

Growth and characterizations of chemically deposited ZnO:Ag NWs

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Abstract: The present paper reports synthesis of thin films of Ag decorated ZnO nanowires (ZnO@Ag) on FTO substrate by using a two step Chemical Bath Deposition and ultra-sonication techniques. Effect of Ag decoration on structure, morphology and optical properties of ZnO NWs were studied. A denser growth of NWs is observed after decoration of Ag on ZnO in SEM. Hexagonal wurtzite phase with well-defined crystalline peaks were observed in XRD studies. The PL spectra of ZnO@Ag NWs show visible peaks in the range of 575nm-600nm.

Keywords: ZnO, CBD, FTO, nanowires, Ag decorated ZnO NWs, PVP (Polyvinyl pyrrolidone), ethylene glycol (EG),

1. INTRODUCTION:

The II-VI semiconductor nanocrystals are the group of nanostructures that have been investigated because of their high luminescence efficiency and easily adjustable optical properties [1-4] from ultraviolet to near infrared region by nanocrystals. Nanostructures such as nanotubes, nanowires, nanorods, nanobelts, nanocables and nanoribbons [5-10] have been successfully fabricated by different methods. One-dimensional ZnO nanostructures such as nanowires have been extensively studied for other applications including chemical sensors [11], solar cells [12], blue and ultraviolet (UV) light-emitting diodes [13], transparent electrodes, hydrogen storage [14] dyes and pesticides [15] and have a wide range of applications in optoelectronic devices, photocatalysis, solar energy conversion and biological imaging and labelling. There are numerous methods and techniques for deposition of noble metals in thin films forms on substrate, such as physical and chemical vapour deposition [16-19], chemical bath deposition (CBD) [20], and microwave [21]. Among various nanoparticles which have found commercial applications, the silver nanoparticles find several applications. In this work, we presented a simplified approach to prepare ZnO seed layer on FTO substrate through Sol-gel followed by annealing. Long and well-aligned ZnO NWs were synthesized through CBD method based on this ZnO seed layer. Silver nanoparticles are among the nano materials widely investigated because they exhibit unusual optical, electronic and chemical properties. Many successful reports on microwave assisted synthesis of silver nanoparticles are available recently [22-26]. Ag NPs are applied in inks, adhesives, electronic devices,

pastes etc. due to high conductivity [27]. 3D hybrid Ag nanocluster decorated ZnO nanowire arrays [28]. Cone-shaped ZnO-NRs decorated with Ag-NPs. Decorated carbon nanotubes (CNTs) with glutaric acid-functionalized Ag NPs [29]. The Ag NP decorated graphene should be more promising nano filler to improve the electrical conductivity Peng et al. [30]. Recently, Liu's research group developed new in situ approaches to decorate the graphene surface with Ag NPs [31-35]. In this study, we synthesized ZnO NWs arrays decorated with Ag NPs. Pristine and decorated nanostructures have been successfully synthesized by Chemical bath deposition and ultra-sonication method. The as synthesized samples were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Photoluminescence (PL).

2. EXPERIMENTAL PROCEDURES

2.1. Preparation of ZnO NWs Arrays:

The two-step method was adopted to fabricate ZnO@Ag thin film decorated NWs arrays. The FTO substrates were ultrasonically rinsed for 1 h in acetone, isopropyl alcohol, and ethanol solution, respectively. The ZnO seed layers were first deposited on FTO substrates by dip-coating method. After heat treatment at 400 °C for 1 hour the FTO coated seeded substrates were immersed into the aqueous solution (100ml) containing 25 Mm zinc nitrate ($Zn(NO_3)_2$) and 25 Mm hexamethylene tetramine (HMTA) kept in water bath for 5h at 90 °C for the ZnO nanowire preparation by CBD (Chemical bath deposition method). Fabricated ZnO NWs arrays were washed with deionised water and dried at 350°C in muffle furnace. After that, the furnace was naturally cooled down to room temperature and ZnO nanowires arrays were synthesized on the FTO.

2.2 Synthesis of ZnO @Ag NPs arrays:

(A) The Synthesis of silver nanoparticles and their subsequent coating on ZnO NWs was done as follows:

13.6g of PVP (Polyvinyl pyrrolidone) were dissolved in 75mL ethylene glycol (EG), 50mL of this mixture solution was transferred to a beaker, and agitated with a magnetic stirrer before including 0.30g of AgNO₃. Upon the addition of silver nitrate, the light yellow solution of ethylene glycol–PVP slowly changed to light brown indicating the formation of silver nanoparticles. The dissolution of silver nitrate is gradual and lasted for approximately 15 min. The reaction was allowed to proceed at room temperature for 48 h. Then the resulting solution was centrifuged at 10000 rpm for 8 min and washed two times with ethanol and dried in air and kept for decoration of ZnO Nanowires Arrays [36].

