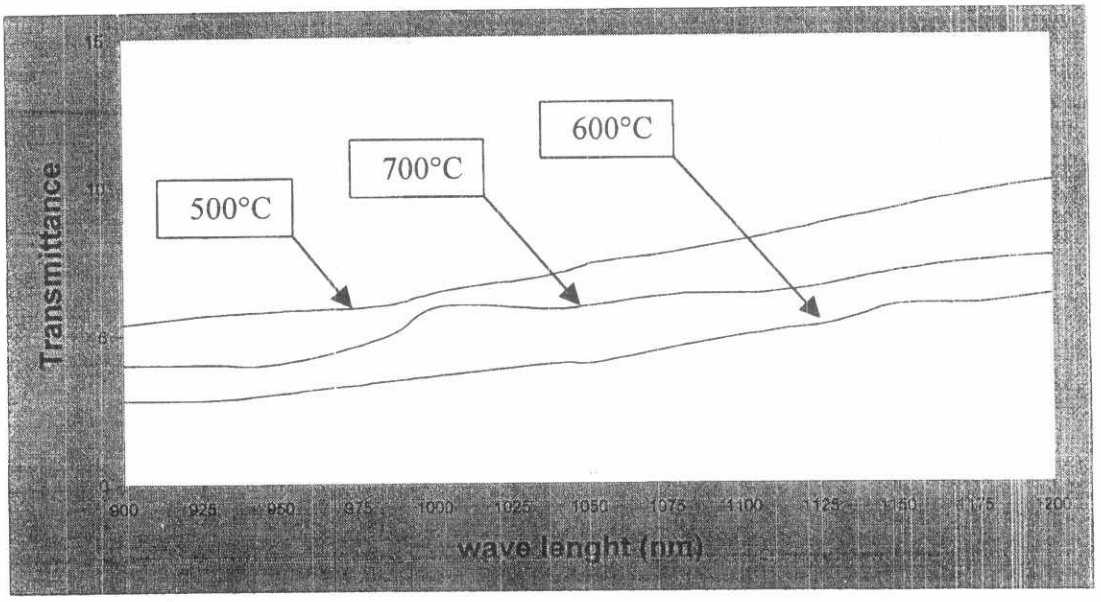


Fig.5. Comparison between thin films with same thickness (9μm) formed at different temperature and their transmittance.

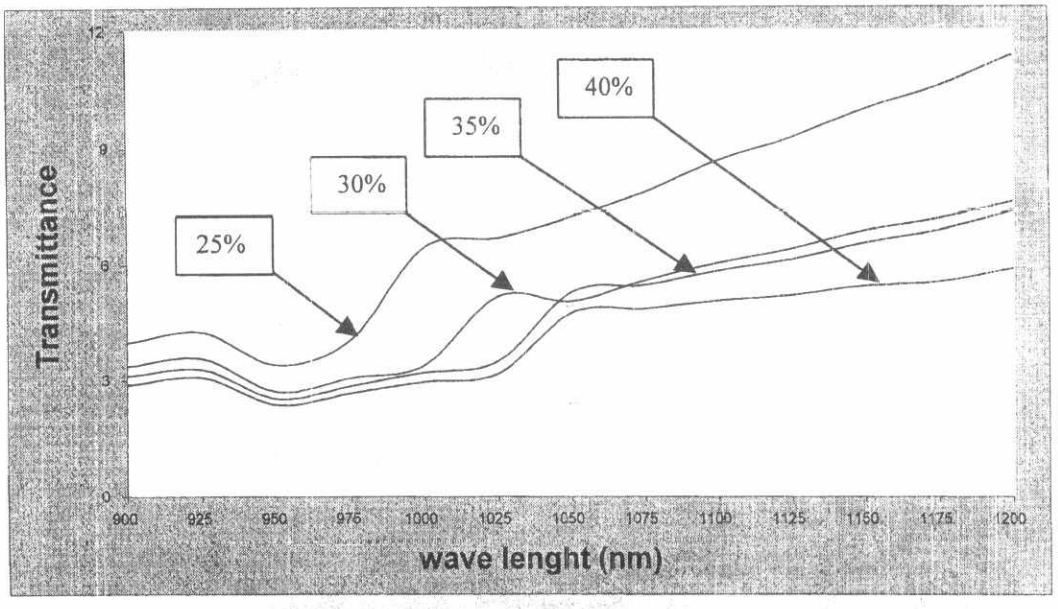


Fig.6. The change of transmittance of thin films prepared with different formamide concentration formed at 600°C.

