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Effect of Dopant Concentration on the Film Properties of In-doped ZnO thin Films Prepared by sol–gel Method

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Abstract

We report on the effect of dopant concentration and substrate temperature on the electrical, optical and structural properties of In-doped ZnO thin films via sol-gel method using spin coating technique to tackle the problem of high instrumental costs for film deposition. In particular, the effect of In dopant concentration will study at wide range (from 1% up to 10%) by using spin coating technique in this work. The result shows that the substrate temperature at 430°C for deposited IZO film exhibited the lowest resistivity. The optimized condition for spin coating of IZO films at 5 at. % In doping which deposited at 430 °C exhibited lowest resistivity (5.58 x 10^{-3} Ω.cm), high bulk concentration (1.06 x10^{20} $cm^2.V^{-1}s^{-1}$) and mobility (10.5 cm^{-3}) with films thickness about 258 nm. Additionally, the optical transmittance spectra for all IZO films show a very good transmittance, between 80 and 90%, within the visible wavelength region. These result indicate that, IZO films were synthesized by low cost way via sol-gel method can be considered as the promising candidate for TCO in thin film solar cell applications.

Keywords: **:** IZO, sol-gel, In-doped ZnO, Optical properties, Electrical properties.

Introduction

The demand for low cost renewable sources of energy is much attention to make the thin film solar cells became a reality in recently. Transparent Conductive Oxides (TCOs) are much attractive due to some their advantages such as abundance, chemical stability and non- toxicity. Films are generally used as transparent electrodes or buffer layers[1]. Tin -doped Indium oxide (ITO) and impurity-doped Tin oxide such as F doped-SnO_2 (FTO) are the usual TCO electrode used in the third generation solar cells. However due to the problem about the cost of these films as well as the induced problems of degradation, in the last few years was challenge that was attributed to impurity-doped zinc oxide[2]. Zinc oxide (ZnO) films are particularly interesting because of their advantageous properties, such as low cost, non-toxicity and for high stability after heat cycle during the fabrication process of amorphous silicon solar cells[3]. Additionally, ZnO thin films have emerged as an attractive option in the design of transparent electrodes in thin films solar cells due to the simultaneous occurrence of high transmittance in the visible region and a low resistivity[4]. For many of these applications it is very important to control the ZnO physical properties by doping. Impurity doped-ZnO thin films have been deposited by a wide variety of physical and chemical techniques such as sputtering[5], Pulsed Laser Deposition (PLD)[6], Atomic Layer Deposition (ALD)[7], Chemical Vapor Deposition (CVD)[8-9] among others. It is well-known that superior quality films are obtained by these above physical techniques, however, the cost is relativity high due to their system need to use the ultrahigh vacuum for deposition processing. Recently, much attention has been centered on the development sol–gel methods that are being employed increasingly for the low cost preparation of ordered high-specification due to its structure and morphology may be developed in order to tailor the properties of this thin film material such as electrical, optical, magnetic properties[10]. Interestingly, the other advantages of this method are the simplicity and the possibilities to scale up it for large area deposition as well[11-14].

According to ZnO based thin films literature, the results show that, among Group III elements (such as Al, Ga, In, B, et.), In has been become one of the n-type doping[15] that exhibit the most promising dopant, since as-grown films with good conductivity and highly optical transmittance[14,16,17]. Therefore, numerous investigations have been carried out to grow the Indium doped Zinc oxide (IZO) films via sol–gel methods with many technique to such as dip coating[18], spin coating[1,19] spray pyrolysis or ultrasonic pray technique[20-22]. However, determining how to synthesize and improve IZO film by low cost fabrication via sol-gel method that can have good conductivity and high optical transmittance used in thin film solar cells still remains a significant challenge.

