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Zinc oxide antireflection thin-film: spin coater parameters effects

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Abstract

Zinc oxide (ZnO) is one of the commonly used materials in antireflective coating (ARC) due to its optical, physical, and chemical properties. In order to enhance optical transmittance, an ARC is essential. Refractive index and film thickness are the key parameters to get an efficient ARC. The aim of this work is to study deposition parameters' effects on thickness evolution and film quality. Spin-coated ZnO film thickness was measured and controlled according to revolutions per minute (rpm) and spin time (t). For this purpose, a sol-gel derived film containing dihydrate Zinc Acetate (ZAD) and ethanolamine was used to be spin-coated on a glass substrate. Thermogravimetric analysis (TGA) was carried out in order to study the film thermal behavior and was followed by X-Ray Diffraction (XRD) measurement in order to confirm the crystallization of ZnO. The film thickness was deduced from its mass measured by a microbalance and its' centrifugal spread over the substrate was checked by an optical microscope. By optimizing the deposition parameters, good film spread was obtained up to 4000 rpm with a spin time of 90 seconds at least. We found that the rpm affects strongly film thickness, in contrast to the spin time which affects the film spread.

Keywords: Antireflective coating; Zinc oxide; Spin coating; Film thickness; Spin time.

1. Introduction

When light crosses two media with different refractive indexes, many fundamental phenomena may occur (reflection, scattering, absorbance, transmittance, and refraction). They are usually correlated according to light propagation law. A part of them can be eliminated in order to keep only the beneficial ones. As in the antireflection coatings, where the reflection will be eliminated in order to avoid power loss; such in LASERs and solar cells; get more transmittance for optical components like cameras, telescopes, and binoculars lenses [1]; and remove glare from ophthalmic lenses, and display devices [2]. The Antireflection effect can be achieved by two approaches, graded-index or destructive interferences [3] based on two key parameters, the refractive index and the thickness [4].

ARC can be manufactured by conventional techniques, like chemical vapor deposition (CVD), Etching (wet chemical, and dry etching), Sol-gel coating (Meniscus, Dip, and Spin coating), etc. As they can be made by unconventional techniques, such as lithography, microreplication technique biological assisted, miscellaneous photo aligning, and photo altering, etc. [5]

A wide variety of metal oxides can be synthesized in order to manufacture antireflection coatings, as Silicon dioxide (SiO_2), Tin dioxide (TiO_2), Zinc oxide (ZnO), etc. [6]. ZnO was chosen because of its optical and mechanical proprieties, as adequate refractive index, high transparency, and good adhesion, it is also low cost, non-harmful, and simple preparation material, especially with a sol-gel technique [7].

The Sol-gel method is widely used in the mass production of anti-reflective thin-films due to its low cost and the highly controlled way [8]. Different optical, electronic, optoelectronic components can be manufactured by combining this method with other techniques like dip coating, spray coating, meniscus coating, and spin coating [9].

Spin coating as a deposition technique has several parameters to control, like rpm, spin time, acceleration, and final speed [10]. A good understanding of these parameters effects is crucial to obtain a given film uniform thickness [11].

This work focuses on the control and evolution of a thickness in spin coated ZnO ARC by sol gel, where the effect of the rpm and the spin time on the film thickness evolution and spread was investigated, using a new approach measurement and characterization, such Thermogravimetric Analysis and differential scanning calorimetry (TGA-DSC) which are never used for this kind of investigation. Zinc Acetate dihydrate (ZAD), ethanolamine, and methoxyethanol was used. The film thickness evolution measurements, centrifugal spread microscope images, thermal decomposition, and crystal structure analysis have been reported.

2. Materials and methods

2.1. Sample preparation

Zinc acetate dihydrate [Zn(CH3COO)2*2H2O, ZAD], ethanolamine [H2NCH2CH2OH, EA], and β-methoxyethanol [CH3O(CH2)2OH, ME] were purchased from Alfa Aesar and were used as received.

