Research Paper

Thickness dependence properties of spin coated ZnO nano crystalline films

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Abstract

Transparent, conducting undoped ZnO thin films were prepared by optimized sol-gel spin coating technique. The influence of film thickness on the structural, optical and electrical properties of ZnO films was investigated. The structural characteristics of the samples were analyzed by X-ray diffractometer and an atomic force microscope. XRD studies revealed the polycrystalline nature of the films with a hexagonal (wurtzite) structure and a preferred orientation with c-axis. The grain size and the surface roughness were found to increase with increased film thickness. The optical properties were studied using a UV-visible spectroscopy. The average optical transmittance in the visible region of all the films was over 80%. The optical band gap (E_g) values decreased from 3.224 to 3.148 when the film thickness was increased from 112 nm to 348nm. A lowest resistivity of 1.46 x 10^{-2} Ω cm was obtained from the film of thickness 384 nm. From the results, it can be concluded that the structural, optical and electrical properties of ZnO thin films can be tuned by varying thickness of the films, making it suitable for optoelectronic device applications.

Keywords: ZnO, sol-gel, thin film, optical properties, electrical properties

1. Introduction

In recent years, the inexpensive, nontoxic and abundant zinc oxide (ZnO) has received extensive attention because of its novel properties such as direct energy wide band gap (3.37eV), large exciton binding energy (60 meV), high thermal and chemical stability and environmental friendly applications **[1].** It is a promising material that possesses various applications such as optoelectronic devices like flat panel displays, light-emitting diodes and transparent antireflection coatings for electrodes in solar cells and gas sensors **[2-5].** A variety of techniques have been used to fabricate ZnO thin films such as chemical vapor deposition (CVD), RF sputtering, spray pyrolysis, thermal vapor deposition and sol-gel process **[6-10].** Among these methods, the sol-gel method is widely used due to several advantages in comparison with other deposition methods such as its low cost of the apparatus and raw materials, safety, simplicity, homogeneity, its excellent control of stoichiometry, ability to prepare high quality thin films in large scale etc. It is well known that the deposition parameters and the preparation method can have an important influence on the properties of the thin film. The device applications mainly depend on the characteristics such as high optical transmittance in the visible region and high conductivity of the film. These parameters are highly influenced by the thickness of the film. Therefore, thickness dependent study of ZnO is essential.

In the present work, ZnO thin films have been prepared by cost effective sol-gel method and the influence of the thickness on the structural, optical and electrical properties were discussed.

2. Materials and Methods

ZnO thin films were deposited by sol-gel spin coating method on glass substrate. The precursor solution was prepared by dissolving an appropriate amount of zinc acetate dehydrate in 2-methoxyehanol. Monoethanolamine (MEA) was used as a sol stabilizer. The total concentration of the sol was maintained at 0.5 mol L^{-1} and the molar ratio of MEA to zinc acetate was maintained at 1.0. The resulting mixture was then stirred at 60°C for 1 hour using a magnetic stirrer to form a clear and transparent homogeneous mixture and was aged for 48 hours at 30°C. The glass substrate was cleaned with standard cleaning procedure and then ZnO films were spin coated on glass substrate at room temperature with a rate of 3000 rpm for 30s. The deposited thin films were preheated at 350°C for 15 min, to evaporate the solvent and to remove organic residuals. The films with desired thickness were achieved by multiple spin-bake process and then the films were annealed in air at 500°C for an hour.

The structural characteristics were investigated by Rigaku Miniflex 600 PXRD. Crystallite size is estimated from XRD data using the Debye-Scherrer formula. The surface topography of the ZnO films was studied using AFM. The thickness of ZnO films was measured by an ellipsometer. Optical properties of the films were measured by a UV-visible spectrophotometer (SHIMADZU 1800) in the wavelength range 300-800nm. Electrical characterization of the films was carried out by the current-voltage measurements using Keithley 236 source measure unit.