Herein, we report on the effect of dopant concentration and substrate temperature on the electrical, optical and structural properties of In-doped ZnO thin films via sol-gel method using spin coating technique to tackle the problem of high instrumental costs for film deposition. In particular, the effect of In dopant concentration will study at wide range (from 1% up to

10%) at various substrate temperature (from 300-460°C) by using spin coating technique in this work. The reason we use the deposition of thin films by spin-coating due to it is a very simple with ultralow instrumental costs and widely used technique to prepare films of uniform thickness of non-volatile materials initially found in liquid solution dissolved in a volatile solvent. Furthermore, deposition by spin coating produces films with thickness that become uniform during spin-off if the viscosity is homogeneous everywhere on the substrate and is independent of the sliding force. The uniformity of the film thickness results from the balance of two opposite main forces: the centrifugal and the viscous forces.

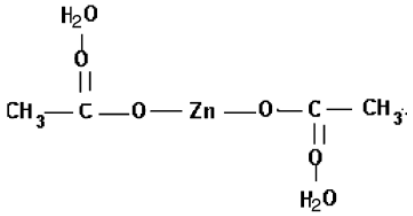
Materials and Methods

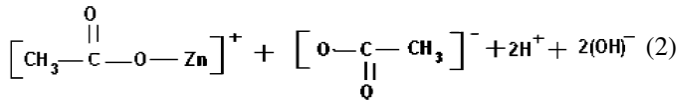
In doped-ZnO (IZO) thin films were prepared by the sol–gel method using spin coating technique. As a starting material, Zinc acetate dehydrate (Zn $(CH_3COO)_2.2H_2O$) 99.999% from the Sigma Aldrich company was used. 2-methoxyethanol 99% and mono ethanolamine (MEA) 99% from Acros Company were used as a solvent and stabilizer, respectively. The dopant source of Indium was indium chloride ($InCl_3$ 99.99% from Sigma Aldrich Company). Zinc acetate dehydrates and dopants were first dissolved in a mixture of 2-methoxyethanol and MEA solution at room temperature. The molar ratio of MEA to zinc acetate ($Zn(CH_3COO)_2$) was maintained at 1.0 and the concentration of zinc acetate was 0.75 M. The In dopant concentration [In/In+Zn] was studied from 1% to 10% in this work. The solution was stirred at room temperature for 2 h to yield a clear and homogeneous solution, which served as the coating solution. The solution was dropped on corning EAGLE 2000 glass (20 mm × 20 mm × 0.7 mm) substrates. The glass substrate was cleaned before by sonication in acetone for 5 min followed by ethanol for another 5 min, then rinsed with DI water and blown dry by nitrogen. The solution was dropped on the glass substrate by spin coating was rotated at 4000 rpm for 20 s. After depositing by spin coating, the films were preheating at different temperature (310°C to 460°C) for several minutes (3-5 min) over a hot plate to evaporate the solvent, remove organic residuals, followed by decomposition and oxidation of the precursor to form doped ZnO, then naturally cooled to room temperature. The procedures from coating to drying and cooling were repeated several times until the thickness of the films was approximately 285 nm. The films were post-heating in vacuum 10^{-3} Torr at 400 °C for 1 hour to get IZO films with preferential orientation.

The crystalline properties of the IZO films were characterized using X-ray (Bruker D2 PHASER) diffraction (XRD). The chemical composition and bonding state of the IZO films were investigated through X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα radiation source. The optical properties of IZO were obtained using UV-visible spectrophotometer (JASCO V-670) in the wavelength from 300 to 1500 nm. The resistivity, carrier concentration and mobility of films were measured at room temperature by Van Der Pauw method using Hall Effect measurement system.

