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Crystallization and surface Morphology following annealing using ZnO thin film

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Abstract - The glass substrates had ZnO thin films produced on them using a sol-gel dip coating process. All sorts of temperatures, from 350 to 550 degrees Celsius, were used to anneal the films. The impact of annealing temperature on the films' structural and morphological features was studied using X-ray diffraction (XRD) and atomic force microscopy (AFM). Different processing conditions are used during manufacturing, all of which might alter the final attributes of a device based on amorphous oxides. Although zinc oxide shows promise as a transparent amorphous oxide, its structure is sensitive to temperature changes. Here, we looked at the phenomenon of surface recrystallization in amorphous zinc oxide layers produced by pulsed laser deposition onto fused silica, sapphire, and Si substrates. Extremely out-of-equilibrium phase structures were found in the three-layer preparation. All the developed ZnO films display strongly (0001)-oriented patterns without in-plane rotation, as evidenced by in situ reflection high-energy electron diffraction (RHEED) and ex situ X-ray diffraction (XRD). As evidenced by atomic force microscopy (AFM) pictures, "ridge-like" and "particle-like" surface morphologies are found for the ZnO films formed in a molecular O2 environment with and without an initial deposition of Zn adatoms, respectively, before ZnO development with oxygen plasma. The ultimate surface shape and optical characteristics of the ZnO film are significantly affected by this artificially constructed interfacial layer.

Keywords - ZnO, Surface morphology, Zinc oxide, Thin films, Nanocrystalline

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INTRODUCTION

Cryogenic pulsed laser deposition (PLD) of ZnO thin films is the topic of this review. In order to undergo "real" recrystallization after annealing, amorphous materials are ideal since they provide unique circumstances for this process. The purpose of the study presented was to examine the recrystallization dynamics from amorphous to wurtzite structures as a function of annealing settings, as well as the characteristics of amorphous undoped ZnO films. Due to its high photocatalytic effectiveness and excellent stability, nanostructure ZnO has gained increasing attention as a promising semiconductor photocatalyst. High photocatalytic efficiencies of ZnO nanoparticles, powders, and colloids have been reported in many research. ZnO thin films, however, are favored for use in water purification because they prevent the catalyst from having to be separated once the degrading process is complete. ZnO thin film's photocatalytic characteristics have been studied in a number of published papers. Coatings based on zinc oxide are of great scientific and technological interest because of their many potential uses. Some examples include thermoelectric and gas sensor devices, transparent electrodes, selective surfaces, piezoelectric devices, and so on. ZnO's broad direct bandgap in the near-UV region and its ability to take on a variety of morphologies—nanorods, thin films, nanoflakes, nanowires, nanoplates, etc.—make it useful in a wide range of contexts. ZnO's shape, as well as its bandgap and conductivity, are said to be controlled by the synthesis technique used.

LITERATURE REVIEW

Ewelina Nowak **et.al (2021)** One of the broad-bandgap semiconductors, zinc oxide (ZnO) has potential uses in a wide variety of electrical, optical, piezoelectric, and scintillating devices. Here we take a look at ZnO microfilms made using the sol-gel technique on a sapphire substrate, analyzing their structure and luminescence. Several annealing temperatures were used on the films. The impact of the substrate on the film's structure was analyzed by using XRD and Raman spectroscopy to examine the structures. Film luminescence was studied by using three different techniques: fluorescence at ambient temperature, radioluminescence, and thermoluminescence.

T. Ivanova et.al (2020) Using a spin coating sol-gel method, nitrogen and gallium co-doped ZnO films have been effectively produced. Films of ZnO with various doping levels (N, Ga, and co-doped) are deposited on silicon and quartz. ZnO:N:Ga thin films are characterized by studying their structural, morphological, and optical characteristics as a function of thermal treatments (300-600 °C) and the two dopants, N and Ga. X-ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM), and UVeVISeNIR spectrophotometry have all been used to examine the doped ZnO films. The co-doped (N, Ga) ZnO films were found to form in the wurtzite structure free of impurity phases. Compared to undoped ZnO films, the optical transparency of ZnO:Ga and ZnO:N:Ga films is much higher, at over 80% in the spectral region of 400-800 nm. In ZnO, co-doping with gallium and nitrogen causes the surface morphologies to transform from wrinkle-like (undoped ZnO) to closed-packed grained.

