Materials Science in Semiconductor Processing 81 (2018) 22–29

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Influence of post-deposition annealing on structural, optical and transport properties of nanocomposite ZnO-Ag thin films

V.V. Siva Kumar*, D. Kanjilal

Inter-University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi 110067, India

ARTICLE INFO

Keywords:
ZnO
ZnO-Ag_xO
Annealing
Photosensitivity
White light
Deep ultraviolet light

ABSTRACT

Thin films of ZnO and ZnO-Ag were grown by rf sputter deposition and post-annealed in air in the 300–600 °C temperature range. Annealing caused variation in strain in ZnO films and significant improvement of ZnO in ZnO-Ag films. The partial oxidation of Ag into AgxO upon annealing of ZnO-Ag films in air resulted in increase of transmittance, absorption due to Ag_xO phase, weakening of surface plasmon resonance absorption due to Ag nanocrystals and an increase in fluorescence. Surface studies indicate temperature induced particle transport cause agglomeration of nanocrystals in ZnO-Ag films during post-annealing. Annealed ZnO films showed a decrease in dark current and a sixteenfold increase in photocurrent at 3 V applied bias under white light illumination due to the formation of charged acceptors / oxygen vacancy centres, which was comparable to the white light photosensitivity of as-deposited ZnO-Ag film. For low applied bias voltages, Metal-Semiconductor-Metal photoconductive detectors made with annealed ZnO-Ag films showed potential for application as efficient deep ultraviolet (DUV) photodetectors with negligible sensitivity to white light and high sensitivity to DUV light.

1. Introduction

Hybrid metal-semiconductor nanocomposite films are studied extensively for potential use in various plasmonic and photonic applications such as optical sensing, light emitters and photovoltaics. The close proximity of metal and wide bandgap semiconductor nanostructures in such nanocomposite films allows for interaction between excitons and surface plasmons, which are collective oscillations of conduction band electrons in the metal nanostructure arising from the dielectric contrast between the metal nanostructure and the surrounding wide bandgap semiconductor such as ZnO. Metals such as silver, gold and aluminium with surface plasmon resonances in the visible and ultraviolet (UV) regions are usually used in semiconductors to fabricate metal-semiconductor nanocomposites. Of these, silver is advantageous due to its low intrinsic losses, high oscillator strength and large optical field enhancement.

ZnO with its direct wide bandgap of 3.37 eV at room temperature and large exciton binding energy of 60 meV is useful for optoelectronic applications such as light emitting diodes, laser diodes and photodetectors, in the blue/UV regions. Various factors such as trap density, surface recombination of carriers, O_2 adsorption-photodesorption and doping influence the UV photoconduction process in ZnO [1,2]. Silver doped ZnO (ZnO-Ag) material was shown to exhibit high sensing performance for flammable and toxic gases with the response proportional to Ag content due to electronic effects promoted by silver nanoparticles [3]. Previous studies showed that the presence of Ag nanocrystals and oxygen vacancies on ZnO nanorods promoted photogenerated electron-hole separation [4] and enhanced photocatalytic activity, and it is well established that the localized surface plasmon resonance (LSPR) effect in Ag due to UV light results in enhancement in UV photosensing by ZnO-Ag nanocomposite film [2,4]. Also, the bandgap emission of ZnO nanorods was significantly enhanced and the defect emission was suppressed after decoration with Ag_2O nanoparticles [5]. Further, the crystallinity, surface roughness and transport properties of ZnO and ZnO-Ag films depends strongly on substrate temperature during deposition [6,7] and on post-deposition annealing [8]. However, conversion of Ag into AgxO can occur due to heating and semiconductor material (Eg: AgxO; $1 \leq x \leq 2$) with bandgap in the range from 1.5 to 2.2 eV embedded in ZnO thin films can influence the optical absorption of the films in visible region. In view of tremendous interest generated in applications based on visible light absorption property of semiconducting metal oxide materials, such as solar water splitting [9], visible light photoconductivity [10], as well as visible blind UV photodetectors, a study on effect of thermal annealing on white light photosensitivity and UV photosensitivity properties of rf sputter deposited nanostructured ZnO and ZnO-Ag films can be useful.

