Determination of the Morphological, Optical and Crystalline Properties of ZnO Thin Film Grown by Pulsed Laser Deposition (PLD)

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***Abstract*—** We have grown ZnO thin films on SLG substrate at room temperature in two different thicknesses, using Pulsed Laser Deposition system. The thicknesses of ZnO (ZnO1, ZnO2 and ZnO3) thin films were measured to be 41 nm, 70 nm and 197 nm, produced applying 18000, 36000 and 54000 laser pulses, respectively. Although ZnO thin films were grown at room conditions, their structures were formed as polycrystalline. If the laser pulse number is increased, the thickness of the thin films is enhanced and it was observed that the crystal structure of semiconductor thin films were developed. Furthermore, it was observed that as the size of the particles forming the thin films are increased, their energy band gaps are decreased. As a result, ZnO2 thin film in 197 nm thickness has been found suitable for use in piezoelectric application areas, thin film solar cell, gas sensor, flat panel displays, thin film transistor and light-emitting devices**.**

***Keywords*—** ZnO thin film, laser pulse number, polycrystalline, PLD.

I. INTRODUCTION

Zinc Oxide (ZnO) is an n-type semiconductor has some spectacular properties such as direct wide band gap (3.37 eV), low electrical resistivity, large exciton binding energy of 60 meV, high transmittance (in visible region), low cost, non-toxicity [1, 2].

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ZnO material is a perfect candidate for use in application areas such as flat panel displays, thin film solar cells, thin film transistor, piezoelectric devices, gas sensors and light-emitting devices. Many coating processes, such as molecular beam epitaxy, sol-gel, spray pyrolysis, magnetron sputtering and Pulsed Laser Deposition (PLD) can be used to grow ZnO thin films [3]. PLD technique has a simple setup and very prominent advantageous for the production of ZnO thin films with its adjustable parameters. By controlling parameters such as background oxygen gas pressure, laser energy, laser pulse number and target-substrate distance as well as substrate temperature, it can be produced that ZnO thin films with ideal crystalline, morphological and optical properties. Especially, the ability to produce polycrystalline and epitaxial thin films at room temperature by PLD system are very important for device performance [4, 5].

In this study, ZnO thin films were deposited on soda lime glass (SLG) at room temperature by 1800, 36000 and 54000 laser pulses. The morphological, optical and crystalline characteristics of ZnO thin films were investigated using Atomic Force Microscopy (AFM), UV-vis spectra and X-Ray Diffraction (XRD) analysis techniques. Thin film thicknesses were measured by a profilometer device. The characteristic changes in ZnO thin film depending on increase the laser pulse numbers have been discussed in detail in this paper.

II. EXPERIMENTAL

ZnO thin films were deposited on p-Si wafers and soda lime glass (SLG) substrates at room temperature by PLD system, using pulses laser beam (at 1064 nm wavelength, 10 Hz repetition rate, 5 ns pulse width. p-Si wafers have a 500 μm thickness, 1 Ω.cm resistance and (111) orientation. Before run the experiment, the following procedure was applied for cleaning the Si wafer and SLG substrates: Si wafers and SLGs were washed with foamy soap, put into and kept in the mixed solution (HCl: H_2O_5: distilled water (1:1:10)) for 10 minutes, put into and kept in distilled water for 5 minutes and then washed in acetone and isopropyl alcohol for 10 minutes in an ultrasonic bath. Si wafers and SLGs were then dried with nitrogen gas jet.

ZnO sputtering target (%99.99 purity from Kurt Lesker) was ablated by pulsed laser beam and the thin films were grown firstly on SLG substrate and then onto p-Si wafers at

room temperature as a function of the number of laser pulses applied to be 18000, 36000 and 54000 pulses. Before all experiments, the vacuum chamber was pumped down to ~8×10^{-6} mbar background pressure and laser fluency was set to 2.2 J/cm^2. The distance between target and substrate was set to be 5 cm and oxygen gas was allowed in up to that the background gas pressure was reached to 1.3×10^{-1} mbar.

