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Optical Properties and Raman Scattering Investigation of Ag Doped ZnO Thin Film Prepared by Two-step Solution-based Deposition Method

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Abstract. Mist-atomization deposition method was applied in order to grow ZnO nanoparticles on Au-seeded glass substrates acting as seeded template. Ag doped ZnO thin films were deposited on ZnO seeded templates by solution-immersion method. The influence of Ag doping content on the optical and Raman scattering properties of ZnO films were systematically investigated by UV-Vis transmittance measurement measured by ultra-violet visible spectroscopy (UV-Vis) and Raman scattering spectrum measured by Raman spectroscopy under room temperature. From UV-Vis transmittance measurement, the incorporation of Ag dopant to the ZnO makes the transmittance wavelength shifted to the shorter wavelength as compared to the pure ZnO. From Raman spectra, 4 cm^{-1} downshift is observed in Ag-doped thin films as compared to pure ZnO thin films. This Raman peak shift shows that a tensile stress existed in the Ag-doped ZnO film.

Introduction

ZnO is a II–VI semiconductor compound with wide direct band-gap of 3.37 eV and large excitation binding energy of 60 meV at room temperature. In recent years, ZnO has been under extensive research because of its broad applications. ZnO also attracted many studies because of their capability and suitability for doping. Doped ZnO shows high electrical conductivity and improved optical properties by doping with suitable elements. Both stoichiometry and dopant impurities affect the electrical and optical characteristics of ZnO which make it either a near insulator or a semi-metal [1]. Usually ZnO is doped by Cu [2], Al [1], Sb [3], etc. Different technologies such as electron beam evaporation [1, 4], sol-gel spin coating [5], hydrothermal [6], ultrasonic spray pyrolysis [7, 8], thermal evaporation [9], RF magnetron sputtering [10], etc. have been reported to produce thin films of Ag doped ZnO with adequate performance for applications.

In order to optimize the optical and electrical properties, these techniques usually coupled with annealing of sample, during or after deposition process. Annealing procedures increase the optical transmittance value of the sample. The defects of the crystalline structures owned by ZnO i.e. O vacancies and Zn interstitial impurities can also be reduced by introducing this post-heat technique to the samples [4].

In this paper, we focus on the synthesis of un-doped and Ag-doped ZnO from solution-based method. We concentrate on the two-step deposition method; mist-atomization and solution immersion. The thin films then went a post-thermal treatment at 350, 400, 450 and 500 ^{o}C. The annealed samples were then compared to un-annealed thin films. The optical properties and Raman spectroscopic of as-prepared samples are studied.

Experimental

Materials. The materials used in this work is zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) Riedel-de Haën brand and stabilizer, hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) of same brand, Riedel-de Haën with 99-100.5 % pure analytical grade. Silver nitrate ($Ag(NO_3).6H_2O$) is used as Ag source. Gold (Au) target is used as the seeded catalyst of the glass substrate.

Synthesis. In this paper, the optical properties and Raman spectroscopic of un-doped ZnO and 1 at. % Ag-doped ZnO were investigated symmetrically. Six nanometer (6 nm) thick gold (Au) was coated on the glass substrates. From previous study, 6 nm found to be the most optimized thickness in synthesizing crystalline ZnO nanostructures [11]. Pure ZnO and Ag-doped ZnO were derived from an aqueous precursor solution prepared by combining $Zn(NO_3)_2.6H_2O$ and HMTA with deionized water only for pure ZnO, meanwhile for Ag-doped ZnO, the starting materials were add up together with deionized water containing the appropriate amount of silver nitrate. The details of the experimental preparation are as follows. For the preparation of Zn^{2+} solution, $Zn(NO_3)_2.6H_2O$ was dissolved in deionized water and stirred well to make sure it is homogenous. Then, HMTA solution is added to the Zn^{2+} solution. The ratio between $Zn(NO_3)_2.6H_2O$ to HMTA is 1:1. The mixture was then stirred and heated on hot-plate stirrer at 60 ^oC. After one hour of heating, the solution then aged for another 24 hours.

