Research Paper

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Effect of pH on the Poroperties of ZnO thin Films Grown by Chemical Bath Deposition

Physics

KEYWORDS : Zinc Oxide, Chemical bath deposition; Structural, morphological and optical properties

G. R. Patil Department of Physics, Bharati Vidyapeeth Deemed University, Yashwantrao Mohite College, Pune 38,India

B. N. Pawar Department of Physics, Bharati Vidyapeeth Deemed University, Yashwantrao Mohite College, Pune 38,India

ABSTRACT

Zinc Oxide thin films have been deposited on glass substrates using the chemical bath deposition technique. The depositions were carried out in the pH range of 10 to 11.5. Structure of these films was characterized by X-ray diffraction and scanning electron microscopy. Optical properties were studied by spectrophotometric measurements. Influence of the increased pH value on structural and optical properties is described and discussed in terms of transmission improvement in the visible range. The direct band gap energy is found to be about 3.12 eV for the films prepared at pH equal to 10.3.

1. Introduction

Zinc oxide is one of the versatile and technologically important semiconducting material because of its typical properties such as resistivity control over the range 10-3 to 10-5 Ω cm [1], transparency in the visible range, high-electrochemical stability, direct band gap (3.37 eV), absence of toxicity, abundance in nature, etc. It crystallizes in a wurtzite structure and exhibits n-type conductivity [2]. Stoichiometric ZnO films are highly resistive, but less resistive films can be made either by creating oxygen vacancies, which act as donors or by doping with Al, Ga or In [3]. ZnO is one of the semiconductor having good chemical stability hydrogen plasma [4] and suitable for photovoltaic applications because of its high-electrical conductivity and optical transmittance in the visible region of the solar spectrum [5], which is prime important in solar cell fabrications. Thin films of ZnO can be used as a window layer as well as one of the electrodes in solar cells [4]. Along with these applications, ZnO thin films have been used in varistor [6], gas sensor [7], solar cell transparent contact fabrication [8], etc. In many industrial processes, such as cleaning, drying, painting, coating, adhesion, heat transfer and pesticide applications, wettability is an important parameter.

Different chemical methods such as chemical bath deposition (CBD)[9,10], spray pyrolysis [11] successive ionic layer adsorption and deposition (SILAR)[12] electrodeposition[13,14], etc. have been used to obtain ZnO films. As compared to other deposition methods, CBD also referred to as solution deposition method, has its own advantages such as simplicity, reproducibility, non-hazardous, cost effectiveness, etc.The CBD process uses a controlled chemical reaction to achieve thin film deposition by precipitation. In most of the experimental approaches, substrates are immersed in an alkaline solution containing the chalcogenide source, the metal ion, the added base and a complexing agent. In CBD spontaneous reaction is possible from the liquid phase, whereas in spray pyrolysis technique the reaction takes place from the vapour phase at much higher temperature (300–6000C). Using CBD method, a large number of binary compound semiconductors such as CdS, CdSe, PbS, ZnO have been deposited as thin films. In the present work, we report the chemical bath deposition of ZnO thin films and their characterization. The effect of pH on structural, morphological and optical properties of these films is investigated with the objective to optimize the Conditions of the deposition process.

2. Experiments

Chemical bath deposition of ZnO thin films using NH4OH as complexing agents has been reported by Shinde at el[15] .All chemicals used for preparing ZnO thin films were of A.R.grade as fallows , Zinc nitrate Zn(NO3)2 (Loba .Chem.), Ammonia Solution (NH3) (Loba. Chem.) and double distilled water is used as solvent. The Chemical bath deposion method is based on the formation of solid phase from a solution, which involves two steps as nucleation and particle growth. The rate of deposition depends upon the super saturation condition.[16] Ammonia was added to precursor solution Zn(NO3)2 to adjust the Ph.When ammonia was added to solution white precipitate of Zn(OH)2 occurred, which was dissolved by additional ammonia.

Zn (NO3)2 + 2NH4OH $\Rightarrow$ Zn (OH) 2 + 2NH4NO3
Zn (OH) 2 + NH4OH $\Rightarrow$ (NH4) ZnO2 - + H2O + H+.
When this solution is heated the ionic product exceeds the solubility product and ZnO film formed by the following reaction,

(NH4) ZnO2- + H + ZnO + NH4OH.