3. Results and Discussion

3.1 Structural properties

The X-ray diffraction patterns of ZnO films with different thickness are indicated in Figure 1. XRD patterns show that all spin coated ZnO films are polycrystalline with hexagonal wurtzite structure. For all the samples, (100), (101) and (002) diffraction peaks are observed in the XRD pattern, showing the growth of ZnO crystallites along different directions. The existence of very strong peak along (002) plane indicates that the films are oriented along c-axis **[11].** It can be seen that the intensity of the (002) peak is increased and FWHM is decreased, as the thickness increased from 112 nm to 384 nm. This indicates that within a certain range of thickness, the crystallinity and the crystallite size increases with film thickness (Table 1). The grain size of the ZnO films was calculated using the Debye-Scherrer formula **[12]**

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad 1$$

Where D is the grain size, λ is the X-ray wavelength (0.154059 nm), β is the full width at half maximum of the peaks in radians and θ is the angle of diffraction. The position of the (002) peak depends greatly on the film thickness and shifts from 34.339 to 34.524 when the thickness of the film increased from 112 nm to 384 nm. This can be attributed to the better crystallinity and the relaxation of the lattice strain. The strain along c-axis (ε) and the dislocation density (δ) of films were estimated using the equations and tabulated in Table 1.

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad 2$$

$$\delta = \frac{1}{D^2} \qquad 3$$

It can be observed that the values of strain and dislocation density, which indicates the defects in the film, decreases with film thickness and the strain relaxation was found to be maximum for the ZnO film of thickness 384 nm for which the crystallite size was maximum

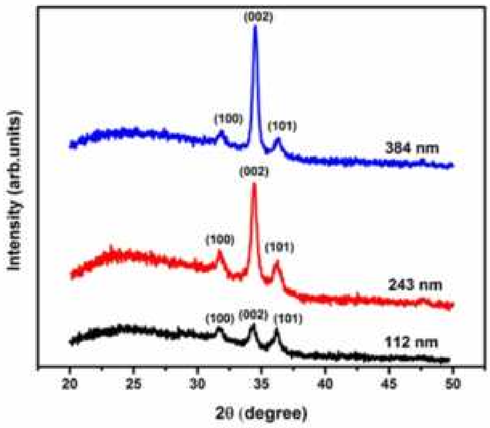

Figure 1. XRD spectrum of the ZnO films

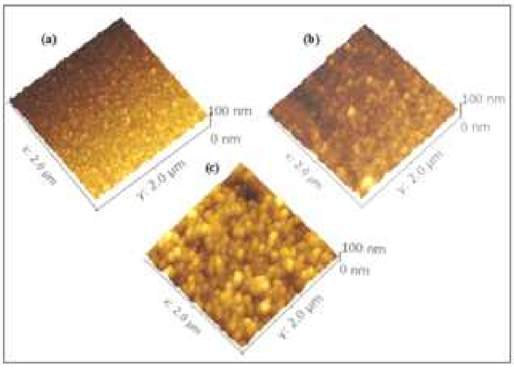

Figure 2. AFM image of ZnO thin films
with thickness (a) 112 nm (b) 243 nm (c) 384 nm

Figure 2 shows the 2 μm × 2 μm AFM images of ZnO thin films for different thicknesses. It can be seen that all the films consist of uniform and spherical like nanoparticles and the grain size increased with film thickness. The grain size is found maximum for the ZnO film of thickness 384nm. As expected, the surface roughness (Sa) also is maximum for the same film (Table.1). These results agree with the XRD results. Thus, in the present investigation, we found that with increase in the film thickness the structural properties of the films improved.

3.2 Optical properties

Figure 3 shows the optical transmittance spectra of ZnO thin films between 300-800 nm wavelengths. The loss due to the plane glass substrate was removed during the measurement. The average transmittance of all the films over visible wavelengths decreased from 89% to 80% with increasing in film thickness. This decrease in the optical transmittance can be attributed to the better crystallization of the film and the dense microstructure of the thicker film as seen in the AFM image (Figure 2). It can also be seen that the transmission in the visible region decreases considerably at shorter wavelengths near the ultra-violet range of all the films. The absorption coefficient α was estimated using the Beer-Lambert relation

$$\alpha = \left(\frac{1}{d}\right)\ln\left(\frac{1}{T}\right) \qquad 4$$

Where T is the transmittance and d is the thickness of the film. The optical band gap (Eg) was estimated using the relatio

[13]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad 5$$

Where h is Planck's constant, ν is the frequency of the incident photon and c is the proportional constant. Since ZnO film is a direct transition semiconductor, the values of energy gap (E_g) of the samples could be estimated by extrapolating the straight line portion at $(\alpha h \nu)^2$=0 as shown in the Figure 4. It can be observed that the optical energy gap deceased with the film thickness indicating the weak Burstein-Moss effect.