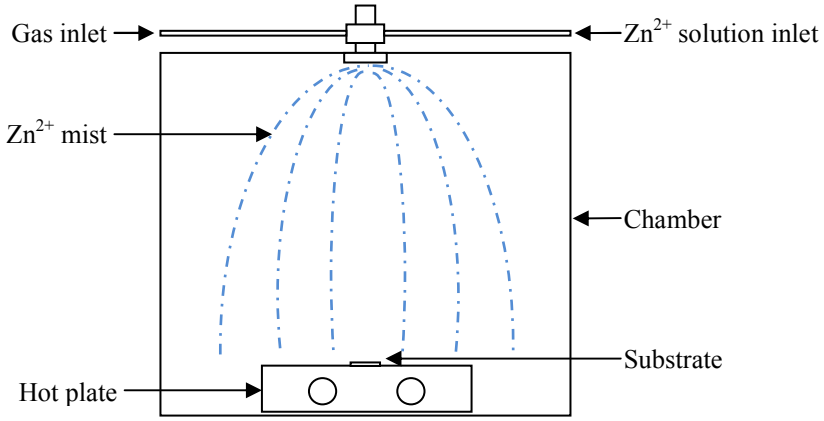

Fig. 1: Mist-atomizer chamber

Next, the solution is ready to be used for the first-deposition method; mist-atomization. The Au-seeded glass substrates were placed on hot plate placed in the mist-atomizer chamber. The substrates were preheated at 250 ^oC for 10 minutes. Then, the ZnO solution was sprayed onto the glass substrates and left for 4 hours to make sure all the ZnO mists settled onto the substrates. The substrates then annealed at 450 ^oC for 1 hour to improve adhesion and remove possible impurities.

After that, the substrates undergo second deposition method; solution-immersion. The solution preparation for this method is the same as prepared for the first deposition method. The difference is Ag dopant is introduced to the mixture solution of Zn^{2+} and HMTA solution. For comparative study, no Ag dopant added for the un-doped ZnO solution. The substrates were placed in boiling tubes and un-doped and Ag-doped ZnO solution was poured into each boiling tubes. The boiling tubes needed to be sealed tightly for the formation of good crystalline ZnO nanostructures. Each sample was immersed in 90 ^oC water bath for 4 hours.

The substrates then rinsed to remove any organic salts and prevent the contamination of the thin film. The glass substrates were annealed at different annealing temperatures of 350, 400, 450 and 500 ^oC. The samples were then compared to an un-annealed substrate.

Characterization. UV–Vis spectroscopy was performed using a Varian Cary 5000 UV–Vis spectrophotometer over the wavelength range between 300 and 900 nm with a data interval of 1 nm. Raman spectra of the synthesized film were measured using Horiba Jobin Yvon-79 DU420A-OE-325 Raman spectrophotometer with a He-Cd excitation laser source operating at 325 nm.

Results and discussions

Optical properties. The uv-vis transmission spectrum of pure ZnO thin film annealed at different temperatures is shown in Fig. 1.