Fig. 1 Plasma image formed by ablated ZnO particles

III. Discussion

A. XRD Analyses

Thin films named as ZnO1, ZnO2 and ZnO3 were grown by applying 18000, 36000 and 54000 laser pulses in thicknesses of 41 nm, 70 nm and 197 nm, respectively. While the number of laser pulses increases, the crystal structure of ZnO thin films improves, according to XRD spectra given in Fig 2, as well as the thicknesses of thin films increases since the deposition rate increases [6]. Thus, ablated particles coming on the substrate and occupy a suitable vacancy in the crystal structure. The compatible crystal directions are formed, and the crystal structure is improved. The important point here is that the formation of polycrystalline ZnO thin films on the substrate is taken place at room temperature. Since the ablated ZnO particles have high kinetic energies and therefore, the particles quickly diffuse towards each other (similar to high substrate or annealing temperature) when they come over the substrate, the particles combine with each other to form a uniform alignment and crystal structure [4, 5, 7]. All ZnO thin films have polycrystalline structure and crystallized at directions of (100), (002), (101) and (110) *hkl* planes appeared at 2Θ=32.1^o, 34.7^o, 36.5^o and 56.6^o, respectively. Mother diffraction peaks of ZnO thin films are in (002) orientation [8]. It has been examined and carried out that, as ZnO thin film thickness increases, their crystal structures develops and the intensity of the mother peak rises.

The main crystalline sizes of the prepared thin films have been calculated by Scherrer equation:

$$D = 0.94\lambda/\beta cos\theta \quad (1)$$

where crystalline size is shown as D, the full-width at half-maximum of diffraction peak exhibits as β, the wavelength ofof X-ray is indicated as λ and θ the Bragg diffraction angle is demonstrated as θ [4]. The main crystalline sizes have been calculated using Scherrer equation for ZnO1, ZnO2 and ZnO3 thin films to be 6.58 nm, 13.31 nm and 27.4 nm, respectively. While the thicknesses of ZnO thin films increases, their crystalline size increases. Thus, the number of defects in the structure decreases and the crystallite of ZnO thin film improves as stated above [6].

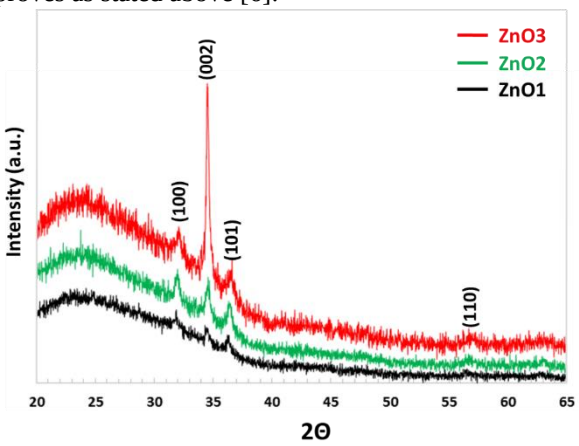

Fig. 2 XRD spectra of ZnO1, ZnO2 and ZnO3 thin films

The dislocation density and microstrain of the thin film [9, 10] are determined by Equation (Eq.) 2 and Eq.3:

$$\delta = \frac{1}{D^2} \quad (2)$$

$$\varepsilon = \frac{\beta cos\theta}{4} \quad (3)$$

The dislocation density and microstrains of ZnO thin film, which identify defect and traps in the thin film. The dislocation density of ZnO1, ZnO2 and ZnO3 thin film have been founded to be 2.31 $\times10^{16}$ (lines/m^2), 5.64×10^{15} (lines/m^2) and 1.33×10^{15} (lines/m^2) while their microstrains have been obtained as 5.5×10^{-3}, 2.72×10^{-3} and 1.32×10^{-3}, respectively. As the thin film thickness increased, the decrease in the dislocation density and microstrain showed that traps and defects in the thin film decreased. According to the results obtained from the XRD results, the most ideal crystalline thin film to be used in different application areas was determined as ZnO3 thin film.

B. Morphologic Analysis

Fig 3. shows AFM images in 10 µm × 10 µm region of ZnO1, ZnO2 and ZnO3 thin films. Since the increase in the laser pulse number rises the amount of ablated and deposited materials, particles reaching the substrate were deposited on top of each other causing the grain size to be increased. ZnO1 thin film has the lowest grain size while ZnO3 has the largest grain size as expected from the increase in the number of laser pulses [11, 12]. ZnO2 thin film has a relatively inhomogeneous size distribution. Increase in the grain size as a function of the laser pulse number applied leads to some decrease in the number of grain boundaries and passivation of

defects and traps within these boundaries. This supports the development of the crystal structure [6]. Therefore, ZnO3 thin film has the most ideal morphology compared to other thin films. style.