(B) Nanowires Arrays decorated with silver nanoparticles (Ag NPs):

To study effect of growth of Ag NPs coating on ZnO NWs arrays, we tried various molar concentration of Ag and various time for deposition of Ag layer. The optimized molar concentration and deposition time for maximum photocurrent and optical absorption was used for further study. For this, we obtained the mixture of weight ratio of 15% of Ag NPs and to these, 45mL ethanol was added and ultrasonicated for 30 min. Solution was divided into three equal parts and all deposited samples were dipped into these solutions and were kept on a magnetic stirrer at 70°C at 700 rpm. After the evaporation of ethanol, the samples were heated at 350°C in a muffle furnace under the same condition. Finally we obtained the sample decorated with Ag NPs arrays. The final products were left to cool at room temperature. The thin films were taken out and dried before the subsequent characterization.

3. RESULT & DISCUSSION

3.1 SEM Studies: The microstructure of the film was analysed using a “Hitachi SU 6600” Scanning electron microscope. The morphology of the as prepared ZnO@Ag were observed in SEM. Fig. 3.1(a)(b) shows the typical SEM images of pristine ZnO NWs sample and ZnO@Ag synthesized by wet chemical methods. From figure 3.1(a) It can be seen clearly that the orderly perpendicular and hexagonal ZnO NWs arrays are grown onto the FTO glass substrates. After decoration of Ag a denser growth of ZnO

NWs is observed in SEM in fig 3.1(b). In fig.3.1 (a) the diameter and length of ZnO are 100-110 nm and ~2μm respectively. After Ag coating the as-prepared ZnO NWs film changed from NWs to a flower like morphology, implying the formation of Ag NPs on the ZnO NWs surface in fig. 3.1(b).

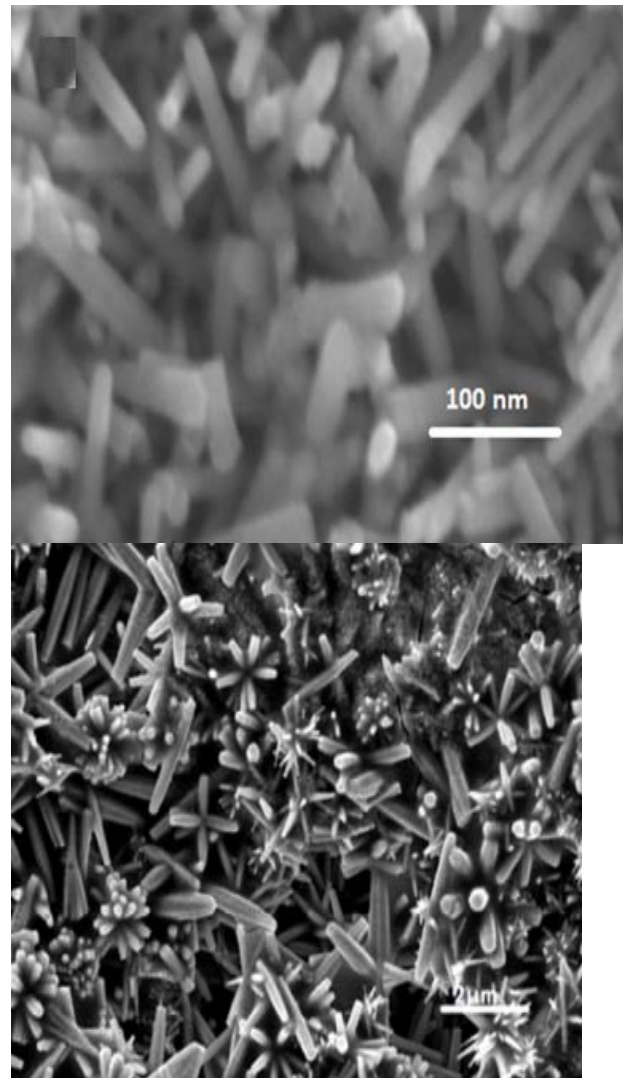


Fig: 3.1 SEM images of (a) Thin film of ZnO NWs grown on FTO (b) ZnO@Ag

3.2 X-Ray Diffraction (XRD) Analysis: The X-ray diffraction (XRD) spectra taken from thin film of pure ZnO NWs arrays and as deposited ZnO @ Ag are shown in fig.3.2 (a) and (b) respectively. Phase identification was carried out by X-ray diffractometer. A diffraction pattern records the X-ray intensity as a function of 2θ (diffraction angle). The peaks in X-ray diffraction pattern are directly

