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Tuning the visible photoluminescence in Al doped ZnO thin film and its application in label-free glucose detection

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ABSTRACT

Herein, we study the effect of thermal annealing on the structural and optical properties of Al doped ZnO (AZO) thin film and its application for the label-free detection of glucose based on fluorescence quenching. AZO thin films grown by radio frequency magnetron sputtering are annealed at different temperatures (250–650 °C) in air environment. The post-growth annealing improves the structural quality of the AZO films, as confirmed from the X-ray diffraction, X-ray photoelectron spectroscopy and micro-Raman analyses. The as-grown and annealed samples show strong photoluminescence (PL) in the UV (~3.33 eV) and visible-NIR (1.6–2.2 eV). The UV PL peak is originated from the near band edge emission of crystalline ZnO, while the broad visible-NIR PL is associated with the radiative transition related to oxygen interstitial (O_i) defects in the ZnO structure. The PL peak intensity is strongly enhanced after annealing due to the partial removal of non-radiative defects. The high intensity visible-NIR PL of the annealed samples is used for the label-free enzyme-based detection of glucose with the help of glucose oxidase based on PL quenching via electron transfer mechanism. Our AZO thin films can efficiently detect ~20 μM concentration of glucose in presence of glucose oxidase (GOx). We have attempted to quantify the nature of PL quenching based on the Stern-Volmer plot and explained the quenching mechanism as collisional quenching due to charge transfer in presence of a quencher. The Stern-Volmer plot of PL quenching of AZO thin film reveals the linear relationship between the quenching effect and the glucose concentration. Higher sensitivity of the sensor can be achieved by tuning the structure and doping density of the AZO films. This report opens up avenues for the non-destructive, label-free detection of biomolecules with high sensitivity using a low cost ZnO thin film.

1. Introduction

In last few decades, metal oxide thin films and nanostructures have drawn enormous attention due to their unique physical and chemical properties, and wide range of applications in different areas of nanotechnology. Among others, ZnO nanostructure has emerged as key player due to its high abundance, cheap fabrication process, chemical/thermal stability, non-toxicity, excellent radiation hardness, low electrical resistivity (ρ) of ~10^{-4} Ω-cm, a wide band gap (E_g) of 3.36 eV, a large exciton binding energy of 60 meV and high transparency at room temperature (RT) [1]. ZnO thin films are extensively studied due to its ease of synthesis, fascinating properties and a wide range of applications, such as solar cells [2], LEDs [3], photodetectors [4,5], FET [6], artificial photosynthesis, photocatalysis[7] etc [8]. ZnO and AZO thin films have been extensively used in different type of sensing applications, such as gas sensing [9–12], bio sensing [13–15] and UV detection [16]. In order to improve the electrical and the photophysical properties of ZnO, a variety of group II or III elements, such as Mg, B, Ga, In, and Al are used as appropriate dopants [17–19]. Besides inorganic materials, polymer and organic molecules can be doped in ZnO to tune its optical properties for various applications [20–22]. Al doped ZnO has better thermal, chemical and mechanical stability, non-toxicity, enhanced electrical conductivity due to the increase in free carrier concentration. Its good optical transparency make it a promising candidate as an alternative of costly Indium Tin oxide (ITO) in thin-film photovoltaic applications [11]. The physical properties of thin films mainly depend on the preparation method and the process parameters. A lot of methodologies have been developed for the growth of high quality AZO thin films, such as spray pyrolysis, hydrothermal, thermal evaporation and sputtering

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methods [23–25]. Among these, the magnetron sputtering method is widely used, since it provides film with high surface uniformity, high packing density and strong adherence to the substrate at a high deposition rate to prevent interfacial degradation in devices [26,27]. AZO thin film shows excellent transparency in the visible range and high intensity photoluminescence (PL), which is usually composed of a visible green-red band, related to a deep level defect emission, and an ultraviolet (UV) emission band originated from the ZnO excitonic emission [28,29]. Earlier studies suggest that the annealing of ZnO/AZO film improves the structure and light emission properties of the thin film.

With the increase of diabetic patients, glucose sensing is of paramount importance for the detection of glucose accurately and efficiently. Optical based techniques for glucose sensing are attractive due to its nondestructive and noninvasive nature [30–33]. Recently, ZnO nanostructures have been used for the sensitive detection of glucose by a non-destructive PL based quenching technique [30,34–36]. However, the nature of quenching has not been studied systematically. Further, there is no report on the use of AZO thin film for the sensitive detection of glucose using PL based optical technique.

In case of enzyme-conjugated sensor, the sensitive detection of biological molecules is associated with the PL quenching of a radiative material due to the charge transfer from the radiative material to a quencher (e.g., H_2O_2). Stern-Volmer plot of PL quenching of a fluorescent system can provide important information on the nature of the interaction between the fluorophore and the quencher (e.g., biological molecules), the selectivity and sensitivity of the sensor based on the fluorescence spectroscopy. Since efficient PL quenching of AZO thin film is highly desirable for a biomolecular sensor, it is imperative to understand the quenching mechanism.