2.1.1. Solution preparation

An amount of ZAD (3.4 g) was dissolved in an equimolar amount of EA (0.94 ml) and stirred at 60 °C for 24 h. The obtained precursor was conserved in a silica gel desiccator for several days until the sol-gel became viscous. It was kept away from light during the experiment in order to avoid any possible photodegradation.

2.2 g of the precursor was dissolved in an amount of 8.82 ml of ME and stirred for 30 min at 60 °C [12]. The obtained solution was passed through a 0.22 µm filter to remove any solid residue.

2.1.2. Substrates preparation

Microscope slides (1 cm 1 cm) were used as substrates. They were washed using liquid soap to eliminate dust, then agitated in distilled water, and finally rinsed in acetone to remove organic impurities.

2.2. Film deposition

ZnO thin-films were deposited on glass substrates by spin coating with different spinning speeds ranging from 3000 to 6000 rpm and different spin times ranging from 45 to 120 seconds using a Laurell WS-650Mz-23NPP spin coater. Spin time was fixed at 120 seconds while changing rpm, then the spinning speed was fixed at 6000 rpm while changing the spin time. The acceleration (Acc) was fixed at 6000 rpm/min during all the experiments.

2.3. Thickness determination

A METTLER TOLEDO XS3DU microbalance was used to determine the average film thickness by weighing substrates with accuracy before and after film deposition. By determining the film mass, we can deduce the film thickness following the next steps:

$$m_i = m_t - m_s \quad (1)$$

Where:

m_i: initial film mass.

m_t: total mass.

m_s: substrate mass.

The film volume can be easily determined by applying the definition of density:

$$\rho_{ZnO} = \frac{m_i}{V_i} \quad (2)$$

Where:

ρ_{ZnO}: ZnO density (5.61 [g.cm^{-3}]).

V_i: initial film volume (V_i = x.y.d).

Where:

x, y, d, are the film length, width, and thickness respectively (Figure 1).

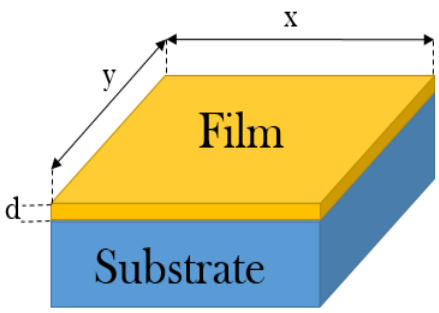

Figure 1. Schematic of ZnO thin-film deposited on glass substrate.

$$\rho_{ZnO} = \frac{m_i}{x.y.d} \quad (3)$$

$$d = \frac{m_i}{\rho_{ZnO}.x.y} \quad (4)$$

The film thickness can be determined by replacing its dimensions (1cm × 1cm × d) and the ZnO density.

$$d[cm] = m_i[g] \times \frac{1}{5.61[g.cm^{-3}] \times 1[cm] \times 1[cm]} \quad (5)$$

The film loses 69% of its mass during decomposition according to TGA.

$$m_f = m_i \times 0.31 \quad (6)$$

Where, m_f is the final film mass.

$$d[nm] = m_i[mg] \times \frac{0.31 \times (10^{-10})}{5.61[g.cm^{-3}] \times 1[cm] \times 1[cm]} \quad (7)$$

$$d[nm] = m_f[mg] \times 1782.53119 \quad (8)$$

2.4. Film characterization

Thermogravimetric analysis (TGA) of the film was carried out using "SETSYS Evolution 1750 TGA/DSC SETARAM" instrument in order to study the solution behavior during the decomposition. A 1.973 mg of the solution was deposited on glass substrates and heated from 50°C to 500°C, in nitrogen flow (40 ml/min) with a heating rate of 10°C/min. XRD measurements were performed by Brucker X-ray diffractometer using a Cu radiation source, at 25°C and a diffraction angle (2θ) lying in the range of 10°- 85°. Optical microscope Carl Zeiss Jenavert was used to evaluate the spread quality of deposited ZnO thin-films.

3. Results

3.1. Thermogravimetric Analysis and differential scanning calorimetry (TGA-DSC).

TGA was performed to study the thermal decomposition and the mass loss of the film. DSC measurement was investigated in order to determine the crystallization critical temperatures of ZnO.