ZnO-Ag nanocomposite films deposited with 8% of Ag coverage of the ZnO target (2 in. dia) showed poor crystallinity of ZnO which

* Corresponding author.
E-mail address: vvsk@iuac.res.in (V.V.S. Kumar).

https://doi.org/10.1016/j.mssp.2018.03.002
Received 4 January 2018; Received in revised form 6 February 2018; Accepted 1 March 2018

deteriorated as the Ag coverage was increased to 40% [11]. In the present study, we investigate the influence of thermal annealing on changes in crystalline structure, SPR absorption, surface morphology, dark current and photocurrent (under white light illumination) of nanostructured ZnO and ZnO-Ag films with low Ag coverage of 3%. Our results show that thermal annealing caused an improvement in crystalline quality of ZnO and Ag nanocrystals, deterioration of surface morphology, variation in dark current and a decrease in white light photosensitivity for low applied bias voltage.

2. Experimental details

Thin films were grown from ZnO and ZnO/Ag (97%, 3%) targets (2″ dia, 3 mm thick) using rf magnetron sputtering method with argon plasma. The ZnO target was made using ZnO powder (3 N pure, MERCK, USA) and the ZnO/Ag target was obtained by fixing silver pieces (4 N pure, Sigma Aldrich, USA) on the ZnO target covering 3% area. A base pressure of 4×10^{-6} Torr was obtained in the deposition chamber using a Turbo Pump (Varian 300 l/s) backed by a Dry pump (Varian Tri Scroll). Argon gas was fed into the deposition chamber at a flow rate of 2 sccm and the chamber pressure was brought to 70 mtorr and maintained using the Scroll pump. An rf power of 150 W was applied to the target holder and the argon plasma was formed between the target holder (cathode) and the substrate holder (anode) which was covered by a shutter operated using a rotatable feedthru (MKS). The shutter was removed and the thin films were deposited on the Si, glass substrates placed on the substrate holder. The temperature of the substrate holder increased to 100 °C during deposition for 1 h, and hence the deposited ZnO and ZnO-Ag films are designated as ZnO100 and ZA100, respectively. After deposition, the thin films were annealed in air for 1 h at temperatures of 300, 400, 500 and 600 °C.

The deposited and annealed films were characterized by X-ray diffraction (XRD), UV–Vis spectrophotometry, Raman spectroscopy, Atomic force microscopy (AFM) and Current-Voltage (I-V) measurements under dark and visible light illumination conditions. Glancing angle XRD measurements were performed using a Bruker D8 (Advanced AXS) diffractometer at a grazing incidence of 3° with Cu Kα (λ = 1.54 Å) radiation. UV–Vis spectrophotometry measurements were performed in transmission and absorbance modes using Hitachi (U-3300) spectrophotometer. Micro-Raman spectroscopy measurements were carried out on the films under backward scattering configuration with incident light normal to the sample surface using InVia Raman spectrometer (Renishaw) system consisting of Ar ion laser with 514.4 nm wavelength and RenCam CCD detector, in the range 100–2000 cm^{-1}. AFM measurements were performed using Nanoscope IIIa scanning probe microscope (Veeco Instruments, Inc). Field emission Scanning Electron Microscopy (FE-SEM) were performed using FE-SEM (MIRA II LHM, TESCAN) fitted with EDAX attachment (Oxford). Dark current and white light illuminated Current-Voltage (I-V) measurements were done using two-probe method by applying the voltage and measuring the current using a Kiethley 2652 A current source. A probe station equipped with a microscope and tungsten (W) pins was used to make pressure contacts of the tungsten pins with the films which formed a Metal-Semiconductor-Metal (MSM) device structure. A schematic is shown in Fig. 1. The current–voltage data was collected using LabView software. White light illumination was done using standard white light source. An oxide layer on the Si substrate, identified from FT-IR studies, prevents the conduction of carriers photogenerated in the ZnO-Ag film through the substrate to the contacts for low substrate bias voltages or the carriers photogenerated in Si substrate from reaching the contacts. Illumination of the ZnO-Ag films with DUV light having wavelength in the 220–260 nm range was done using a pulsed Xenon lamp (PX2, Ocean Optics) and an extremely solarisation resistant (XSR) optical fibre.