At a certain Ph the concentration of metal ion decreases to a level such that the ionic product becomes less than the solubility product and film will not be formed. So, here we will find such optimized Ph which will give the good quality film. In the present case deposition were carried out in range pH,9.7pH,10.3pH,11pH.We keep fixed precursor concentration as 0.08M and reaction temperature 800C for deposition period 2hr.The effect of pH on structural ,morphological and optical properties of these films is investigated to optimize the conditions of the deposition process. The film deposition is carried out with the same bath basic composition. Ammonia solution is added to the chemical bath to adjust the pH from 9.7 to 11.5 under the control of a pH meter..Thickness of ZnO films annealed at various PH was measured by the gravimetric weight difference method. The density of the deposited material is assumed to be the same as that of the bulk material (ρ = 5.675 g/cm3 for ZnO films [17]. Fig. 1 shows the variation of ZnO film thickness as a function of the pH value. The thickness increases from 100 to 580 nm when the pH decreases respectively from 9 to 11.5

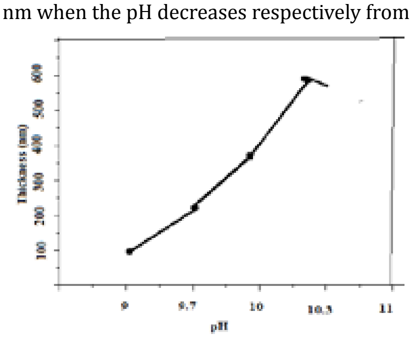

Fig 1: Thickness of ZnO thin films deposited at different pH of the chemical bath for a constant dipping time of 2 h.

The thickness of the ZnO film was measured by weight difference method using sensitive

microbalance. Structural identification of ZnO film was carried out using X-ray diffractometer [chromium target (l = 202895 A °)]. Microstructure of film was studied using scanning electron microscopy (SEM) 2.2895 A°. For this, the film was coated with gold–palladium (Au–Pd) using polaron SEM sputter coating with E-2500. The SEM micrographs were obtained with Cambridge stereoscan 250 MK-3 assembly. The optical absorption studies were carried out within wavelength range 300–850 nm for ZnO film using Systronics spectrophotometer-119, with glass substrate as reference.

3. Results and discussion

3.1. Structural and morphological properties

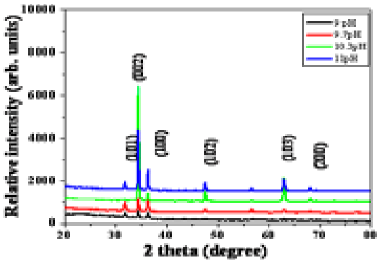

Fig 2. Shows the XRD patterns of the ZnO films deposited with different pH value. All diffraction peaks can be indexed as ZnO crystal with hexagonal wurtzite structure (JCPDS card no. 36-1451).From figure, it is clear that with increasing pH, diffraction intensity of the peak, assigned to (002) plane, is markedly increased and that from the other crystal planes are found to be decreased. At Ph 10.3 the (002) plane having highest intensity which indicates the complete formation of ZnO. Again we increase pH the intensity of (002) plane decreases.[18] Fig 3. shows the SEM images of ZnO thin films deposited with 9Ph, 9.7Ph, 10.3Ph, 11Ph respectively.

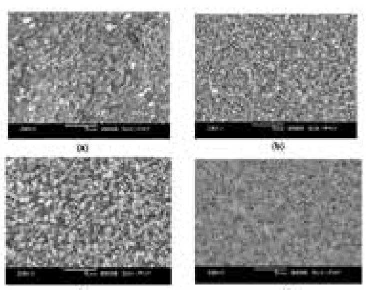

Fig 3- SEM images of ZnO thin films deposited with 9Ph, 9.7Ph, 10.3Ph, 11Ph respectively.