Results and Discussion

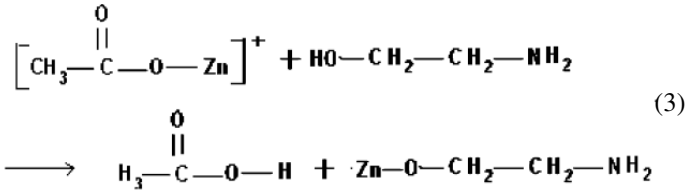
Reaction mechanism for Indium doped Zinc oxide: The chemistry of the precursor solution of In doped Zinc oxide by using 2-methoxyethanol and mono ethanolamine was proposed the mechanism as below: The solvent (2-methoxyethanol) and the stabilizer (mono ethanolamine (MEA)) play important role of In doped-ZnO formation. Consider water molecules in zinc acetate dihydrate are bonded through oxygen in the C=O bonding[23] then they can obtain the following molecular picture projected on a horizontal plane for zinc acetate in 2-methoxyethanol[24]:


(1)


(2)

Zinc acetate $Zn(C_2H_3O_2).2H_2O$ transforms to mono-acetate $Zn(C_2H_3O_2)$ in 2-methoxyethanol, which can result in a composition from Equation-1, as follows:

MEA acts as a complexing agent, also retarding Zn (II) condensation. However, the presence of this amine also increases the pH, which should promote the formation of ZnO. The reaction between mono-acetate Zn ($C_2H_3O_2$) and MEA are listed below, with the presence of $InCl_3$ doping (not show here in Equation-3) which results in the formation of doped-ZnO.


(3)

Effect of Indium doping concentration on the film properties: To investigate the effect of doping concentration on the properties of the IZO films, we varied the content wide range of indium from 1 up to 10 at.%.

After depositing by spin coating, the films were dried at temperature 430°C for several minutes (3-5 min) over a hot plate. Finally, the films were annealed in vacuum 10^{-3} Torr at 400°C for 1 h. IZO thin films with thickness were fixed about 258 nm. Figure-1 shows the XRD patterns of the films doped with various indium concentrations.

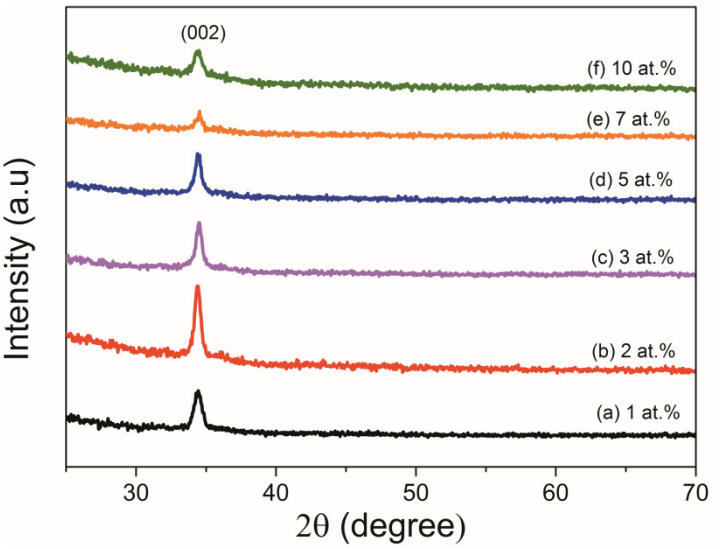


Figure-1
XRD patterns of ZnO films doped with (a) 1 at.%, (b) 2 at.%, (c) 3 at.%, (d) 5 at.%, (e) 7 at.%, and (f) 10 at.% indium doping