related to the atomic distances. For a given set of lattice planes, with an inter planer distance of ‘d’, the condition for a diffraction peak to occur can be simply written as $2d\sin\theta = n\lambda$ which is known as the Bragg’s law. The positions and the intensities of the peaks are used for identifying the underlying structure or phase of the material. This phase identification is important because the material properties are highly dependent on structure. We can calculate the particle size of the sample from XRD analysis using Debye Scherer’s formula $d = K \lambda / \beta \cos\theta$ where ‘ λ ’ is the wavelength of X-rays, β is the FWHM(Full width of Half Maxima) of diffraction peak and θ is the angle to the corresponding peak[39]. Comparing the XRD pattern of thin films of ZnO NWs Fig. 3(a) with the standard ZnO diffraction pattern (JCPDS, No. 36–1451), we observe all three characteristics peaks (100), (101) and (002) of a wurtzite structure in the as-obtained ZnO NWs; with the most prominent peak along (101) direction. The average crystalline size of the nanostructure array is calculated as 38.9nm for ZnO. However the crystalline size was decreased to 24.7nm when we decorate the thin film of ZnO sample with Ag NPs (cubic jcpds-04-0783).

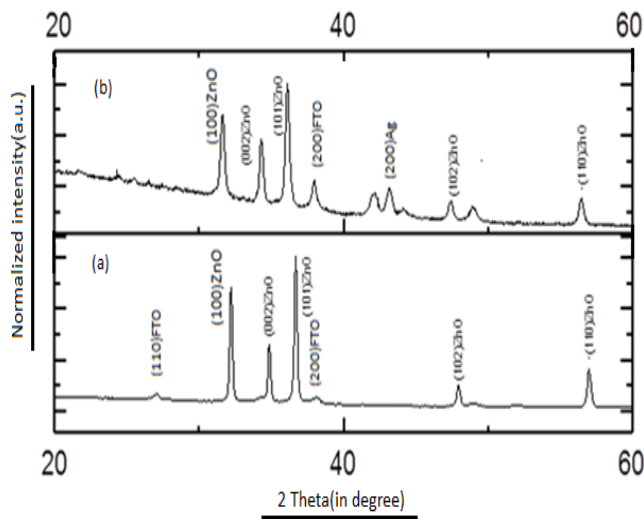


Fig 3.2: XRD graphs of (a)Thin film of ZnO NWs grown on FTO (d) ZnO@Ag NWs grown on FTO

3.3. PL Analysis (Photoluminescence):

The PL emission spectra were recorded with the help of “Shimadzu RF 5301” PC Spectrofluoro-photometer. PL spectra are often used to examine the efficiency of charge carrier trapping and transfer, as well as to understand the fate of photo generated e^-/h^+ pairs in semiconductor particles [40]. Fig 3.3(a) and (b) show the room temperature PL spectra; with 325 excitation of (a) Thin film of ZnO NWs grown on FTO (b) ZnO @ Ag decorated NWs. In fig 3.3(a) UV emission at wavelength 380nm is

observed due to the deep level states such as dislocations, interstitials and Zn^{2+} vacancies in the film, whereas after Ag decoration (fig 3.3(b)), the peaks were shifted to 600nm, which can be associated to presence of Ag. This broad peak can be thought of superposition of various peaks corresponding to various visible transitions, covering the whole visible region, making it a favourable material for solar cell application. The peak observed in the UV region corresponding to direct band to band transition of ZnO is completely suppressed, showing formation of new bands in the band gap region due to decoration of Ag.

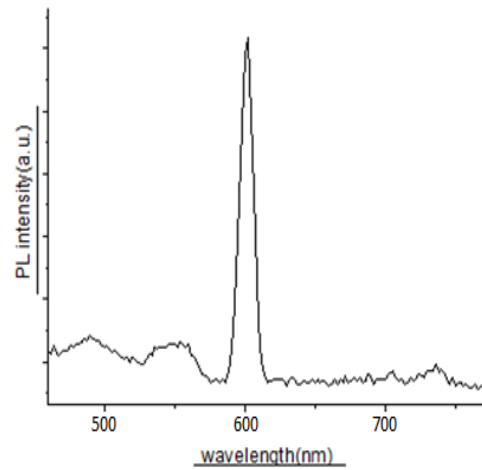


Fig: 3.3 PL spectra of (a) Thin film of ZnO NWs grown on FTO (b) Ag decorated ZnO

4. CONCLUSION: In conclusion, it can be summarized that pristine as well as thin film of ZnO@Ag NWs, are successfully synthesized at room temperature and pressure. The optimum deposition conditions were established for ZnO@Ag thin film fabrication by chemical deposition wet chemical Method. The effect of the Ag NPs decoration on the structural and luminescent properties of decorated thin films ZnO@Ag has been investigated. SEM show a denser growth of particles. The XRD patterns exhibited that the decorated ZnO NWs have excellent crystal qualities and high c-axis orientations. The improvement of film crystalline quality by decoration leads to the appearance of the new peaks with a remarkable red shift in the PL spectrum from 380nm to 600 nm. These decorated thin films of II-VI compounds can be used for solar cell applications, as well as in optoelectronic and display devices.

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