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International Journal of Current Research
Vol. 4, Issue, 12, pp.026-028, December, 2012

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

THE INFLUENCE OF NI DOPING ON THE PHOTOLUMINESCENCE PROPERTIES OF ZNO THIN FILMS GROWN BY SILAR METHOD

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ARTICLE INFO

Article History:
Received 13th September, 2012
Received in revised form
08th October, 2012
Accepted 28th November, 2012
Published online 18th December, 2012

Key words:
SILAR,
Ni doped ZnO,
Band gap,
Structural studies,
Morphological studies

ABSTRACT

The influence of Ni doping on the Photoluminescence properties of ZnO thin films grown by SILAR method are discussed in detail. The diffraction XRD patterns revealed good crystalline quality without any appreciable changes from pure ZnO films and are genuinely polycrystalline with a hexagonal wurtzite structure. The observed 'd' spacing values are in good agreement with the standard values of ZnO. X-ray diffraction results provide the evidence that Ni is incorporated into the ZnO lattice at Zn site. Also ZnO films with (*002*) texturing is a promising candidate for solar cells, photo detectors, light-emitting devices, thin film transistors and surface acoustic wave guide applications. The optical properties revealed a decrease of band gap with Ni doping. The PL studies revealed the increase of near band gap emission intensities and the PL properties may be tailored with a limited extent of Ni doping by SILAR mthod.

INTRODUCTION

ZnO is an excellent material because of its low-voltage and short wavelength electro-optical devices applications including light emitting diodes, solar cells and laser devices due to its wide band-gap (3.37 eV at room temperature) and large exciton binding energy (60 meV). An array of hierarchical assembly of nanoscale building blocks such as nanocantilever, nanocombs (NCs), is a crucial step toward realization of functional nanosystems and represents a significant challenge in the field of nanoscale science [1]. In order to utilize the applications of nanostructure materials, it usually requires that the crystalline morphology, orientation and surface architecture of nanostructures can be well controlled during the preparation processes. In this background, the purpose of this investigation is to study the influence of Ni doping on the physical properties of ZnO thin films. Successive Ionic Layer by Adsorption and Reaction (SILAR) is an excellent method for the fabrication of undoped and doped ZnO thin films [2-5]. The photoluminescence property of ZnO is of interest for many years [6,7] and the doping effect on the PL properties of SILAR prepared Ni doped ZnO has not been reported by any group. In this report the PL properties of SILAR grown Ni doped ZnO thin films are reported.

Experimental details

ZnO thin films were prepared using double dip technique. The 'Ni' doping was carried out by adding the respective metallic salts in the solution bath at the proportion of Zn:Ni as 100:3,5,10 respectively. ZnO thin films were grown using a two-step chemical bath deposition technique using a solution comprising 0.1 M Zinc Sulphate (99% e-Merck) , 0.2 M sodium hydroxide with a pH value of 9±0.2 deposited at bath temperature of 90 °C under optimized condition. For Ni doped ZnO (NZO) thin films $NiSO_4$ was used at a concentration of 0.1mM. Before deposition, the glass substrates were cleaned by chromic acid followed by cleaning with acetone. The well-cleaned substrates were immersed in the chemical bath for a known standardized time followed by immersion in hot water for the same time for hydrogenation. The process of solution dip (step 1) followed by hot water dipping (step 2) is repeated for known number of times. The cleaned substrate was alternatively dipped for a predetermined period in sodium zincate bath and water bath kept at room temperature and near boiling point, respectively The addition of MSO_4 in the ratio of Zn:M as 100:3, 100: 10 respectively in the first dip solution leads to the formation of M doped zinc oxide nano thin films where M stands for Ni here. The ZnO thin film formed was confirmed by XRD (Rigaku Ultima III) analysis and the micro structural analysis of the samples were performed using SEM (JEOL Model JSM - 6390LV). The optical properties were estimated by transmittance and absorption measurements using UV-Vis NIR spectrophotometer (PerkinElmer UV WinLab 6.0.3.0730). The room temperature PL measurements were carried out by using the Xe lamp with an excitation wavelength of 360 nm. There are two obvious PL regions for the three different annealing temperatures.