W. Matysiak et.al (2018) In this research, zinc oxide thin films were made utilizing sol-gel and spin coating processes from Zn(COO)2 x 2H2O dissolved in ethanol and acetic acid with ZnO monocrystalline nanoparticles of 0 and 10% (wt.) relative to the final concentration of generated solutions. The impact of calcination procedure on ZnO thin films at 600°C were evaluated using atomic force microscope to analyze the shape of semiconductor coatings, infrared spectroscopy to verify the chemical structure of material. Besides, optical characteristics were assessed on the basis of absorbance in the function of wavelength spectra and the values of energy band gaps were analyzed. The topography examination of ZnO thin films indicated an increase in roughness with the increasing of zinc oxide nanoparticles in the thin film's material. In addition, the investigation of the optical characteristics of ZnO thin films demonstrated a reduction in absorption level in the region of near-ultraviolet wavelength for the produced layers after annealing. It was observed that ZnO thin films made by spin coating and calcination process are an appropriate material for photoanode in dye-sensitized solar cells, since zinc oxide layers give greater conductivity throughout the photovoltaic cell.

Iping Suhariadi et.al (2018) Using atomic force microscopy, we examine the surface morphology of ZnO thin films formed through the nitrogen assisted crystallization process at varying nitrogen flow rates. At first, the deposited ZnO thin film had a rough surface replete with spiky granules with a skewness and kurtosis of 0.48 and 4.80, respectively. The films' skewness and kurtosis values reduce dramatically with the addition of a little quantity of nitrogen, which is also correlated with a flatter topography. Roughening of the surface is most evident in the increased kurtosis value to 3.30 as a result of increasing the nitrogen flow rate to 16 sccm. These findings suggest that introducing a trace quantity of nitrogen during the deposition process improved the film quality by increasing the grain size and facilitating the mobility of adatoms on the surface. All of the films contain self-affine fractal geometry with total fractal values between 2.14 and above 3.00, as determined by a two-dimensional power spectral density study.

Bakri, A S et.al (2017) The sol-gel dip coating process is used to create thin layers of titanium dioxide (TiO2) on silicon substrates. The film's surface appearance, structure, and electrical characteristics were studied in relation to the annealing temperature. X-ray diffraction, field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), and a four-point probe were used to study the crystalline structure, surface morphology, and electrical characteristics. The findings demonstrate that when annealing temperature is raised, the strength of the (101) peak grows while the full-width at half-maximum narrows. Surface roughness and grain size both increase when thin films are deposited at high annealing temperatures. When the annealing temperature is changed from 300 to 900°C, the electrical characteristics of these films reveal that the resistivity changes from 1.40 x 105 to 7.19 x 102.cm, respectively. In comparison to other films, the resistivity of the TiO2 thin films annealed at 900 degrees Celsius was much reduced. Findings indicate that TiO2 thin films' surface morphology, structural, and electrical characteristics are all affected by the annealing temperature.

METHODOLOGY

The glass substrates had ZnO thin films produced on them using a sol-gel dip-coating technique. The raw material was zinc acetate dehydrate [Zn(CH_3COO)2•2H_2O], and the solvent and stabilizer were isopropanol and diethanolamine (DEA), respectively. Precursor solution Zn ion concentration was kept constant at 0.3 M by keeping the molar ratio of DEA to [Zn(CH_3COO)2•2H_2O] at a constant 1:1. After mixing, the solution was heated to 70 degrees Celsius and agitated for an hour to catalyze the hydrolysis process, yielding a clear and homogenous solution that could be used as a coating solution after it had cooled to room temperature. To get the best results from the dip coating procedure, it is customary practice to let the coating solution sit out for at least 24 hours.