Table 1. Characteristic properties of ZnO thin films.

Thickness	$(2\theta)_{(002)}$	FWHM(°)	D(nm)	⍰ (10^{-3})	⍰ (10^{15})	S_a (nm)	T (%)	E_g (eV)
112nm	34.339	0.589	14.123	2.454	5.014	11.328	89.107	3.224
243nm	34.432	0.460	18.089	1.916	3.056	18.675	84.483	3.181
384nm	34.524	0.394	21.124	1.641	2.241	23.015	80.863	3.148

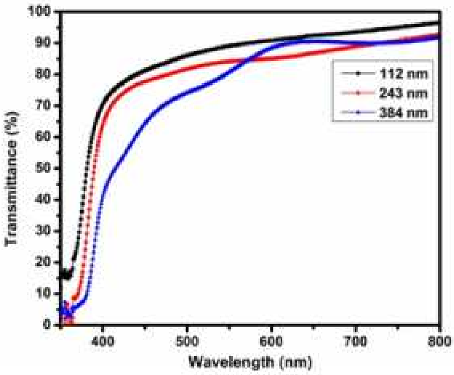

Figure 4. $(\alpha h\nu)^2$ vs. $(h\nu)$curves of the ZnO films

3.4 Electrical properties

The sheet resistance (Rs) of the films was measured by soldering two wires to the ends of the films with silver contacts. I-V characteristics of the samples were recorded using Keithley 236 measuring unit. Then by using I-V data, the sheet resistance of the films was calculated by the relation,

$$R_S = \frac{\pi}{\ln 2} \times \frac{V}{I} \qquad 6$$

Where V is the applied voltage and I is the measured current. Then the resistivity of the ZnO films were determined by the relation [14]

$$\rho = R_S \times t \qquad 7$$

The dependence of electrical resistivity (p) on film thickness is shown in Figure 5. It can be seen that the resistivity decreases with an increase in the film thickness. A lowest resistivity of 1.46×10-2 Ω cm was obtained from the film of thickness 384 nm. This may be because the crystalline size increases with increasing film thickness, which reduces the grain boundary scattering. From the obtained results, it is clear that the film resistivity strongly depends on the film thickness.

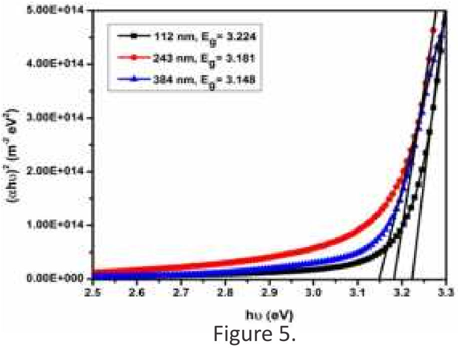

Figure 5.

Dependence of Electrical resistivity on thickness of the film

4. Conclusion

ZnO thin films with different thickness were prepared by cost effective sol-gel spin coating method. Structural analysis revealed the polycrystalline nature of the films. The grain size was found to increase with increasing film thickness. The optical transmittance of all the films was above 80%. The optical energy gap was decreased from 3.224 to 3.148 when the thickness of the film was increased from 112 nm to 384 nm. The lowest electrical resistivity of 1.46×10-2 Ω cm was obtained from the film of 384 nm thickness. We observed that the structural, optical and electrical properties of synthesized ZnO thin films were dependent on the film thickness and can be tuned by selecting the appropriate thickness. The good performance of ZnO thin film indicates that it can be used as promising materials for optoelectronic applications.

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The puzzle of neutrino – an elementary particle in the Universe

- Navin N Bappalige

Pauli stated that “I have done a terrible thing, I have postulated a particle that cannot be detected”. This was the theoretical birth of an electrically neutral, weakly interacting and very light particle called neutrino. But as the time elapsed this tiny particle revolutionised both particle physics and cosmology.