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RESULTS AND DISCUSSIONS

The structure, morphology and other properties of these systems are presented in our paper elsewere [8]. Figure 1 and 2 gives the PL spectra obtained at room temperature. It is found that the strongest ultraviolet (UV) emission peak centered at about 3.2 eV (*372 nm) and a weakest broad green one band centered at 3 eV (408 nm) are from ZnO sample. The effect of Ni doping enhances the intensity slightly and a very low shift towards higher energy in both the excitation and emission spectra. The PL property of Ni doped Nanostructures annealed grown by hydrothermal route [**9**], however has been reported that, the green emission peaks happen into magnification intensity whereas counterparts of UV emissions are decreasing.

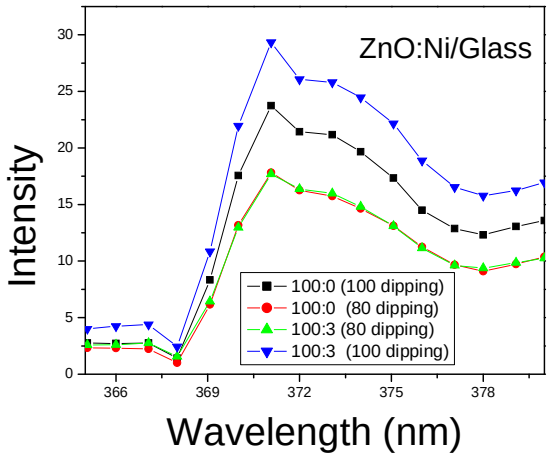

Figure 1. PL emission spectra obtained for Ni doped ZnO films prepared by SILAR with Zn: Ni as 100:0 and 100:3 with various number of dippings excited with 415 nm.

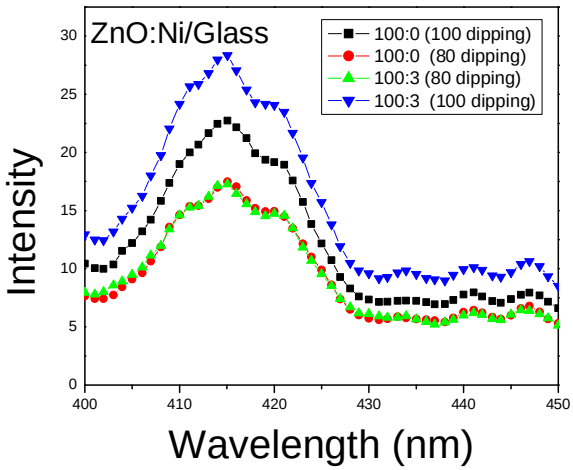

Figure 2. PL excitation spectra obtained for Ni doped ZnO films prepared by SILAR with Zn: Ni as 100:0 and 100:3 with various number of dipping.

For example, the green peak the highest while the UV emission changes into the weaker. The UV peak of ZnO is generally attributed to a recombination of free excitons, namely a near-band-edge transition of wide band gap of ZnO, and the green emission is thought that originates from the recombination of the holes with the electrons occupying the singly ionized oxygen vacancy [10]. After samples are annealed at high temperatures, the excess carriers supplied by the impurities to the conduction band contribute to decrease the electrical conductivity of ZnO. The intensity of the green emission increases strongly, which means that the oxygen vacancy concentration in Ni-doped ZnO NCs increases after annealing at high temperatures [10,11].

It is reasonable because oxygen atoms are easily evaporated during the higher temperature, especially in inert ambient. The red-shift of the UV peak is attributed mostly to the larger grain size and the increase in the peak intensity indicates an improvement of the crystal quality of the ZnO films, which usually occurred during annealing at higher temperatures. Commonly with ZnO a broad green band emission is also observed. While the UV emission corresponds to the near band-edge emission, the green band emission has been attributed to the singly ionized oxygen vacancy in ZnO and results from the recombination of a photo-generated hole with an electron occupying the oxygen vacancy. The stronger the intensity of the blue-green luminescence, the more singly ionized oxygen vacancies there are. The absence of the visible luminescence indicates that there is no substantial oxygen vacancy concentration in the annealed ZnO films.

Conclusions

It is concluded from the PL studies that the ZnO and choice of Ni as dopant can be introduced with ease and an emission panel could be fabricated for many display devices including plasma panels covering a wide range of properties. The increased number of dippings increases the thickness of the film and hence the improvement in intensity is quite visible. The effect of Ni doping enhances the PL intensity slightly and a very low shift towards higher energy in both the excitation and emission spectra.

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