In this article, we report on the growth of AZO thin films on Si substrate by a RF magnetron sputtering method using a high quality AZO target. As-grown films were annealed at different temperatures in a muffle furnace. The AZO thin film shows highly efficient visible PL before and after annealing, due to the intrinsic defects in ZnO. The post-growth annealing not only improves the structural quality of the AZO films, but also enhances the intensity of UV (~3.3 eV) and broad visible-NIR PL (1.6–2.2 eV) emission. The UV PL peak is originated from the near band edge emission of crystalline ZnO, while the broad visible-NIR peak is usually associated with the radiative transition related to oxygen interstitial (O_i) defects in the ZnO structure. The high intensity PL of the annealed samples was utilized for the label-free detection of glucose based on the PL quenching process. Our results show that AZO films can efficiently detect ~20 μM concentration of glucose in presence of glucose oxidase and the sensing follows a linear behaviour over a wide range of glucose concentrations (20 μM – 10 mM). We attempt to quantify, for the first time, the nature of PL quenching of AZO thin film in glucose-GOx medium using the standard Stern-Volmer plot. This enables us to quantify the sensing efficiency of AZO thin film and to explore the nature of interaction between the fluorophore and the quencher.

2. Experimental details

2.1. Deposition of AZO thin film

AZO thin films were grown on Si(100) and quartz substrates by RF magnetron sputtering at room temperature. At first, Si wafers and quartz substrates were cleaned by standard protocol and dried under Ar gas flow. Commercial AZO target (purity = 99.99%, Kurt J Lesker, USA) with ZnO:Al_2O_3 = 98:2 (wt%) was used for the growth of AZO thin films. We optimized the growth of AZO film by RF sputtering and found that a RF power of 100 W gives rise to reasonable deposition rate and good quality (polycrystalline) film. As-grown AZO thin films (Sample code, AZO) were thermally annealed in a muffle furnace at temperatures 250 °C, 450 °C and 650 °C for 1 h in air environment and the annealed samples are named as AZO250, AZO450 and AZO650, respectively.

2.2. Characterization techniques

The thickness of the AZO films was measured by a profilometer (Vecco, Dektak 150) and the thickness was found to be ~415 nm. The morphology and topography of AZO samples before and after annealing were characterized using a field emission scanning electron microcopy (FESEM, Sigma, Zeiss) and atomic force microscopy (AFM, Bruker). For structural characterizations, X-ray diffractometer (XRD) (Rigaku RINT 2500 TRAX–III, Cu Kα radiation) and an energy-dispersive X-ray spectrometer (EDX) were used. X-Ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI X-Tool automated photoelectron spectrometer (PHI X-tool, ULVAC-PHI Inc.) using Al K_α X-ray beam (1486.6 eV) with a beam current of 5 mA. Carbon 1s spectrum (284.8 eV) was used for the calibration of the XPS spectra recorded for various samples [38]. XPS measurement was performed with a step size of 0.2 eV. The steady state PL spectrum of different samples was recorded using 355 nm and 405 nm diode lasers (CNI Laser) excitation with the help of a commercial fluorimeter (Horiba Jobin Yvon, Fluoromax-4). Raman scattering measurement was carried out with a 532 nm Ar laser excitation using a micro-Raman spectrometer (LabRAM HR-800, Jobin Yvon). UV–vis absorption spectra were recorded in a Shimadzu 2450 UV–vis spectrophotometer. Time resolved PL (TRPL) measurements were performed using a 405 nm pulsed laser excitation, with an instrument time response of <50 ps (LifeSpecII, Edinburgh Instruments).

2.3. Glucose sensing measurement

For the glucose sensing measurement, Glucose oxidase (GOx) from Aspergillus Niger (Sigma-Aldrich) in 0.01 M phosphate buffer solution (PBS, pH7) stock solution was prepared with concentration 2 mg/ml. Simultaneously, D-glucose (Merck) solutions with concentration 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 4, 5, 7, 10 and 20 mM were prepared in PBS. 1 mL D-glucose solutions were mixed with 1 mL GOx solution in a 5 mL centrifuge tube and AZO samples (size ~8 × 8 mm^2) were dipped for 40 min in dark at room temperature. The samples were taken out and the sensing measurements were performed using a commercial fluorimeter (Horiba Jobin Yvon, Fluoromax-4) along with external laser excitation source (405 nm, 10 mW). PL intensity for each sample was measured at room temperature under identical conditions.

3. Results and discussion

3.1. Morphology and structural analysis

3.1.1. Atomic force microscopy (AFM)

AFM micrographs of AZO thin films on Si wafer before and after annealing (at 450 °C) are shown in Fig. 1(a) and (b), respectively. The corresponding line profiles are shown in Fig. 1(c) and (d), respectively. AFM confirms that the roughness of the sample is marginally increased and the average grain size is also increased after annealing. The RMS roughness of the as grown AZO sample is found to be 3.00 nm for a 2 × 2 μm^2 AFM image, while it is 3.05 nm for AZO450. Note that the shape of the grains is arbitrary and looks like “disc”, which is also confirmed from the FESEM analysis, as shown in Fig. S1(a) (as-grown sample) and S1(b) (annealed sample) (Supporting information).