Substrate was withdrawn from the coating solution at a steady rate of 15mm/min while at room temperature. Following coating, the film was preheated in a furnace at 160 °C for 20 minutes to totally eliminate any organic residuals and evaporate the solvent. To get nine layers of film, we repeated the coating and pre-heating procedure nine times.

After that, the ZnO films were annealed at temperatures of 350 C, 450 C, and 550 C.

By using X-ray diffraction (XRD) with Cu K radiation (= 0.15406nm), the films' structures were examined. In order to determine the surface morphology, an atomic force microscope was used (AFM).

Before being inserted into the MBE growth chamber at ultra-high vacuum, the MgO (111) substrates were ultrasonically cleaned in acetone and ethanol, then dried with nitrogen. All the substrates were heated to 490 degrees Celsius for 60 minutes in an oxygen plasma at a power of 250 watts and a partial pressure of 5 x 105 mbar. Different ZnO films were then produced from scratch using the settings described in Table 1 and Additional file 1. An essential step in altering the surface morphology is step (b), which involves growing the initial buffer layer (BLI) without plasma after step (a) heat treatment of the substrate.

RESULT AND DISCUSSION

Effect of annealing temperature on the structural properties of the films

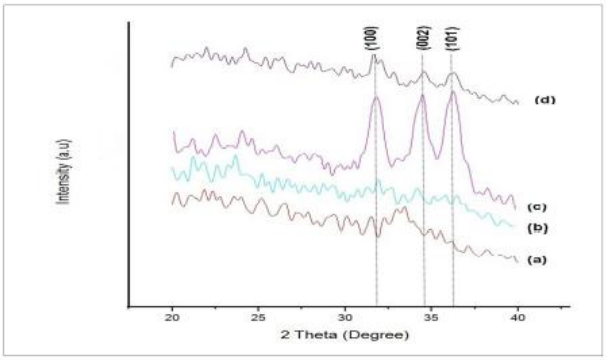

Figure 1: XRD spectrum of ZnO thin films annealed at different temperatures of (a) as grown, (b) 350 °C, (c) 450 °C, (d) 550 °C

The XRD patterns of ZnO films annealed at different temperatures are shown in Fig. 1. Diffraction peaks for the (100), (002), and (101) plane of reflections may be seen in the XRD pattern. Based on these findings, it may be concluded that annealed ZnO films have a polycrystalline, hexagonal wurtzite structure. The XRD pattern for unprocessed, as grown ZnO films is shown in Fig. 1(a). The amorphous-like structure of ZnO films is suggested by the XRD pattern in Fig. 1(a), rather than the polycrystalline structure that would be expected. This might be because of the amorphous nature of the glass substrates utilized, making the lower pre-heating temperature of 160 °C unnecessary for obtaining the desirable orientated ZnO films.

For ZnO films annealed at 450 °C, the reflection intensity is greatest in the (002) plane, which corresponds to the c-axis orientation. It can be seen in Fig. 1 that after annealing at 550 °C, the (002) peak intensity drops and the (100) peak becomes dominants in the film (d). These results suggest that the ZnO film annealed at 550 °C has a crystalline orientation with a preferential a-axis. When the annealing temperature is raised, the zinc ions and oxygen ions on the surface get the necessary energy and mobility to be removed and relocated. Because of this, the (002) peak along the c-axis would be the most successful in terms of growth. Instead of providing enough energy to move onto the stable position, increasing the annealing temperature (>450 °C) may break the bonds within Zn-O, speeding up the rate of re-evaporation.M.Vishwas et al. also reported that Al doped ZnO films annealed at higher temperatures exhibit a preferred (100) a-axis orientation. The current films have crystal lattice constant values of a = 3.2498 angstrom and c = 5.2066 angstrom, which are similar to the a = 3.253 angstrom and c = 5.209 angstrom values of ZnO crystal (JCPDS Card No. 80-00075).