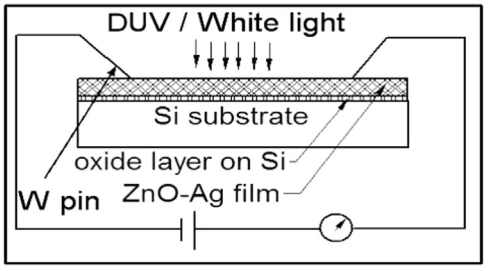

Fig. 1. Schematic of I-V measurement of ZnO-Ag films and structure of the Metal-Semiconductor-Metal (MSM) photoconductive device formed using tungsten (W) pins.

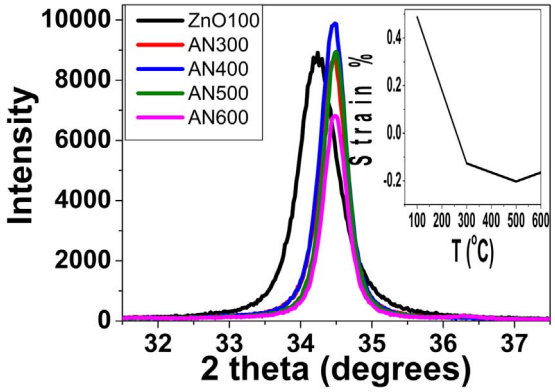

Fig. 2. XRD spectra of the deposited (ZnO100) and annealed ZnO films, with inset showing the trend of strain with annealing temperature.

3. Results and discussion

The XRD patterns of the deposited and annealed ZnO films are shown in Fig. 2. The deposited film (ZnO100) has high c-axis orientation indicated by the presence of a strong peak at 2 theta value of 34.24° corresponding to (002) planes of hexagonal wurtzite ZnO phase. With annealing upto 500 °C, the position of this peak shifts towards higher values of 2 theta and thereafter it shifts marginally to a lower 2 theta value in the spectrum of the film annealed at 600 °C. Further, the intensity of the (002) peak increased for annealing at 400 °C after which it decreased, which suggests improvement in crystalline quality of ZnO for 400 °C annealing and deterioration in it with annealing at 600 °C temperature.

The average crystallite size (D) of ZnO nanocrystals in the films, calculated using Scherrer's formula ($D = 0.9\lambda / B\cos(\theta)$) and (002) peak, increased with annealing from a value of 14 nm for the deposited film to a value of 22 nm for the film annealed at 600 °C. This suggests that smaller grain present in the deposited film are consumed by larger grains due to Ostwald ripening. Also since the films are deposited at low temperature, i.e. RT to 100 °C, it may be assumed that they are composed of ZnO grains in an amorphous ZnO matrix and the amorphous ZnO is converted into crystalline ZnO due to annealing. The strain in the deposited and annealed ZnO films were calculated using the formula:

$$\varepsilon_z[\%] = [(c_f - c_o)/c_o] \times 100 \quad (1)$$

where c_f is the strained lattice parameter of wurtzite ZnO (hexagonal cell) and c_o is the unstrained lattice parameter of bulk ZnO (i.e. 0.52066 nm).

Further, the average strain (ε) was calculated using the relation (2):

$$\varepsilon = (\beta/4)tan(\theta) \quad (2)$$

and the dislocation density (δ) were calculated using the formula (3):

$$\delta = 15*\varepsilon/c_f*D \quad (3)$$