Interestingly, only a strong (0002) ZnO peak was observed in the films, no additional diffraction peak was detected for all IZO films, corresponding independent of the Indium doping concentration. The 0002 peaks indicate that the films are highly oriented with their crystallographic c-axis perpendicular to the substrate. This strongly asserts that there is no significant change in orientation for the films deposited at various doping concentration. In other words, the Wurtzite-type crystal structure of ZnO is dominantly formed to produce the IZO films at any doping concentration. No signal corresponding to a single metallic phase of Indium or to phase separation between Indium and Zinc oxide (Figure-1) of all films was detected, which provides evidence that the Indium present could be substituted in the Zinc oxide lattice with the Wurtzite structure. The crystallite properties of all films under different In doping concentration were also evaluated by the full width half maximum (FWHM) of (002) peak of IZO films. It is found that as increasing the In doping concentration from 1 at.% to 5 at.%, the FWHM first decreases with a value from 0.639° to 0.481° in Figure-2. However, further increasing the In doping concentration over 5 at.% up to 10 at.%, the FWHM value increases 0.481° to 0.678° (Figure-2), suggesting that a further increase in In doping concentration deteriorates the crystallinity of the films, which may be effect of the formation of the compressive stresses due to more ions In occupies in the interstitial sites of ZnO under high doping level of In and the segregation of dopants in grain boundaries for high doping concentrations[19]. In addition, the lattice constant of IZO films was larger than that of the pure ZnO films[14, 25]. Due to the radius of In^{3+} ion (0.84 A°) not only was larger, but also was substituted for the Zn^{2+} ion (0.74 A°) when the indium was doped. This result can be attributed to indium ions substituting for the zinc atoms and suppressing the growth of ZnO[11]. This implies that the crystal quality of IZO films is improved by In doping. It is found that the FWHM of 5 at. % In doping reaches to minimum value (0.481) among various In doping, indicating the good crystallinity of IZO film could be enhanced at 5 at.% In doping.

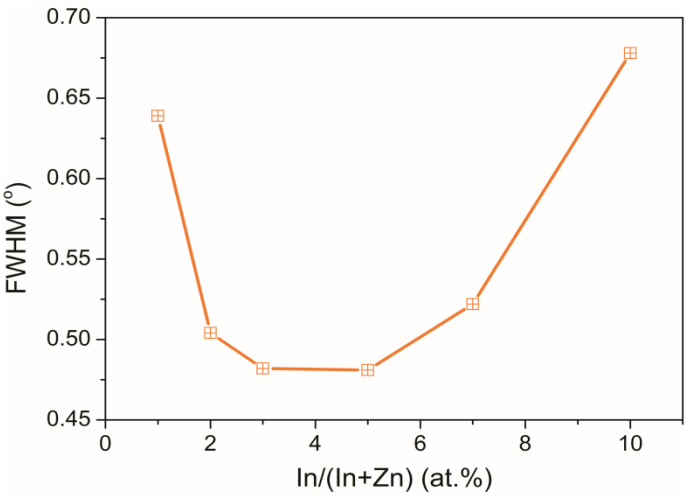


Figure-2
The full width half maximum (FWHM) value of IZO films with different In dopant concentration. FWHM value was calculated by the (002) peak of IZO films

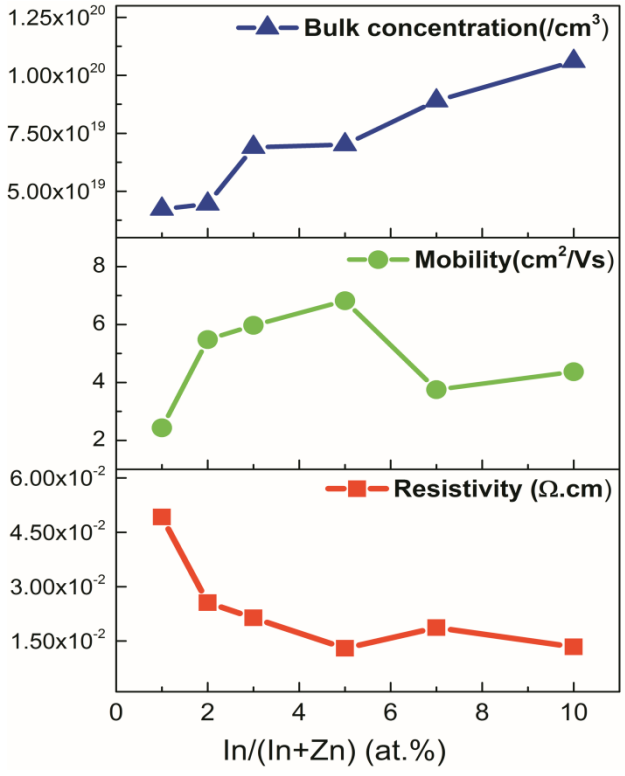


Figure-3
Electrical properties of IZO films for various dopant concentration of In/(In+Zn) at. %