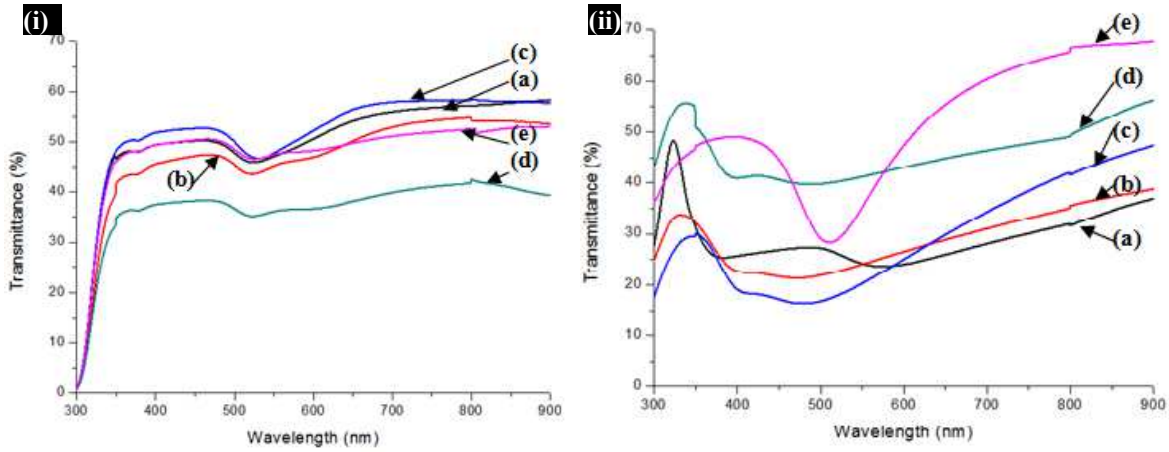

Fig. 2: UV-vis transmittance spectra of (i) pure ZnO annealed at (a) 0, (b) 350, (c) 400, (d) 450 and (e) 500 °C and (ii) Ag-doped ZnO annealed at (a) 0, (b) 350, (c) 400, (d) 450 and (e) 500 °C

From Fig. 2(i), it can be seen that the transmission values of the film are low at short wavelengths; meanwhile at long wavelengths, the transmissions values are high. At short wavelengths, which is at the UV region, the pure ZnO exhibits good absorbance properties. The film acted as a dense material because of its high absorbing properties at UV region and as a transparent material at visible region. This condition is associated to the energy of the incident light [7]. When energies of photons are smaller than the band gap of ZnO film, they are insufficient for excitation of electrons from valence band to conduction band. Some of the photons have smaller energy compared to the band gap energy of ZnO. The deficient of energy make them did not able to excite from valence band to the conduction band. These low energies remain at that certain level until some outer stimuli help to make some changes.

The natural defect of ZnO i.e. oxygen vacancies and interstitial Zn atoms, acted as donor impurities. These impurities may be ionized by these low energies. These impurities caused the film to have small absorbance and high transmittance values at visible region. From Fig. 2(i), it can be observed that at about 521–530 nm wavelength range, the transmittance values slightly increased as the wavelength increased. This range refers to the fundamental absorption region. Pure ZnO with 400 °C annealing temperature have the highest transmittance value amongst all samples. Meanwhile, ZnO thin film annealed at 450 °C have the lowest transmittance value.

From Fig. 2(ii), it shows that the Ag-doped sample annealed at 400 °C has the lowest transmittance value, meanwhile the sample annealed at 450 °C has the highest transmittance value. The incorporation of Ag dopant to the ZnO makes the transmittance wavelength shifted to the shorter wavelength as compared to the pure ZnO as in Fig. 2(i). From Fig. 2(ii), it can be observed that at about 360–400 nm wavelength range, the transmittance values slightly decreased as the wavelength increased. Meanwhile, the transmittance value of Ag-doped ZnO thin film annealed at 500 °C at 510 nm wavelength increased as the wavelength increased.

Raman studies. From the group theory, one will theoretically expect $A_1+2B_1+E_1+2E_2$, all will have two modes at the center of Brillouin zone [10]. The A_1, E_1 and $2E_2$ modes are Raman active. Only the two B1 modes are forbidden for Raman excitations. According to the selection rules we expect to observe the two E_2 modes and the A_1 (LO) mode in unpolarized Raman spectra taken in backscattering geometry. The frequencies of the fundamental optical modes in pure ZnO are E_2 (low) is 101 cm^{-1}, E_2 (high) is 437 cm^{-1}, A_1 (TO) is 380 cm^{-1}, A_1 (LO) is 574 cm^{-1}, E_1 (TO) is 407 cm^{-1}, and E_1 (LO) is 583 cm^{-1} [12].

Fig. 3(i) shows the Raman spectra of the undoped ZnO films with different annealing temperatures which are 0, 350, 400, 450 and 500 °C. From Fig. 3(i), it is clear that the A_1 (LO) mode and the E_2 (high) mode of ZnO appear at about 577.9 cm^{-1} and 436.4 cm^{-1} for all the samples, respectively. Meanwhile, Fig. 3(ii) shows the Raman spectra of the 1 at. % Ag-doped ZnO with different annealing temperatures of 0, 350, 400, 450 and 500 °C. As shown in Fig. 3(ii), the A_1 (TO) and A_1 (LO) modes were observed at 347.9 and 560 cm^{-1}, respectively The E_2 (high) mode appeared at about 433 cm^{-1}.

