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Optical and Surface Morphology Studies of Hydrothermally Grown Nanostructured ZnO for Optoelectronic Applications

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Abstract: Nanostructured Zinc Oxide (ZnO) thin film has been deposited with different annealing temperature (350 ℃, 450 ℃ and 550 ℃) on glass substrate by film coating technique followed by hydrothermal method. The structural behavior of ZnO samples have been confirmed without any impurity by XRD and the crystalline size of the samples were 15 nm, 19 nm, 26 nm which has been calculated from Scherer's formula. The effect of synthesis condition on ZnO growth was systematically studied by field emission scanning electron microscopy (FE-SEM). The FE-SEM image shows that the synthesized ZnO particles are like clusters in a large-scale area, which are highly disperse in the space without any aggregation and have approximately uniform morphologies. From this study, it has shown that the ZnO nanoparticles are distributed in uniformly dense particles, and exhibit the wurzite hexagonal structure. Optical study was carried out for the coated ZnO nanoparticles, and the obtained result has shown that the grown ZnO nanoparticles exhibit good crystal quality with the band gap of 3.15 eV. Moreover, the d.c. conductivity value is 2.7 E^{-7} Ω^{-1}cm^{-1} for 550 ℃ annealed ZnO sample.

Keywords: ***Nanoparticles; Zinc Oxide; thin film coating technique; Optical Properties; FE-SEM.***

I. INTRODUCTION

ZnO is considered as a workhouse of technological development exhibiting excellent electrical ,electrical and optical properties. Zinc oxide is a II – IV semiconductor, which has a wide band gap of about 3.37 and large excition binding energy of 60 meV [1] which has attracted much interest in the areas of optoelectronic devices, such as solar cells , light emitting diodes (LED) and acoustic – optical devices.[2,3].In solar cells ,the zinc oxide nanorods are used as an anti-reflective coating due to their high optical transmittance in the visible light region. Zinc oxide is widely used as functional material because of their wide and direct band gap, and excellent chemical and thermal stability. Recently One dimensional ZnO nanostructures has received much attention ,due to its controlled morphology, growth parameters and physical properties of these nanostructures[4].The use of well aligned nanostructures such as naowires, nanorods because of their controlled morphology has a impact on the working performance of the nanoscale optoelectrical devices. In addition, ZnO possesses a large number of intrinsic and extrinsic deep-well impurities which is capable of emitting light in all directions.[7].From the application point of view , the properties of high aspects ratios and small sizes of ZnO nanowires/nanorods improve the stability of the electrical devices and sensibility of chemical sensing [8].The Zinc Oxide nanorods show n-type semiconductor behavior due to their native effects such as oxygen vacancies and zinc interstitials. The Zinc Oxide nanorods are important for Dye-sensitized solar cells because of the electronic mobility of the Zinc oxide nanorods is about 2-3 orders of magnitude faster than that in TiO_2 naoparticles.[9-12]. It is well known that purity of ZnO is important for its application demanding extreme thermal treatment after its synthesis or coating. This is with intension of reducing or elimination the organic species that absorbed on the surface of ZnO, which are the methods used for the synthesis of ZnO nanoparticles. By employing extreme heat treatment process after coating of ZnO particles on the paper surface is not applicable. For this reason ,use of performed heat-treated ZnO nanoparticles for coating on substrates is desirable, although ZnO nanoparticles could be formed and grown on the substrate.[13-15]

The Zinc Oxide nanorods are prepared by various methods such as Chemical vapour deposition, chemical deposition, sol-gel process, pulsed laser deposition, and spray pyrolysis[16-17].In the present study , the zinc oxide nanorods are prepared by hydrothermal method by coating on glass substrates. The zinc oxide nanorods are annealed for different temperatures like (350°,450°, 550° C). In the deposition of ZnO nanoparticles ,by hydrothermal method are cheap and safe and can be implemented easily in the standard laboratory, as it was used in this work.[18-20].