In Italian language neutrino means "little neutral one”!!. Pauli postulated the emission of neutrino particle in a desperate attempt to explain conservation of energy in beta decay as there was discrepancy in energy and momentum during beta (β) decay. In a research paper in December 1930, he suggested that some of the energy is carried away by the β particle during the radioactive decay process. The word "neutrino" entered the international vocabulary through Enrico Fermi, who used it during a conference in Paris in July 1932.

The original equation of β decay, $n \longrightarrow p + e^{-}(\beta)$, is Fermi,s theory of β decay and indicates that an electron i.e., β particle is emitted during the radioactivity due to the conversion of neutron into proton in the nucleus. However it has taken a quarter of a century for the discovery of neutrino particle with the streaming of the neutrinos from nuclear power plants then being built in 1950’s. In June 1956, two American physicists, Frederick Reines and Clyde Cowan sent a telegram to Wolfgang Pauli stating the neutrinos had left traces in their detector. This discovery showed that the ghostly neutrino, or Poltergeist as it had been called, was a real particle. Frederick Reins and Clyde Cowan were jointly awarded the Nobel Prize in Physics in the year 1995 for the discovery of leptons and neutrino particle.

Solar neutrino problem

In fact we live in a world of neutrinos. Billions of neutrinos are flowing through our body every second. We cannot see them and do not feel them. Neutrinos rush through space almost at the speed of light and hardly ever interact with matter and the question is where do they come from? Some were created already in the Big Bang, others are constantly being created in various processes in space and on Earth – from exploding supernovas, the death of massive stars, to reactions in nuclear power plants and naturally occurring radioactive decays. Even inside our bodies an average of 5,000 neutrinos per second is released when an isotope of potassium decays. The majority of those that reach the Earth originate in nuclear reactions inside the Sun. Second only to particles of light[electromagnetic spectrum]- photons, the neutrinos are the most numerous particles in the entire universe.

Since the 1960s, scientists had theoretically calculated the number of neutrinos [using energy mass relation] that are created in the nuclear reactions that make the Sun shine. But while carrying out measurements on Earth, up to two thirds of the calculated number of neutrino was missing. Where did the neutrinos go? One suggestion was that there was some error in the theoretical calculations of how the neutrinos are produced in the Sun. Second suggestion that came to solve the solar neutrino puzzle was that the neutrinos change identities. According to the Standard Model of particle physics there are three types of neutrinos – electron-neutrinos, muon-neutrinos and tau-neutrinos. The second suggestion was more realistic as explained later.

In order to detect the neutrinos , the search was on day and night, in colossal detectors built deep underground, in order to shield out noise from cosmic radiation from space and from spontaneous radioactive decays in the surroundings.

Following this search, in 1998 Takaaki Kajita presented the discovery that neutrinos seem to undergo metamorphosis i.e., they switch identities during their passage in the Super-Kamiokande underground detector in Japan. The neutrinos captured there are created in reactions between cosmic rays and the Earth’s atmosphere.

Meanwhile, scientists at the Sudbury Neutrino Observatory in Canada, SNO, were studying neutrinos coming from the Sun. In 2001, the research group led by Arthur B. McDonald proved that these neutrinos, too, switch identities.

Together, the two experiments have discovered a new phenomenon – neutrino oscillations. A far-reaching conclusion of the experiments is that the neutrino, for a long time considered to be massless, must have a mass. This is of great importance for particle physics and for our understanding of the universe.

In summary, the neutrino particle took birth in *Pauli’s theory to explain the discrepancy in the explanation of beta decay. At that time this massless particle was only a hypothesis. Pauli himself expressed the doubt about its real existence. Later, Frederick Reines and Clyde Cowan proved the existence of the neutrino particle. But the massless assumption of the neutrino particle again created the problem of number or quantity of the particle as the energy has to be conserved. Last year, Takaaki Kajita and Arthur B. McDonald with their discovery of neutrino oscillations showed that neutrinos indeed have mass. For solving the neutrino puzzle they were jointly awarded with the Nobel Prize in Physics 2015.

**Pauli got the Nobel prize in 1946 not for his prediction of beta particle but for the discovery of exclusion principle.*

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