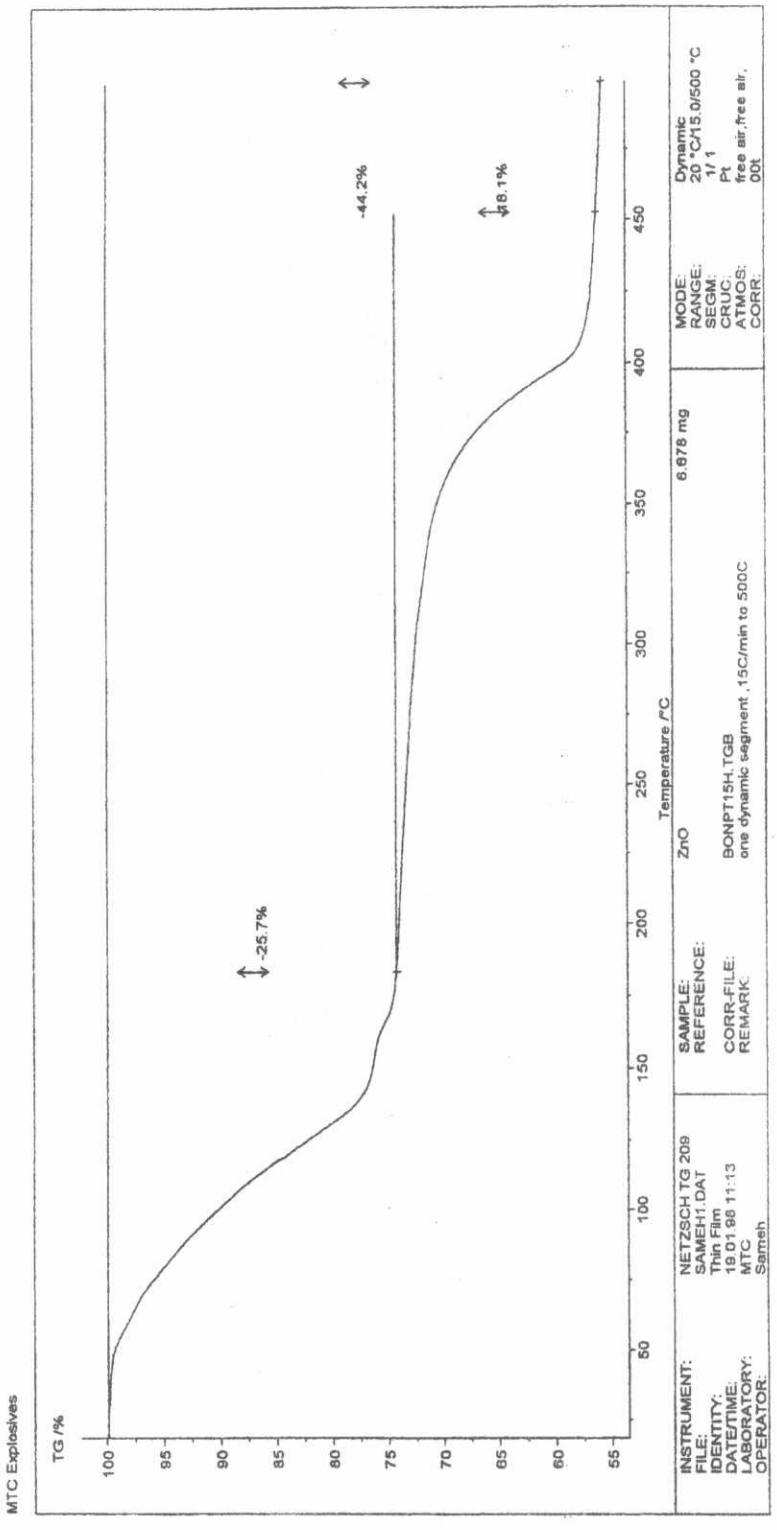


Fig.7. Thermogravemetric analysis of a sample formed under ultrasonic effect for 1 hr.

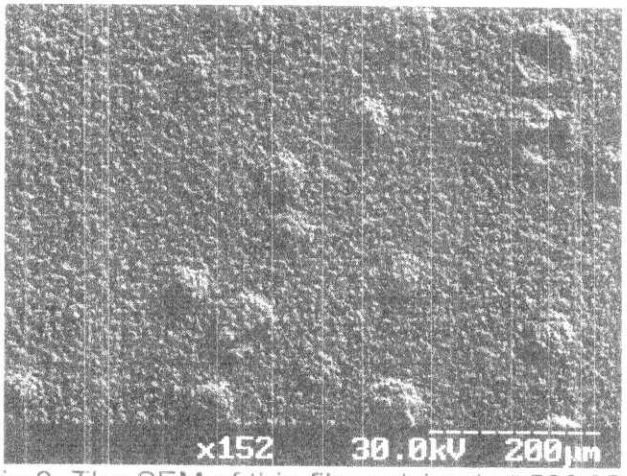


Fig.8. The SEM of thin film calcined at 500 °C (Thickness 7µm).