The Hall measurements were performed at room temperature in Van Der Pauw configuration. The negative sign of Hall co-efficient confirmed n-type conductivity. The variation of electrical properties is schematically shown in Figure-3 as a function of In doping. The resistivity behavior clearly shows an important effect of the doping level. The electrical resistivity decreases as the dopant concentration in the solution increases. It can be seen that the resistivity of IZO film is gradually decreased with an increase in In doping to reach 1.3 10^{-2} Ω cm at 5 at. % In doping.

The resistivity decreases initially upon doping due to indium dopant acts as additional charge carrier and the mobility increases[12]. However, the resistivity increases slightly again with higher indium content (>5at.%) that can be attributed to a decrease in of mobility with high Indium doping concentration. The lowest resistivity of 1.30 x 10^{-2} Ω. cm is achieved at 5 at. % doped film and corresponding carrier concentration and mobility are about 7.015 x 10^{19} cm^{-3} and 6.82 $cm^2.V^{-1}s^{-1}$, respectively.

The optical transmittance spectra with wavelengths from 300 to 1500 nm of the doped ZnO thin films are presented in Figure-4. The optical transmittance spectra for all IZO films show a very good transmittance, between 85 and 90%, within the visible wavelength region. An increase in In dopant concentration, leads to a slight decrease in optical transmittance, but still maintain above 85% transmittance.

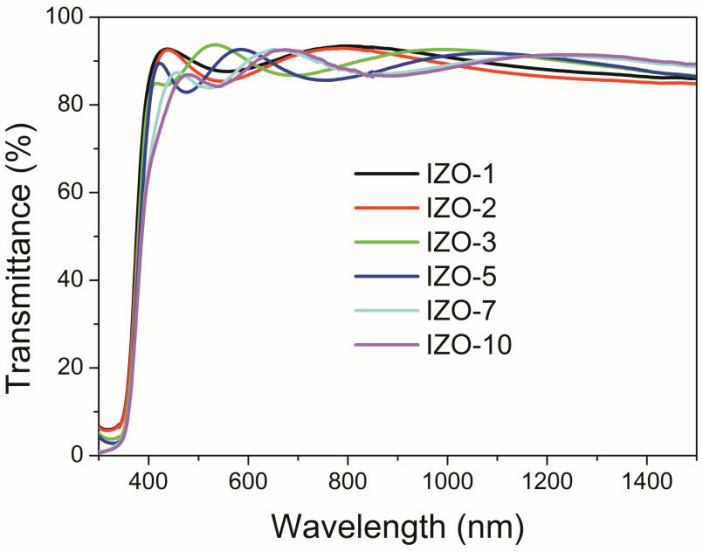


Figure-4
Optical properties of IZO films for various dopant concentration of In/(In+Zn) at.%

Conclusion

In-doped ZnO (IZO) films were prepared successfully by a sol-gel method using spin coating technique in this work. It is confirmed that the amount of 5 at. % Indium doping concentration is an optimum at which the lowest electrical resistivity can be achieved in this work. Furthermore, the pre-heating time on hot plate was carried out for short time (3-5 minutes) compare with previous work (10 min) to vapor the solvent, remove organic residuals, followed by decomposition and oxidation of the precursor to form doped ZnO. The optimized condition for spin coating of IZO films at 5 at. % In doping which deposited at 430 °C exhibited lowest resistivity (5.58 x 10^{-3} Ω.cm), high bulk concentration (1.06 x10^{20} $cm^2.V^{-1}s^{-1}$) and mobility (10.5 cm^{-3}) with films thickness about 258 nm. Additionally, the optical transmittance spectra for all IZO films show a very good transmittance, between 80 and 90%, within the visible wavelength region. These result indicate that, IZO films were synthesized by low cost way via sol-gel method can be considered as the promising candidate for TCO in thin film solar cell applications.

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