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II. SYNTHESIS OF ZINC OXIDE NANOPARTICLES.

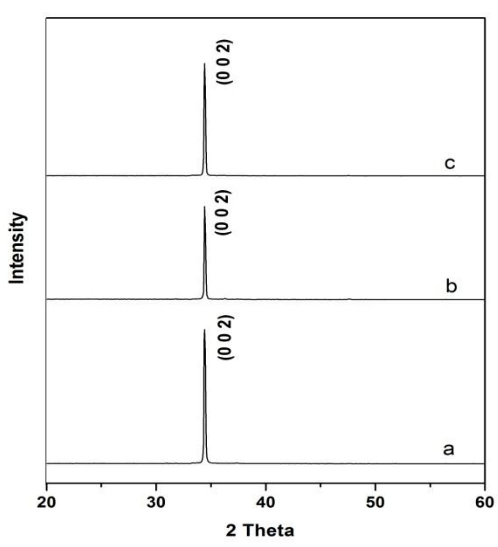
All the chemicals were of analytical grad and were used without any further purification. In this work Glass slides was used for coating of ZnO nanoparticles. The Glass slides was cleaned by Chromic acid and Sodium Hydroxide, then the glass slide was treated by sonificator for further purification. The deposition of ZnO nanoparticles are prepared by two step process. First the seed layer was prepared .For the seed layer preparation , the ethanol ammine (0.2 M) was mixed with 20 ethanol ,the ethanol solution was prepared. Then the Zinc acetate was added to the above prepared ethanol solution and allowed to stirrer for few hours, after few hours a transparent solution was formed. The cleaned glass substrates are dipped in the transparent solution and the dipped glass substrates are kept in the vaccum oven at 150^{o} C for 4 hours.

In the next step, for the second layer coating the hexaammine (0.2 M) was mixed with the 35 ml of distilled water and Zinc nitrate was added and stirred, a white color solution was prepared. The prepared white color solution was transferred into the auto-clave and the coated glass substrates are dipped in the solution and sealed off. The auto-clave are kept in the vaccum oven of about 110^{o} C for 10 hrs.

The coated glass substrates are annealed for different temperatures of (350^{o},450^{o}, 550^{o} C).

III. RESULTS AND DISCUSSION.

Fig 1 shows an XRD pattern of ZnO nanorods prepared by hydrothermal method and annealed at (350^{o},450^{o}, 550^{o} C). The pattern which was indexed as the pure hexagonal phase of ZnO nano rods with the lattice parameters a = 3.274 Å and c = 4.197 Å, which were very close to the reported data (JCPDS, 89- 0501). XRD pattern was indexed using POWDER-X software. It can be clearly seen from the pattern that the sample showed a single-phase nature with a nano rod structure. No diffraction peaks from any other impurities were detected and the sharpness of the peaks implied the high crystallinity of the as-prepared ZnO nanorods. A strong peak occurs at 2θ = 34.8° which corresponds to the (002) reflection. These peaks indicate that the prepared ZnO nano rods are of hexagonal phase. Using the Scherer's formula, the calculated value of the crystalline size of the samples were **15 nm, 19 nm, 26 nm.** Fig 2 shows the uv graph, UV–vis absorption spectrum as shown in Figure 6.3 is carried out to evaluate the potential optical properties of the as-prepared ZnO nanorods.