Effect of annealing temperature on the surface morphology the films

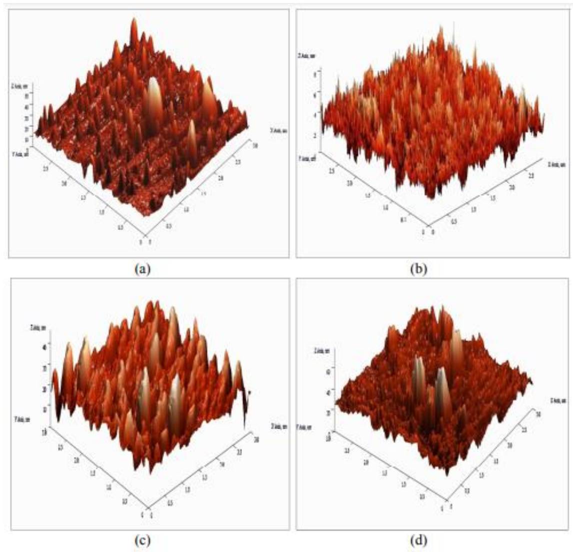

Figure 2: AFM surface morphology images of the ZnO films annealed at the temperature of (a) as grown, (b) 350 °C, (c) 450 °C, (d) 550 °C

Surface morphology photos of annealed ZnO films captured by an atomic force microscope are shown in Fig. 2. ZnO films at 350 °C, 450 °C, and 550 °C had RMS roughness values of 0.897 nm, 5.653 nm, and 7.975 nm, respectively. Similarly, Hwang et al. assert that ZnO films show an increase in RMS roughness with increasing temperature. According to the XRD pattern in Fig. 1, the as developed ZnO films have an amorphous structure rather than a polycrystalline one, as seen in Fig. 2(a) (a). As a result, its surface is relatively rough, with a root-mean-square roughness (RMS) of 5.466 nm. This may be because some leftover organic material was vaporized during the preheating process. ZnO films' RMS roughness rises as their annealing temperature rises over 550 degrees Celsius because their grain distributions become less uniform when the grains agglomerate. This might be because the glass substrate was annealed at a very high temperature, very close to its melting point. ZnO films annealed at

350 °C and 450 °C had larger average grain sizes, at 32.1 nm and 176.0 nm, respectively, whereas those annealed at 550 °C have smaller average grain sizes, at 56.1 nm. The reductions in average grain size for the 550 °C annealed films may be explained by the poorer uniformity in grains size and its distribution, as illustrated in Fig. 2. (d).

In this case, AFM was used to investigate the surface morphologies of ZnO films grown under a variety of circumstances. Surface morphologies of the thin films were significantly affected by the implanted interfacial layer. Figure 3a is an AFM picture of a ZnO-P film, which reveals a distribution of nanoparticles. However, as can be seen in Fig. 3b and c, the ZnO-R1 and ZnO-R2 AFM pictures exhibit more ridge-like characteristics. Zooming in on the square region indicated by the dotted black lines in Figures 3a-c (Figures 1d-f), we see the enlarged photographs. In Fig. 3d, the mean particle diameter of ZnO-P is about 70 nm, and in Fig. 3e, the mean ridge width of ZnO-R1 is about 70 nm, with the presence of numerous apertures between the ridges. The ridges in the modified ZnO-R2 sample are denser and larger (with an average width of 90 nm) compared to the ridges in ZnO-R1, and there are fewer voids in the ZnO-R2 sample. The RMS values of 4.15, 7.51, and 3.10 nm for the ZnO-P, ZnO-R1, and ZnO-R2 films provide additional confirmation of the surface roughnesses. The influence of BLI on the morphology of our samples is significant. It can be shown in Additional file 1 that although all of the BLI samples created at varying substrate temperatures have ridge-like surface morphologies, some of the samples also have surface flaws. Films with and without BLI were compared, and it was discovered that the initial nucleation of ZnO was responsible for dictating the final particular shape. Furthermore, oxygen pressure played a significant role in the nucleation process, exhibiting great sensitivity, since Zn atoms may rapidly desorb without surrounding oxygen owing to their poor stickiness.

