Thin Solid Films 558 (2014) 378–384

Contents lists available at ScienceDirect

Thin Solid Films

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

Annealing effects on zinc oxide-silica films prepared by sol–gel technique for chemical sensing applications

Atif Mossad Ali [a,b,*], Adel A. Ismail [c,d], Rasha Najmy [e], Ali Al-Hajry [c,f]

[a] Department of Physics, Faculty of Science, King Khalid University, Abha, Saudi Arabia
[b] Department of Physics, Faculty of Science, Assiut University, Assiut 71516, Egypt
[c] Promising Centre for Sensors and Electronic Devices (PCSED), Najran University, PO Box 1988, Najran 11001, Saudi Arabia
[d] Central Metallurgical R&D Institute, CMRDI, Helwan, Cairo 11421, Egypt
[e] Science Department, Girls' College of Education, King Khalid University, Saudi Arabia
[f] Department of Physics, College of Science and Arts, Najran University, Saudi Arabia

ARTICLE INFO

Article history:
Received 22 May 2013
Received in revised form 14 February 2014
Accepted 14 February 2014
Available online 21 February 2014

Keywords:
Zinc oxide
Silicon dioxide
Composite
Sol–gel deposition
Chemical sensors
Optical band gap
Photoluminescence
Structural properties

ABSTRACT

ZnO:SiO_2 films are prepared by sol–gel technique on Si substrates. The effect of annealing temperatures (T_a) on the structure, surface morphology, and optical and photoluminescence (PL) properties of these films is studied. The X-ray diffraction analysis revealed that the *c*-axis orientation and the grain size of ZnO:SiO_2 films increased at high T_a. High-resolution transmission electron microscopy results showed that the ZnO nanoparticles are spherical in shape with their size increasing from 5 to 15 nm with T_a while PL spectroscopy showed few separated PL bands. In addition, two optical band gaps located at 3.0 eV and 4.2 eV are observed and showed a redshift with T_a up to 600 °C, and then a blueshift is observed at 800 °C. ZnO:SiO_2 film was tested as sensors for the detection and quantification of phenyl hydrazine. It is found that ZnO:SiO_2 films showed good sensitivity of 390 μA mM^{-1} cm^{-2} and a lower limit of detection of 3 mM with linear dynamic range of 0.05 mM to 3 mM and rapid reaction kinetics (in the order of seconds). The cycling tests indicated that the ZnO:SiO_2 films are quite stable since no significant decrease in sensitivity was observed even after being used repetitively for 3 times, showing a good potential for practical applications.

1. Introduction

Zinc oxide (ZnO) is a wide band gap (~3.3 eV) and large exciton binding energy (60 meV) semiconductor with high sensitivity to combustible and reducing gases. It exhibits many characteristics leading to its promising application in many devices such as ultra-violet (UV) light-emitting devices, solar cells, surface acoustic wave devices, transparent electronics, and chemical, gas, vapor, and humidity sensors [1–5]. In recent years, the silica-based nanocomposites are considered the most challenging system for the quantum confinement of semiconductor nanocrystallites for a better control of shape, size and properties. Among these, zinc oxide-silica (ZnO:SiO_2) nanocomposite films are considered as an important assembly for the optoelectronic applications and gas sensing materials [5]. Zinc oxide films are prepared by different techniques such as pulsed laser deposition, sputtering, spin coating, chemical vapor deposition (CVD), and spray pyrolysis [6–10]. In addition, various techniques have been employed, including impregnation [11], molecular capping [12], sol–gel [5,13], etc., for the dispersion of ZnO nanoparticles in silica [5,11,13] or polymeric [12] matrices in order to avoid the tendency of nanoparticles to aggregate. However, the sol–gel method provides easy control of chemical components, high yield, short time, low power consumption, and efficient and low-cost process for the deposition of meso- and microporous silica-based films to investigate optical and structural properties of ZnO:SiO_2 films [5]. Nanostructured zinc oxide is one of the most promising metal oxide semiconductors for gas sensing due to its high surface to volume ratio. Moreover, it is a high chemical sensitive material because it has more chemically active centers. In this work, nanostructured ZnO:SiO_2 films prepared by sol–gel technique on Si substrates, are characterized, and the effects of annealing temperatures (T_a) on the microstructure and optical properties of the films are investigated. Then these films were used as a phenyl hydrazine chemical sensor as a promising application for this material.