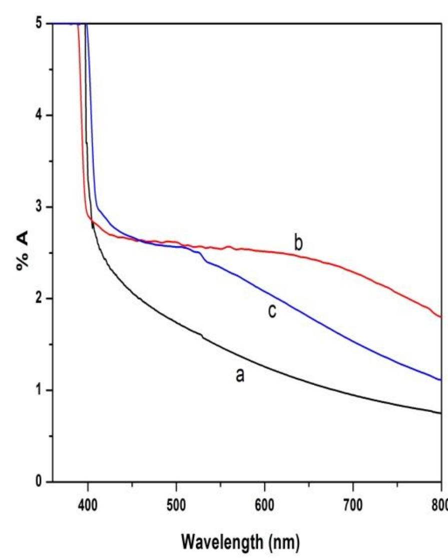


Fig 1&2 XRD and UV graph of a) 350^{o} b) 450^{o} c) 550^{o}

The spectrum was corrected for the solvent contribution. The absorption spectrum of ZnO nanorods show well-defined exciton band at ~399 nm (calculated band gap of ~3.10 eV) which is red shifted by ~26 nm relative to the bulk excition absorption (423 nm). The reason of the shifting of absorption band could be due to the oriented attachment of the nanoparticles by microwave irradiation, may lead to defect formation in the nanorods, which is in good agreement with the XRD studies of the as-prepared nanorods. The UV–

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Vis transmittance spectra shows that absorption edge shifts to longer wavelength with increase in heat treatment temperature and the red-shift of absorption edge can be attributed to the increase in grain size of ZnO nano rods on annealing. The calculated band gap

Figure 1 (350°)

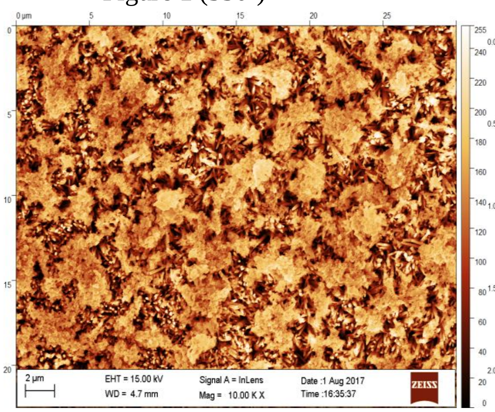


Figure 2(450°)

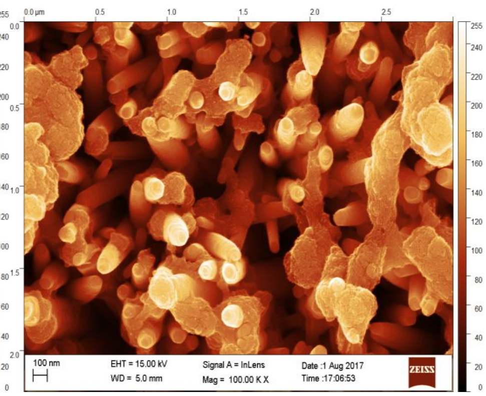
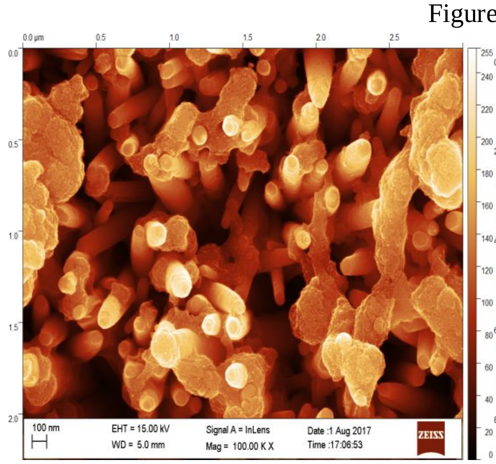


Figure 3(550°)