Table 1: Detailed growth conditions for the ZnO films

Samples	Growth processes and detailed parameters
ZnO-P	a) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 250 W, t = 60 min b) ——— c) T = 250 °C, $P(O2) = 1 \times 10^{-5}$ Torr, O-plasma = 180 W, Zn = 330 °C, t = 5 min d) T = 420 °C, $P(O_2) = 1 \times 10^{-5}$ Torr, O-plasma = 180 W, Zn = 330 °C, t = 90 min
ZnO-R1	a) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 250 W, t = 60 min b) T = 315 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, T(Zn) = 310 °C, t = 30 min c) T = 250 °C, $P(O2) = 1 \times 10^{-5}$ Torr, O-plasma = 180 W, Zn = 330 °C, t = 5 min d) T = 420 °C, $P(O_2) = 1 \times 10^{-5}$ Torr, O-plasma = 180 W, Zn = 330 °C, t = 90 min
ZnO-R2	a) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 250 W, t = 60 min b) T = 370 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, T(Zn) = 340 °C, t = 30 min c) T = 250 °C, $P(O2) = 5 \times 10^{-5}$ Torr, O-plasma = 200 W, Zn = 340 °C, t = 5 min d) T = 490 °C, $P(O_2) = 5 \times 10^{-5}$ Torr, O-plasma = 200 W, Zn = 340 °C, t = 60 min

T temperature (°C), P oxygen partial pressure (mbar), plasma oxygen plasma power (W), t time (min)

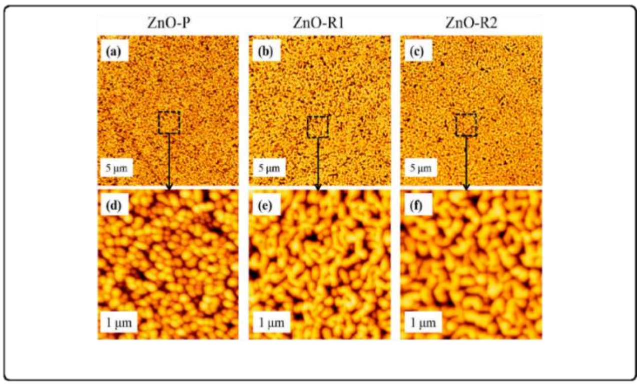

Figure 3: AFM results. a–c AFM images of the ZnO film surface morphologies (5 µm). d–f Magnified images of the square areas (marked by dashed black lines) in a–c

This unique ridge shape is reminiscent of another work in which 3D columnar grains with a particle-like morphology were driven to merge laterally into nanoridges during a 30-minute HT post-annealing. Lateral coalescence, however, is seen here as a normal part of development. Zn atoms, much like the AlN nuclei, preferentially migrate to the substrate's unique step edges, where they combine with O2 to produce ZnO at the edges despite the fact that O2 is not activated by plasma, resulting in the ridge-like morphology. Adatoms migrating to the surface during the first stage of development (when the surface is quite flat) would produce ZnO crystals of superior quality. When O is activated by plasma during deposition of the ZnO film onto the substrate surface in the absence of BLI, the resultant surface morphology is that of typical nanoparticles.