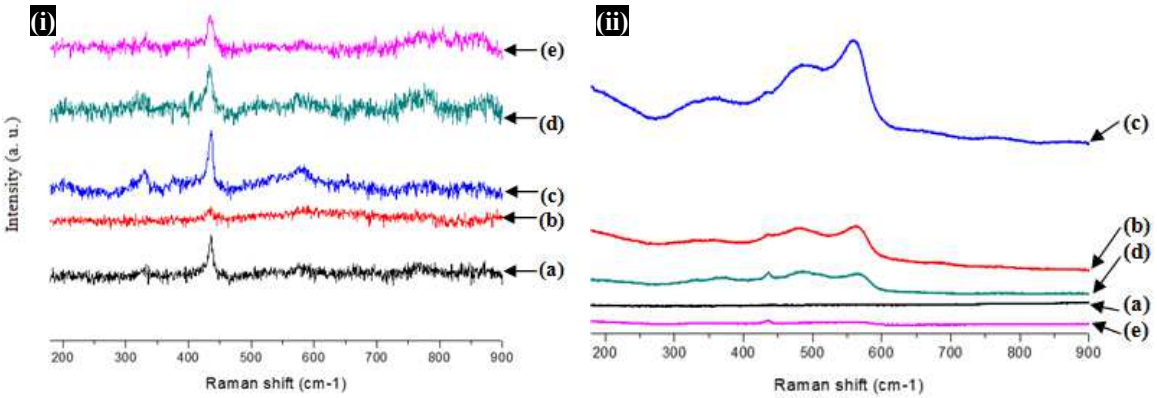

Fig. 3: Raman spectra of (i) pure ZnO annealed at (a) 0, (b) 350, (c) 400, (d) 450 and (e) 500 °C and (ii) Ag-doped ZnO annealed at (a) 0, (b) 350, (c) 400, (d) 450 and (e) 500 °C

According to literature, the shift of the E_2 mode can give the information on stress. The phonon frequency shifts related to the individual single crystal value that can be used to estimate remaining stress in the thin film [13]. Previous investigations have shown the relation between stress and E_2 (high) mode: under a compressive stress the E_2 (high) up shifts, where as a tensile stress will lead to its downshift [10, 12]. Compared to the E_2 (high) mode of the standard ZnO which is 437 cm^{-1}, a downshift of 4 cm^{-1} was observed for the E_2 (high) mode of the Ag doped ZnO film. This Raman peak shift shows that a tensile stress existed in the Ag doped ZnO film. The A_1 (LO) mode with very high intensity was also observed in the Raman spectra of the Ag doped ZnO samples. The A_1 (LO) mode is known to be related to the defects such as oxygen vacancy and Zn interstitial in ZnO.

The high-frequency E_2 mode at 436.4 and 433 cm^{-1} is associated with vibration of the oxygen atoms [13]. Generally, the phonons of E_2 symmetry have two frequencies E_2 (high) and E_2 (low). E_2 (high) is related with the oxygen atom and E_2 (low) related with the Zn sub lattice [14, 15]. The incorporation of impurities, in this study is Ag dopant in the host lattice can introduce additional local vibrational modes (LVMs) in the Raman spectra. A possible physical mechanism for explaining LVMs is that defects induced by impurities break the translational symmetry of the crystal, thus relaxing the conservation of the wave vector and leading to the scattering of phonons with the wave vectors far from the Brillouin zone center [12]. Compared with undoped ZnO films, the LVM at about 485 cm^{-1} can be clearly observed in the patterns of ZnO:Ag films, such as shown in Fig. 3(ii).

Conclusion

As-prepared ZnO and Ag-doped ZnO have been deposited by two-step deposition methods; mist-atomizer and solution-immersion. The solution processing methods offer an economical route to the preparation of pure and Ag-doped ZnO thin films. Apart from that, the amount of dopant can be controlled easily by this method. The Raman investigation shows that Ag-doped ZnO have a downshift of 4 cm^{-1} which is observed at E_2 (high) mode of the Ag doped ZnO film. This Raman peak shift shows that a tensile stress existed in the Ag-doped ZnO film.

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