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Morphological, optical and structural studies of deposited ZnO films by silar method for solar energy applications

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ABSTRACT

The deposited ZnO films were grown on glass substrates using the Successive Ionic Layer Adsorption and Reaction. The morphology of the deposited ZnO is that of flower-like bud.The optical properties were characterized using UV/VIS spectroscopy, the optical band gap decreases with increasing reaction time, and these films have band gap values of 3.19eV, 3.22eV, 3.24eV and 3.25eV. The crystal structure of the films were also characterized using the X-Ray Diffraction spectroscopy, Prominent among them are the peaks at 2θ values of around 32.5^0, 35.9^0 and 38.5^0 corresponding to the diffraction lines produced by (100), (002) and (103) planes respectively.

INTRODUCTION

Zinc oxide is an inorganic compound and has the molecular formular ZnO. It appears as a whitish powder in nature, nearly insoluble in water. The powder has being widely used as an additive in the manufacturing of numerous materials such as; plastics, ceramics, glass, cement, rubber (e.g., car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, etc. ZnO is present in the Earth's crust as a mineral known as zincite. However, most ZnO used commercially is produced synthetically[1].

Zinc oxide as a compound is often called II–VI semiconductor because zinc and oxygen belong to the second and sixth groups of the periodic table, respectively. It has numerous favorable properties such as; strong room temperature luminescence, good transparency, wide band gap, high electron mobility, etc. These properties have already been used in emerging applications as transparent electrodes in liquid crystal displays and in energy-saving or heat-protecting windows, photovoltaic and electronic applications of ZnO as thin-film transistor and light-emitter[1].

The semiconductor is an important material due to its direct energy gap (3.4 eV) and large excitation binding energy (60 MeV) at room temperature which have made it to have a variety of uses in applications such as high transmittance conductive oxide coatings for solar cells[2], UV photodetector[3], laser diode[4], gas sensor[5], bulk acoustic wave resonator[6], light emitting diode[7], etc.

Full Paper

Several methods have already been used in the deposition of ZnO thin films, including molecular beam epitaxy (MBE)[8], sol-gel[9], spray pyrolysis[10], cathodic electrodeposition[11], sputtering[12], pulsed laser deposition (PLD)[13], and other solution methods. Many of these techniques are expensive and require high vacuum and controlled formation condition[14]. Very limited works have been reported on the preparation of ZnO using chemical bath deposition technique[14].

Solar energy conversion has the potential to satisfy the electricity and even the total energy consumption of the world. Indeed, one hour of solar irradiation on earth is equivalent to the total world energy consumption in one year (about 130 petawatt hour). Photovoltaic (PV) or the direct conversion of sunlight into electricity is a promising technology which can be easily installed without affecting neither the landscape nor the natural environment if directly integrated into building. Solar energy conversion is a highly attractive process for clean and renewable power for the future. Excitonic solar cells (SCs), including organic and dye-sensitized solar cells (DSSC), appear to have more significant value as a low cost alternative to conventional inorganic photovoltaic (PV) devices. The synthesis and application of nanostructures in solar cells have attracted much attention. Metal oxide nanowire (NW) arrays with large surface area and short diffusion length for minority carriers represent a new class of photoelectrode materials that hold great promise for photoelectrochemical (PEC) hydrogen generation applications. Up to now, various metal oxide nanostructures such as TiO_2, ZnO, Fe_2O_3, ZrO_2, Nb_2O_5, Al_2O_3, and CeO_2 have been successfully employed as photoelectrodes in Solar cells[15]. Among the above-mentioned metal oxide nanostructures, the study of ZnO is of particular interest due to the fact that it is one of the best candidates as photoelectrode used in Solar cells[15].