The addition of base in the bath allows the properties of the films to be modified. [19]

From the fig it is observed that at lower ph the film is seems to be powdery, on uniform and poorly adherent to the substrate. As ph increases the uniformity of film going on increasing at 10.3 ph nearly all nanorods are perpendicularly oriented to the substrate. The top surface is seems to be hexagonal shape and film is uniform, adherent and good quality. Above 10.3 Ph films were obtained but they were poorly adherent with rough surface. Which is inconsistent with XRD results.

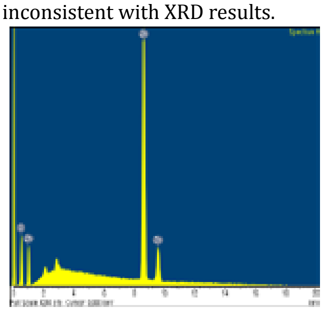

Fig 4- EDAX of ZnO film prepared with 10.30 Ph

In order to confirm the presence of Zn and O in the synthesized ZnO nanorods, EDX measurements were performed. Fig. (4) shows the representative EDX spectra of ZnO sample with pH 10.3. From the similarity of the Zn and O peak intensity line traces, it is clear that after the synthesis process, zinc and oxygen were homogenously distributed inside the nanorod. From the EDX line traces it can be also concluded that O was successfully substituted in to the crystal structure of ZnO nanorods. The estimated amount of atomic weight percentage of Zn and O in deposited thin film approximately are71.84%and 28.15%. The ZnO nanorods are stable without an excess adsorption of oxygen and OH radicals.

3.2 Optical properties:

The optical properties of ZnO thin films prepared at various pH were investigated from variation of optical absorbance with wavelength. The variation of absorbance (at) of ZnO film is shown in Fig. 5. This spectrum reveals that as prepared ZnO film has low-absorbance in the visible region, which is a characteristic of ZnO.The theory of optical absorption gives the relationship between the absorption coefficient a and the photon energy hν for direct allowed transition as

$\alpha = (h\nu - Eg)1/2\ h\nu$

This equation gives the band gap (Eg), when straight portion of $(\alpha h\nu)2$ against hν plot is extrapolated to the Point α= 0. Fig. shows the plot of $(\alpha h\nu)2$ versus hν for ZnO film.

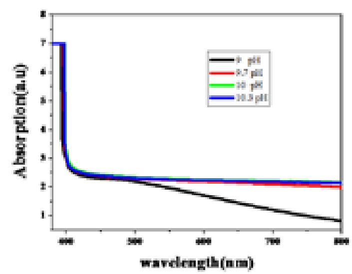

Fig 5- Absorbance of ZnO samples prepared by various Ph value.

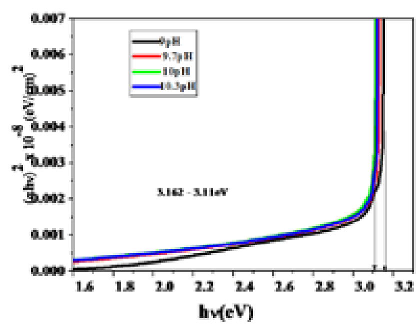

Fig 6-Band gap ZnO samples prepared by various Ph value.

Fig shows UV-vis absorption spectra of samples prepared by various Ph value.

The absorption spectra [Fig.5] reveal that as Ph value increases the absorption going on increasing. At ph 9 the ZnO film having low absorbance. The film prepared with 10.3 ph value having highest absorbance. Again when we increases the ph 9 to 11 the band gap decreases. The film prepared with ph 10.3 shows good optical property.

4. Conclusion

Zinc Oxide thin films are prepared on glass substrates by the CBD technique. There is a good agreement between XRD, SEM, and optical results. These studies show that the pH contributes noticeably to the growth and to the structure of deposited films. The thickness increases from 100 to 580 nm when the pH decreases respectively from 9 to 11.5.

It is particularly observed that the best crystallinity of the ZnS thin films is obtained at pH=10.3. At Ph 10.3 the (002) plane having highest intensity which indicates the complete formation of ZnO.As ph increases the uniformity of film going on increasing at 10.3 ph nearly all nanorods are perpendicularly oriented to the substrate. The band gap is found to be increased from 3.11 to 3.16 ev.The film prepared with ph 10.3 shows good optical property.

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