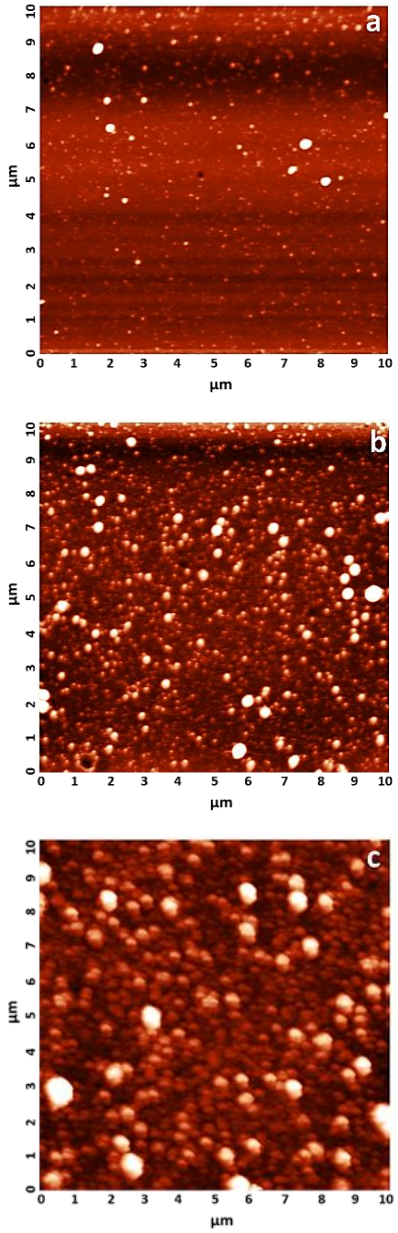

Fig. 3 AFM images (in 10 µm × 10 µm area) of ZnO1, ZnO2 and ZnO3 thin films

C. Optical Properties of ZnO thin films

According to the graph of the absorbance versus wavelength, as given in Fig 4a, as the thickness of the thin films increases, the grain sizes increase, so more photons are absorbed by ZnO thin films [13]. While the photon transmission in the visible region is performed by ZnO1 and ZnO2 thin films at the lowest thickness, the lowest photon transmission in this region was obtained with ZnO3 thin film at the highest thickness. ZnO3 thin film absorbs photons especially in the range of 400-600 nm, which can be attributed to large size grains.

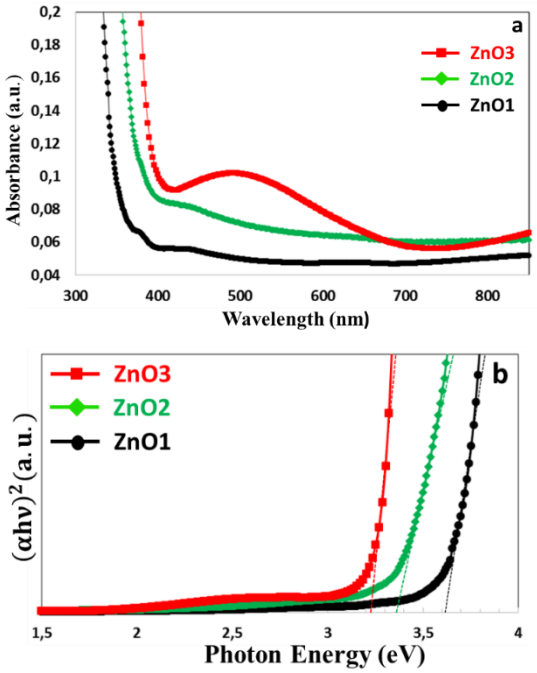

Fig. 4 Absorption spectra and **b)** Tauc Plots of ZnO1, ZnO2 and ZnO3 thin films

Energy band gap values of thin films have been calculated using Tauc equation given below:

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right)^{1/2} \tag{4}$$

where the energy of the photon is shown as hν$h\nu$, the constant of equation is exhibited as A, the energy band gap value of thin films is presented as E_g and it is definedby extrapolation of straight line of $(\alpha h\nu)^2$ $(\alpha h\nu)^2$ versus (hν) in Tauc ploting and presented in Fig 4b. E_g values of ZnO1, ZnO2 and ZnO3 thin films were calculated to be 3.61 eV [14], 3.37 eV [15] and 3.23 eV [16] relating to Tauc plot given in Fig 4b, respectively, and these are compatible with studies in literature. Grain size rises since the thin film thickness increases and thus, the absorption intensities of thin films become superior and the energy band gaps of ZnO thin film reduces [17]. All ZnO thin films with wide band gap include suitable optical properties for micro electrical devices.