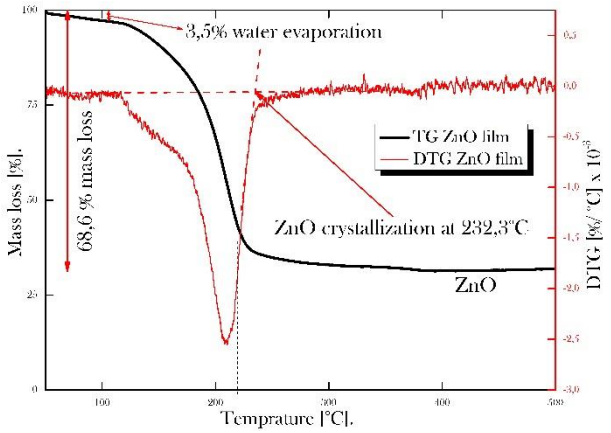

Figure 3. TG and DTG thermograms of ZnO.

TG curve (figure 2) shows that the ZnO loses 68.6% of its total mass during thermal pyrolysis where 3.5% was lost as water evaporation. The ZnO theoretical mass represents 64.8% of the total mass.

M [ZnO] / M [Zn(H2NCH2CH2O)] = 81.39 / 125.46 u.m. a = 0.648.

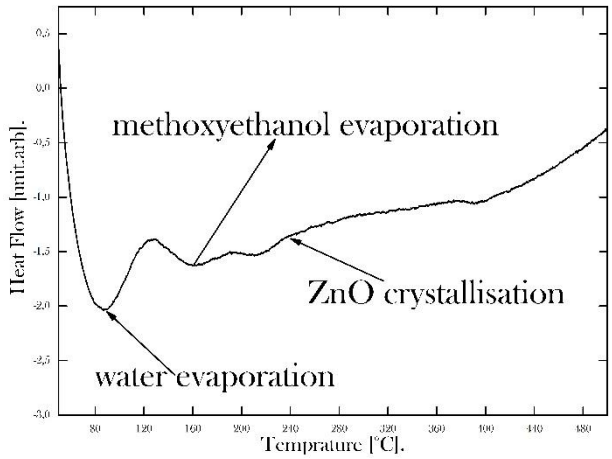

Figure 4. DSC thermogram of ZnO.

The difference between the ZnO theoretical mass and the remaining mass (64.8% - 31.4% = 33.4%) is due to its evaporation during the pyrolysis process.

The critical temperatures of the major phenomena occurring during ZnO pyrolysis are shown in figure 3. They are respectively the water evaporation at around 120°C, the methoxyethanol evaporation at 177°C which are endothermic phenomena observed, and an exothermic phenomenon related to ZnO crystallization beginning at 250°C.

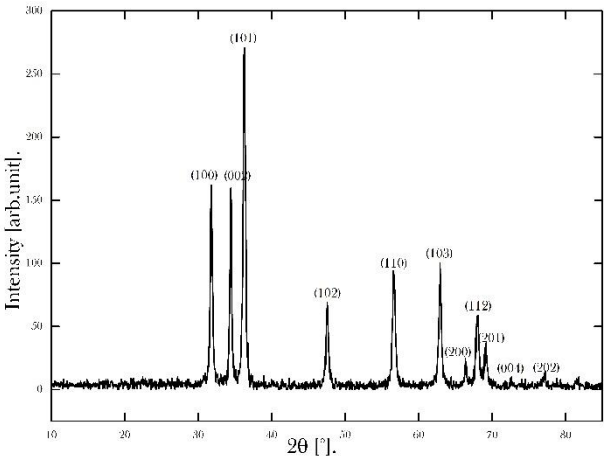

Figure 2. Diffractogram of ZnO annealed at 400°C for 2h.

3.2. X-Ray Diffraction (XRD).

To check the ZnO film prepared crystallinity, an amount of it was annealed at 400°C for 2 hours, and analyzed using an XR diffractometer.