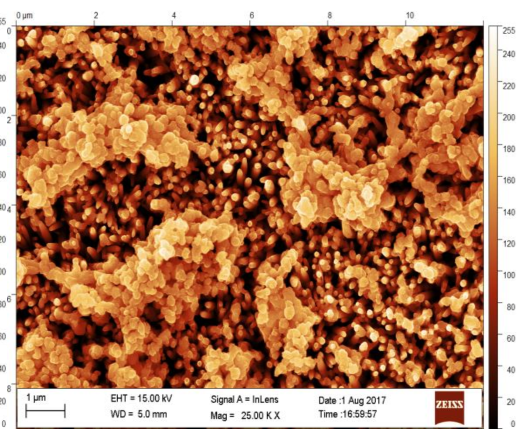
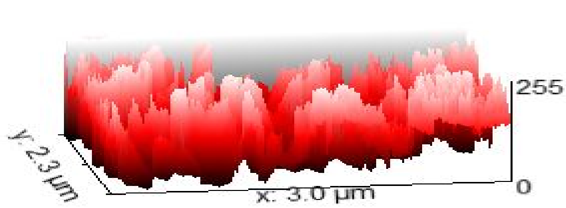
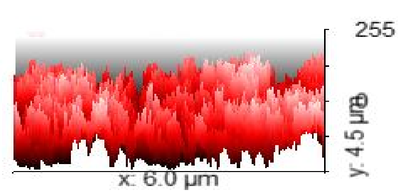


Fig 1,2,3,4 shows the Zinc oxide nanorods at (350°,450°, 550° C).From the image of ZnO nano rods and it represents the morphology of the ZnO nanorods. Typical FESEM images of the ZnO nanostructures at different annealing temperatures are shown in Figure It is clear from the fig 1 that at 350 C the as synthesized ZnO are nano rod like clusters in a

Figure 4 & 5 3d view of Zinc Oxide Nanorods





Large-scale area, which are highly disperse in the space without any aggregation and have approximately uniform morphologies. But at 450C and 550C the growth of the nanorods was uniform and the size of the nanorods was also increased of about 3 µm to 6µm.This is clear from the morphological studies at higher annealing temperatures the growth of the nanorods was uniform and the conductivity was also increased on increasing the

DC conductivity of 550C

50.Ivm	70 .Ivm	90.Ivm	110.Ivm	130.Ivm	rt.Ivm
9.13E-09	1.05E-08	1.19E-08	1.15E-08	1.22E-08	8.48E-09
2.05E-08	2.39E-08	2.61E-08	2.55E-08	2.61E-08	1.76E-08
3.31E-08	3.80E-08	4.17E-08	4.08E-08	4.11E-08	2.75E-08
4.56E-08	5.31E-08	5.72E-08	5.62E-08	5.73E-08	3.82E-08
5.85E-08	6.77E-08	7.34E-08	7.28E-08	7.29E-08	4.99E-08
7.20E-08	8.32E-08	9.03E-08	8.98E-08	8.96E-08	6.15E-08
8.61E-08	9.94E-08	1.06E-07	1.07E-07	1.07E-07	7.19E-08
1.00E-07	1.15E-07	1.23E-07	1.25E-07	1.24E-07	8.45E-08
1.14E-07	1.31E-07	1.40E-07	1.42E-07	1.41E-07	9.75E-08
1.28E-07	1.47E-07	1.57E-07	1.60E-07	1.57E-07	1.08E-07

Table shows the dc conductivity values of 550 C at different temperatures. On comparing from the three annealing temperatures 550 C only shows good conducting values and it was proved from the FESEM image that the Size of the nanorods was increased on increasing the annealing temperature. The d.c. conductivity value is 2.7 E^{-7} $\Omega^{-1}cm^{-1}$ for 550 °C annealed ZnO sample.

IV. CONCLUSIONS

In Conclusion, ZnO nanorods had been successfully synthesiszed by Hydrothermal method and annealaed different temperatures at (350°,450°, 550° C) . The Prepared ZnO nanorods were characterized by XRD and FESEM .It is clear that ,the size of the nanorods increases on the increasing the annealing temperature. FESEM image shows that the growth of the nanorods was very uniform .The UV- Vis results shows that on increasing the temperature the band gap decreases. From the above results DC conductance was taken for 550° C and the calculated conductance is about 2.7 E^{-7} $\Omega^{-1}cm^{-1}$. Experiment shows that the Different growth temperature would influence structure and morphology of the prepared ZnO nanorods.

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