IV. Conclusion

In this study, ZnO thin films in three different thicknesses were produced by applying 18000, 36000 and 54000 laser pulses and according to the number of laser pulses applied, thicknesses of thin films were measured to be 41 nm, 70 nm and 197 nm, respectively. All ZnO thin films were formed in polycrystalline structure on the substrate at room temperature. While the thicknesses of ZnO thin films are increased, the crystal structure of these thin films are improved, and then their crystalline sizes and particle size increased. In addition, ZnO thin films absorbs more photons and their band gap

decreases with increasing thickness. As a result, ZnO3 in 197 nm thickness was determined as the most ideal thin film for application areas such as flat panel displays, thin film solar cell, thin film transistor, piezoelectric devices, gas sensors and light-emitting devices.

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REFERENCES

1. Al-Hardan, N., et al., *A wide-band UV photodiode based on n-ZnO/p-Si heterojunctions.* Sensors and Actuators A: Physical, 2014. **207**: p. 61-66.
2. Sharma, S. and C. Periasamy, *A study on the electrical characteristic of n-ZnO/p-Si heterojunction diode prepared by vacuum coating technique.* Superlattices and Microstructures, 2014. **73**: p. 12-21.
3. Soylu, M. and O. Savas, *Electrical and optical properties of ZnO/Si heterojunctions as a function of the Mg dopant content.* Materials Science in Semiconductor Processing, 2015. **29**: p. 76-82.
4. Gezgin, S.Y. and H.Ş. Kılıç, *The electrical characteristics of ITO/CZTS/ZnO/Al and ITO/ZnO/CZTS/Al heterojunction diodes.* Optik, 2019. **182**: p. 356-371.
5. Gezgin, S.Y. and H.Ş. Kiliç, *Determination of electrical parameters of ITO/CZTS/CdS/Ag and ITO/CdS/CZTS/Ag heterojunction diodes in dark and illumination conditions.* Optical and Quantum Electronics, 2019. **51**(11): p. 360.
6. Gezgin, S.Y., A. Houimi, and H.Ş. Kılıç, *Production and photovoltaic characterisation of n-Si/p-CZTS heterojunction solar cells based on a CZTS ultrathin active layers.* Optik, 2019. **199**: p. 163370.
7. Chávez-Urbiola, I.R., et al., *Development and characterization of photodiode n-ZnO/p-Si by Radio Frecuency Sputtering, a sensor with low voltage operation and its response to visible and UV light.* Thin Solid Films, 2019. **669**: p. 364-370.
8. Shaban, M., M. Zayed, and H. Hamdy, *Nanostructured ZnO thin films for self-cleaning applications.* RSC advances, 2017. **7**(2): p. 617-631.
9. Kalita, P.K., B. Sarma, and H. Das, *Structural characterization of vacuum evaporated ZnSe thin films.* Bulletin of Materials Science, 2000. **23**(4): p. 313-317.
10. Prabahar, S. and M. Dhanam, *CdS thin films from two different chemical baths—structural and optical analysis.* Journal of Crystal growth, 2005. **285**(1-2): p. 41-48.
11. Đekić, M., et al., *Influence of deposition parameters on pulsed laser deposition of K0. 3MoO3 thin films.* Bulletin of the Chemists and Technologists of Bosnia and Herzegovina, 2017. **48**(1): p. 1.
12. Vakulov, Z., et al. *Size effects in LiNbO3 thin films fabricated by pulsed laser deposition*. in *Journal of Physics: Conference Series*. 2018. IOP Publishing.
13. !!! INVALID CITATION !!! [14, 15, 20].
14. Al-Asadi, A.S., et al., *Fabrication and characterization of ultraviolet photosensors from ZnO nanowires prepared using chemical bath deposition method.* Journal of Applied Physics, 2016. **119**(8): p. 084306.
15. Davis, K., et al., *Band gap engineered zinc oxide nanostructures via a sol–gel synthesis of solvent driven shape-controlled crystal growth.* RSC advances, 2019. **9**(26): p. 14638-14648.
16. Husna, J., et al., *Influence of annealing temperature on the properties of ZnO thin films grown by sputtering.* Energy Procedia, 2012. **25**: p. 55-61.
17. Dai, P., et al., *Band-gap tunable (Cu2Sn) x/3 Zn 1− x S nanoparticles for solar cells.* Chemical Communications, 2010. **46**(31): p. 5749-5751.

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