Figure 4 shows XRD pattern of the ZnO thin-film heated at 400°C in order to get the powder to be analyzed. After the decomposition process, the crystalline nature of the ZnO film clearly appears on the XRD pattern with several diffraction peaks. All peaks have been indexed and were found to be in agreement with those of the hexagonal wurtzite phase of ZnO with lattice parameters a = 3.24982 Å; b = 3.24982, c = 5.20661 Å. In addition, no other peaks were detected, suggesting that the prepared material is pure ZnO.

3.3. Effect of spin coating deposition parameters

The film thickness is related to several parameters like: dispense volume, solution concentration, acceleration, final speed, etc. It is strongly related to the variation of rpm and Spin time which we have tested in different intervals to get the desired thickness and a good quality spread.

After film deposition, there are four possible results:

(1) uniform film spread with the desired thickness. If the viscosity and the evaporation rate of the solvent are compatible with the spin coater parameters.

(2) non-uniform film spread with the desired thickness. When the solution parameters; viscosity and/or evaporation rate are not suitable several cases can occur.

- For the high viscosity of the solution spiral vortices appear.

- when the rotation speed is not correlates with the evaporation rate of the solution the film shrinks.

To solve this problem, we can reduce the viscosity of the solution, change the solvent or reduce the rotation speed to correlate with the evaporation rate.

(3) uniform film spread with an unreached thickness which means that the viscosity and the evaporation rate are appropriate but the spin coater parameters settings are not appropriate (we are in intervals that do not perform the function despite the good film spread).

To solve this problem, we can change either spin coater parameters (the final speed, the acceleration), or the solutions' parameters (the concentration, the viscosity).

(4) non-uniform spread with an unreached thickness. In this case, we are facing two problems, not only the spread is non-uniform, but the thickness desired is not achieved as well. This means that all the parameters are not suitable.

To solve this problem, it's necessary to adjust the solution parameters as a first step to get a good spread then adjust the spin coater parameters to achieve the expected thickness.

3.3.1. Effect of spin time (t)

Figure 5 is the ZnO film thickness evolution according to spin time, where the insets a, b, c, and d, are the microscopic images for 75, 90, 105, and 120s spin time respectively. It shows that film mass decreases according to spin time except for the first sample where we suspect that it's due to manipulation error. For the sample of the inset (a), the microscope image shows a non-uniform spread of the film at 3500 rpm due to the short time of spinning.

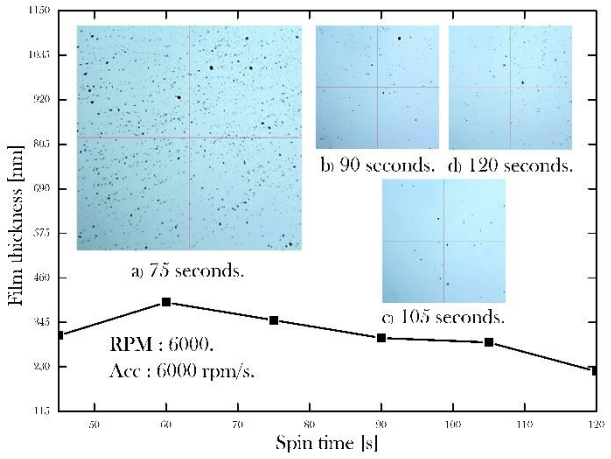

Figure 5. Evolution of film thickness according to spin time. a), b), c) and d) are images taken by optical microscope at 5X magnifying of a 2mm area.

For the samples on the insets b, c, and d the film obtained presents a uniform spread. Therefore, it's important to notice that the film spread becomes non-uniform below 90 seconds.

When the substrate finishes its rotation, we obtain the final film thickness regardless of its spread quality. The thickness evolution interval is limited. Outside of this interval, the film becomes non-uniform for short spin time and thin for long spin time. In these cases, the film is non-efficient and inappropriate for the anti-reflection applications because the two conditions have not been verified. These two conditions; thickness expected and good spread promise the adequate thickness to get antireflective effect and eliminate the destructive interferences of the either interferential and graded-index ARCs.