EXPERIMENTAL DETAILS

ZnO thin films were prepared by Successive Ionic Layer Adsorption and Reaction (SILAR) method, based on alternate immersion of substrate in Zn^{2+} source and H_2O_2 solutions, both kept at room temperature (300K). The Zn^{2+} source is a solution of zinc nitrate which was made alkaline by the addition of aqueous ammonia solution. The H_2O_2 solution was formed by addition of distilled water to hydrogen peroxide at the volume ratio of 10:2 respectively. The cleaned-dried glass substrate was immersed in the alkaline zinc nitrate solution so as to get zinc complex adsorbed on the substrate. After immersion of the substrate in H_2O_2 solution, the reaction occurred on the glass surface to form ZnO. The process is repeated for 50 oscillations in other to increase the overall film thickness of ZnO. The dipping period of substrate in zinc bath is known as "Adsorption time" and that of the solution of H_2O_2 is called "reaction time". For ZnO to have different level of properties, the reaction timing was varied from 30s to 60s with an interval of 10s, the adsorption time was kept constant i.e. 30s. Substrates were rinsed in distilled water, dried in air and kept in air tight container after annealing at a temperature of 623K to remove the hydrogen phase[16].

Process in the formation of zno film

The mechanism of ZnO film formation by the SILAR method can be enlightened as follows: The first precursor, an alkaline $Zn(NO_3)_2$ of pH ~12.0 adjusted by additional ammonia, give complex ions that can be as follows[16]:

$$Zn(NO_3)_2 + 2NH_4OH \rightarrow Zn(OH)_2 + 2N_4NO_3$$

$$Zn(OH)_2 + NH_4OH \rightarrow (NH_4)ZnO_2^- + H_2O + H^+$$

When the glass substrate was immersed in the solution, the zinc complex ions get adsorbed on the substrate due to attractive forces between ions in the solution and that on the surface of the substrate. These forces may be cohesive or Van-der Waals or chemical attractive[17,18]. The glass substrate is then immersed in H_2O_2 solution to convert the zinc complex into zinc oxide by the reaction which can be represented as[17,18]

$$(NH_4)ZnO_2^- + H^+ ZnO + NH_4OH.$$

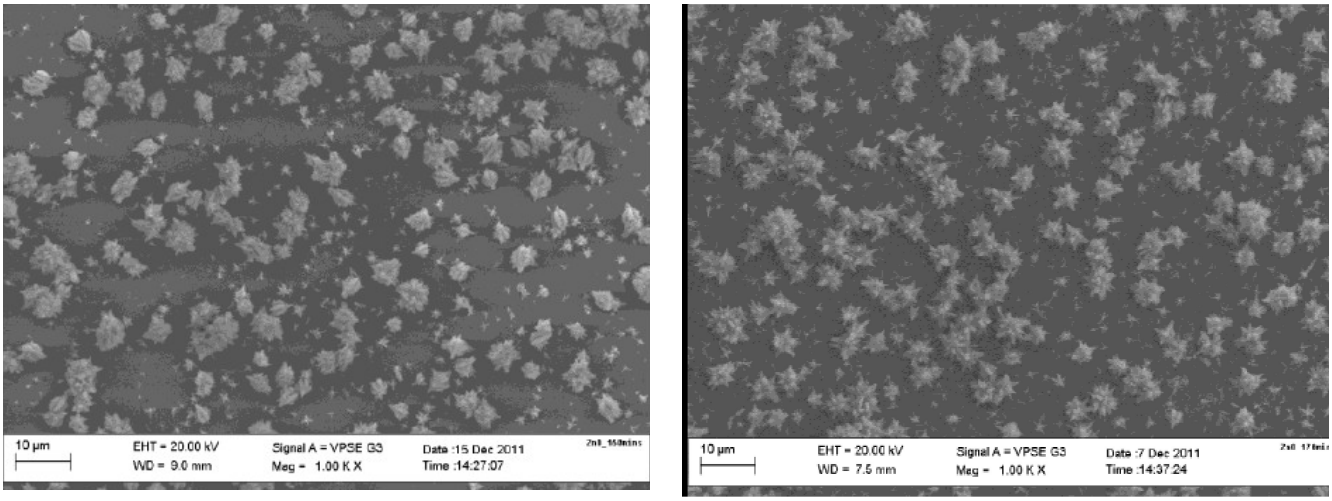
RESULTS AND DISCUSSION

Morphological studies

Figure 1 shows the SEM images of the films deposited at 40s and 50s as in (a) and (b) respectively, the morphology of the deposited ZnO films is flower-like, the flower becomes more developed with petals as the reaction time increases.