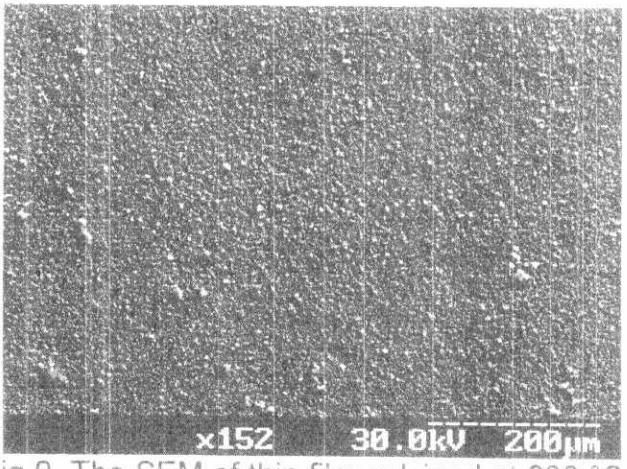


Fig.9. The SEM of thin film calcined at 600 °C (Thickness 19µm).

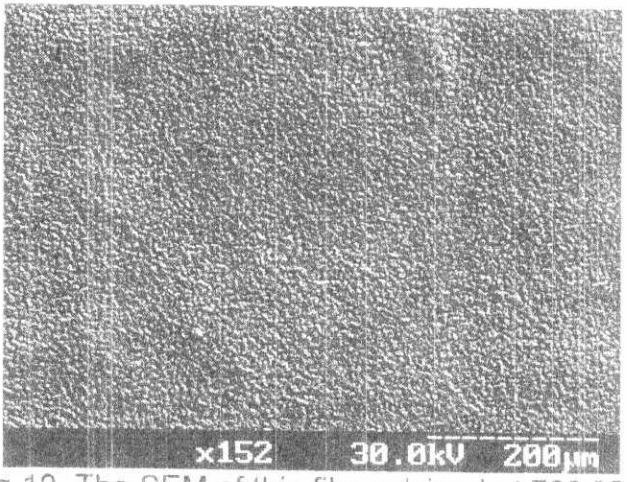
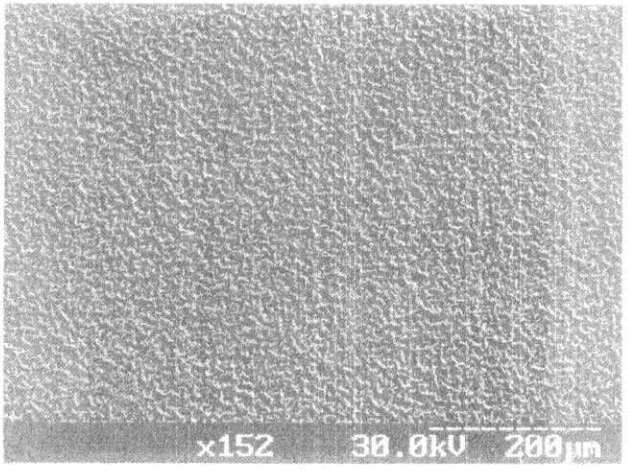
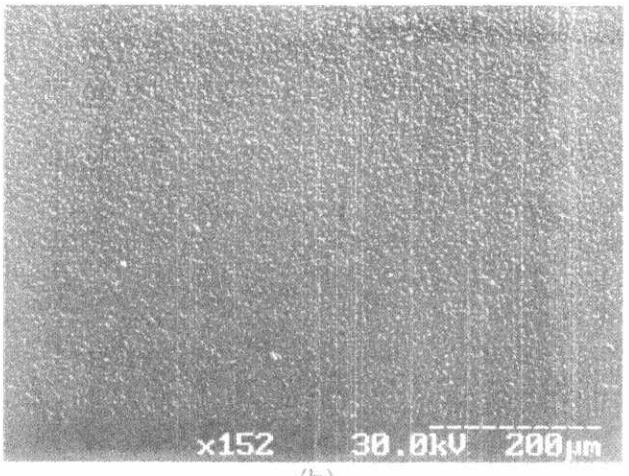


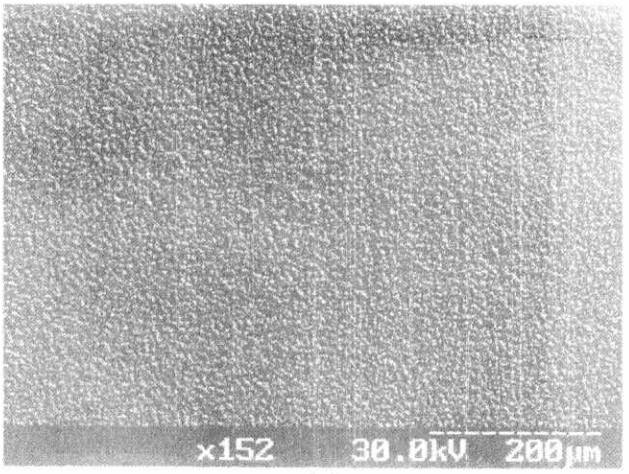
Fig.10. The SEM of thin film calcined at 700 °C (Thickness 16µm).



(a)



(b)



(c)

Fig.11 The SEM of thin films calcined at 600 °C with different formamide concentration
(a) 40% formamide (Thickness 15µm). (b) 35% formamide (Thickness 14µm).
(c) 30% formamide (Thickness 21µm).