CONCLUSION

The glass substrates had ZnO thin films produced on them using a cheap sol-gel dip-coating method. After being exposed to temperatures between 350 and 550 degrees Celsius, the films were annealed. In contrast to the amorphous structure displayed by as-grown ZnO films, polycrystalline hexagonal wurtize structures were observed in annealed films, with a preference for the (002) c-axis orientation with increasing annealing temperatures. The highest peak intensity was observed in films annealed at 450 °C. ZnO films with ridge-like surface morphologies, which were shown to be sensitive to the initial oxygen pressure, were generated on MgO(111) substrates and compared to a conventional particle-like ZnO film in this study. The elements that affect the morphology were studied using a battery of studies.

REFERENCE

1. Ewelina Nowak et.al “The Influence of Recrystallization on Zinc Oxide Microstructures Synthesized with Sol–Gel

Method on Scintillating Properties” https://doi.org/10.3390/cryst11050533

2. Bakri, A S et.al **“**Effect of Annealing Temperature of Titanium Dioxide Thin Films on Structural and Electrical Properties” https://doi.org/10.1063/1.4968283

3. W. Matysiak et.al “Manufacturing process and optical properties of zinc oxide thin films as photoanode in DSSC” Volume 86 • Issue 1 • January 2018

4. Iping Suhariadi et.al “Morphology Evolution OfZnO Thin Films Deposited By Nitrogen Mediated Crystallization Method” https://doi.org/10.1051/matecconf/201815902031

5. T. Ivanova et.al **“**Structural and optical characterization of nitrogen and gallium codopedZnO thin films, deposited by sol-gel method “Journal of Molecular Structure (2020), vol. 1206, 127773 DOI: 10.1016/j.molstruc.2020.127773

6. T. A. Vijayan, R. Chandramohan, S. Valanarasu, J. Thirumalai and S. P. Subramanain, J. Mater. Sci., 43, 1776 (2008).

7. A. Alivisatos,"Semiconductor Clusters, Nanocrystals, and Quantum Dots. Science", 271, 933-937, (1996).

8. T. Obata , K. Komeda , T. Nakao , H. Ueba , and C. Tasygama , "Structural Characterization of Si0.7Ge0.3 Layers Grown on Si(001) Substrates by Molecular Beam Epitaxy," J. Appl. Phys. Vol. 81, P.199, (1997) .

9. S. Boninelli, “Properties and Evolution of Si Nanoclusters Studied by Energy Filtered Transmission Electron Microscopy”, University of Catania, Ph.D thesis, December (2004).

10. Y. V. Gassenbauer and A. Klein, (2006)"Electronic and Chemical Properties of Tin-Doped Indium Oxide (ITO) Surfaces and ITO/ZnPc Interfaces Studied In-situ by Photoelectron Spectroscopy", J. Phys. Chem,Vol.110, pp.4793-4801.

11. A. J. Ghazai1, E. A, Salman and Z. H. (2016) " Structural Properties of Zno Thin Films Prepared Using Different Techniques". Swift Journal of Physical Sciences Vol 2(1) pp. 001-004

12. O. Shane,C. Mehmet, Paul ,T. G. Mark, A. Jeff, P. Ian et al. (2011)"The effect of dopants on the morphology, microstructure and electrical properties of transparent zinc oxide films prepared by the sol-gel method". Thin Solid Films, 520, pp. 1174-1177.

13. Z. Xiaofeng, J. Tao, Z. Jian and W. Xiaohua, (2007)"Humidity sensor based on quartz tuning fork coated with sol-gel-derived nanocrystalline zinc oxide thin film". Sensors and Actuators B,123, pp.299-305.

14. K. S. Khashan and F. Mahdi, (2017)" Synthesis of ZnO: Mg Nanocomposite by Pulsed Laser Ablation in liquid". Surf. Rev. Lett., 1750101

15. A.R. Phani, M. Passacantando, and S. Santucci, (2001)"Synthesis and characterization of zinc aluminum oxide thin films by sol-gel technique". Materials Chemistry and Physics, 68, pp. 66-71.

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