Energy dispersive spectroscopy analysis

Energy dispersive X-ray spectroscopy (EDS or



(a) **(b)**

Figure 1 : SEM images of the SILAR deposit at reaction timing of (a) 40s and (b) 50s.

EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. The EDS result in Figure 2 is for the sample with the deposition time of 150 min. The EDS of the ZnO sample was done by the SEM (JEOL-JSM 5800) machine. The EDS results reveal that the required phase has both Zinc (Zn) and Oxygen (O) present in the sample. Again the graph shows the presence of Mg, Si and Ca, probably from the glass substrate used for the deposition of ZnO thin films.

Optical properties

Figure 3a shows the transmittance of the deposited ZnO films for different reaction time, its shows that the films have low tranmsmittance at reaction timing between 40s to 60s and a average transmittance for the reaction timing of 30s, and also observed is the increase in the transmittance as the wavelenght increase from 200nm (UV region) to near infra red(1100nm), ie higher transmittance at Visible and near infra red than ultravoilet region.

Figure 3b shows the energy band gap of the deposited ZnO films for different reaction time. From the theory of optical absorption, the relation between the absorption coefficient (α) and photon energy (hυ) for direct allowed transition is

$$\alpha h\upsilon = (h\upsilon - Eg)1/2 \quad (1)$$

This equation (1) gives the band gap (Eg). When straight portion of (αhυ) is extrapolated to the point α = 0, the intercept in the x-axis gives the band gap (Eg). From the Figure 3b the band gap of ZnO films was found to be 3.19eV, 3.22eV, 3.24 eV and 3.25eV for the reaction timing of 60s, 50s, 40s and 30s respec-

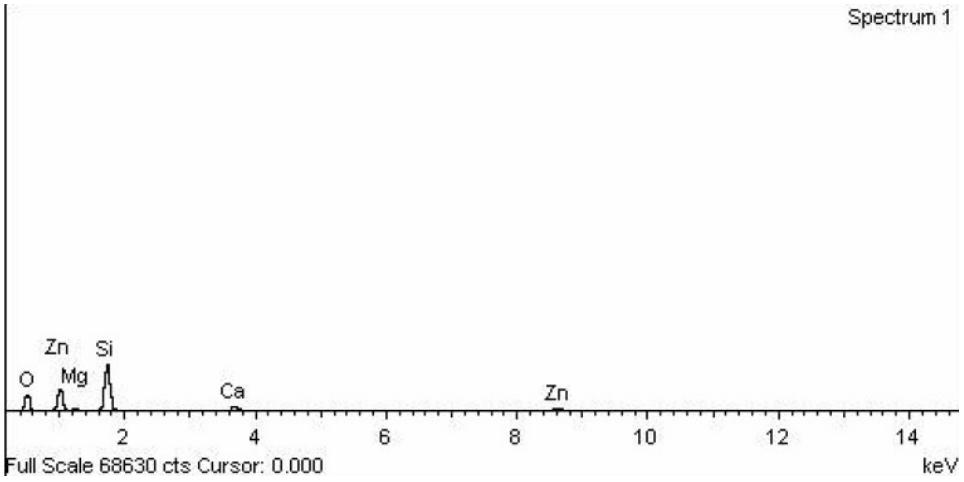


Figure 2 : Energy Dispersive Spectroscopy EDS for reaction timing of 50s.

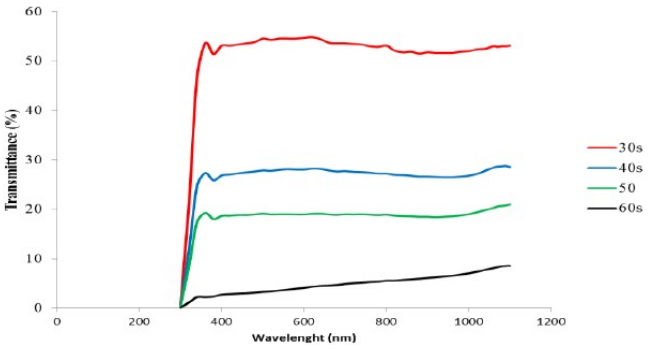


Figure 3a : transmittance of deposited film for different reaction time.