3.3.2. Effect of rotation per minute (rpm)

When the substrate reaches the wanted rotation speed, the film begins to spread on the substrate due to the centrifugation force. After film spread, it gradually becomes thinner before achieving the final thickness according to the rotation rate.

If the rotation speed is low, the film present spiral vortices.

If the rotation speed is high, the film obtained will be very thin therefore useless for the application domain or it shrinks due to solvent evaporation rate that isn't compatible with the substrate rotation rate.

If the film is rotated at an adequate speed, the film obtained will have a uniform spread with desired thickness for the application.

Figures 6 is the ZnO film thickness evolution according to rpm and while insets a, b, c, and d, are the microscopic images for 3500, 4000, 4500, and 5000 rpm respectively. It shows as a general trend that ZnO film mass decreases with the increase of rpm. For the sample of inset (a), the microscope image shows streaks and a non-uniform spread due to the low rotation rate. A good film spread was obtained up to 4000 rpm as shown on images of the insets b, c, and d.

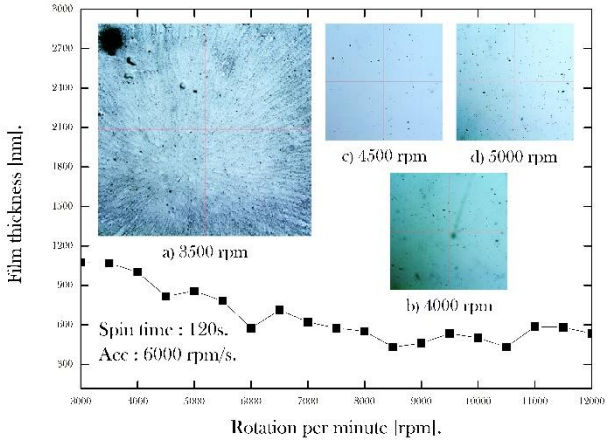

Figure 6. Evolution of film thickness according to rpm. a), b), c) and d) are images taken by optical microscope at 5X magnifying of a 2mm area.

Insufficient spin time and/or insufficient rotation speed, both lead to a non-uniform film spread (as shown in insets (a) in figures 5 and 6) because of the high

viscosity of the solution as explained above. To achieve the wanted results in term of uniform film spread and expected thickness, we need to verify some initial conditions such minimum spin time and minimal rpm. These two parameters (spin time and rpm) which seem independent, are in fact related. This relation confirms that a minimum revolution number at a minimum spin speed is required to get a uniform film spread, in our case 4000 rpm, 1.5 minutes and 6000 revolutions.

If we combine the minimum speed rate with the minimum spin time, we'll get the thickest layer. This combination is considered as the maximum thickness that we can achieve without losing the uniform film spread. By increasing these parameters, the film gets thinner gradually until it reaches the maximum speed rate with the maximum spin time where we get the thinnest layer. This combination provides the minimum thickness that can be achieved before the film gets shortened and cracked due to the solvent evaporation rate that is not compatible with these parameters, for example 4000 rpm with 90 seconds and 12000 rpm with 120 seconds. Other parameters can influence the spread quality, but we have focused only on these two parameters because of their strong influence on the thickness and the film spread quality.

4. Conclusion

The spin coated ARC is used for long time in the industry. A few studies on the effect of spin coating parameters on film thickness have been found. Therefore, we have studied spin time and rpm as independent parameters in order to understand how they affect the ZnO film thickness and its spread quality.

Pure ZnO films were synthesized by a sol-gel process and characterized by powder XRD and TGA-DSC. Optical microscope images of as-deposited ZnO films indicate that the high viscosity of the solution affects film spread at low rpm and short spin time. Thus, it was demonstrated that below 4000 rpm and 90 seconds the centrifugal film spread becomes non-uniform. On the other hand, it has been noticed that the decrease in spin time affects the film spread quality much more than its thickness. This study has been launched to facilitate the tasks done on thin ZnO films, either in ARC or other applications. It can be considered as a starting point leading ZnO deposition experiments. Further investigations are conducted on the efficiency of this technique in the control of the film thickness on more complex geometries in mineral ophthalmic lenses as it can also be used to control the film thickness of multilayers thin-film system.

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