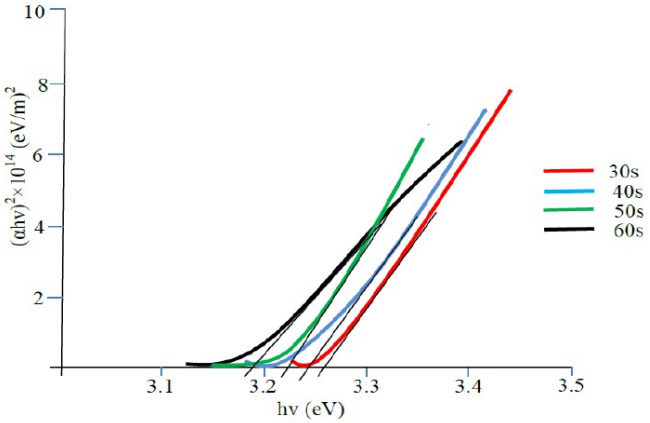


Figure 3b : plot of $(\alpha hv)^2$ versus hv

tively, these all lie in the range of ZnO standard band gap. The properties of high band gap values exhibited by these films together with higher transmittance in the visible region suggest that these films could be employed as window layer in solar cell architecture which agrees as reported in literature[19].

The band gap of ZnO is found to increase with a decrease in film thickness; the theory behind this is called quantum size effect. In thin films the particle size of crystallites is of the order of film thickness and proportional to thickness of films[20]. The band gap decreased to 3.19eV as the reaction time increased to 60s, which is common phenomenon in chemical deposition[21].

Structural studies

The crystal structure and orientation of the ZnO thin film were investigated by X-ray diffraction (XRD). The X-ray diffraction spectrum for the crystalline ZnO thin film is shown in Figure 4. The diffraction peaks of each sample were quite consistent with bulk ZnO, which could be indexed as the hexagonal wurtzite structure ZnO and diffraction data were in agreement with JCPDS (36-1451) of ZnO. The sharp diffraction peaks indicated the good crystalinity of the prepared crystals and lack of any other peaks than ZnO. The XRD pattern displayed in Figure 4 show several peaks. Prominent among them are the peaks at 2θ values of around 32.5^0, 35.9^0 and 38.5^0 corresponding to the diffraction lines produced by (100), (002) and (103) planes respectively. A close examination of Figure 4 shows that the intensity of the peaks increased with increase in deposition time. This means that better crystallization of ZnO film takes place at higher reaction time.

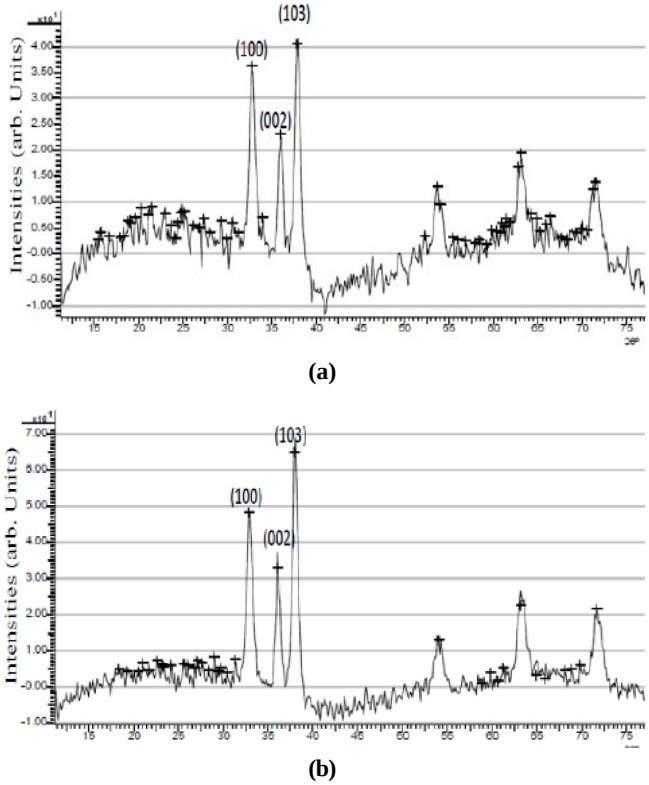


Figure 4 : The XRD structure of deposited ZnO films at

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