2. Experimental details

2.1. Film preparation

SiO_2 sol was obtained from the addition of a tetraethoxysilane, H_2O, C_2H_5OH, and HCl. The equivalent molar ratio of each was 1:4:5:0.25. The

* Corresponding author at: Department of Physics, Faculty of Science, King Khalid University, Abha, Saudi Arabia. Tel.: +966 17 241 7099; fax: +966 17 241 8319.
E-mail address: atifali@kku.edu.sa (A.M. Ali).

http://dx.doi.org/10.1016/j.tsf.2014.02.058
0040-6090/

mixture was stirred for 30 min at room temperature (RT) to complete hydrolysis then forming the sol. To prepare the ZnO:SiO_2 nanocomposite films, $Zn(CH_3COO)_2$ was added to SiO_2 sol under vigorous stirring for 3 h to obtain 5 % wt% ZnO:SiO_2 composites. The films then were deposited on a silicon (Si) substrate (P(100)), by spin coating technique. Si substrates were washed with acetone, submerged in a beaker containing aqueous solution of HF (5%) for surface treatment, and rinsed with water, and then air dried. Spin speed was fixed at 2000 rpm with a spinning time of 60 s. After aging in air for 24 h, the samples were annealed at different temperatures for 4 h.

2.2. Films characterization

The structural properties of the overall films were studied by X-ray diffraction (XRD) technique using a SHIMADZU XD-D1 with Cu Kα radiation (λ = 1.5406). The vibrational spectra were measured by a Fourier transform infrared (FTIR) spectrometer (JASCO FT/IR-610) at a normal incident light under vacuum, using the same Si wafer with the Si substrate as a reference. The Raman spectra were measured by a Raman spectrometer with a double monochrometer (Jobin Yvon RAMANOR HG 2S) coupled with a cooled photo-multiplier tube (Hamamatsu R649S) and an Ar-ion laser at 488 nm.

Photoluminescence (PL) spectra were determined with a monochrometer and photomultiplier tube (PMT) detector over the visible range using excitation by a He–Cd laser (λ = 325 nm). PL excitation spectra were obtained using 300 WXe lamp as the excitation source with a monochromator and a PMT detector. To examine the optical properties of ZnO:SiO_2 nanostructures, RT UV–Visible spectroscopy (Perkin Elmer-UV/VIS-Lambda 950) was used.

Field emission-secondary electron microscope (FESEM) images were obtained with an FE scanning electron microanalyzer (JEOL-6300 F, 5 kV) equipped with energy dispersive spectroscopy, while the nanoscale structure of the films were studied by a high-resolution transmission electron microscope (HRTEM). TEM was conducted at 200 kV with a JEOL JEM-2100 F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. In addition, the general morphology of the ZnO:SiO_2 films was examined by atomic force microscopy (AFM). Tapping mode AFM experiments were performed on a Solver Next AFM microscope (Molecular Devices and Tools for Nano Technology (NT-MDT Co)).

2.3. Fabrication of phenyl hydrazine chemical sensor using current–voltage (I–V) technique

For the fabrication of phenyl hydrazine sensor, a typical two-electrode setup was employed using the electrochemical workstation, Zahner Zennium, Germany. Si-coated ZnO:SiO_2 thin film was used as a working electrode with a surface area of 1 cm^2, while a Pt wire was used as a counter electrode. The electrical contact for silicon substrate was made on the backside using Ag paste and a Cu wire as a current collector. A phosphate buffer solution (0.1 M, pH 7.0) was prepared by mixing 0.2 M from both Na_2HPO_4 and NaH_2PO_4 in 100 ml pure water. If necessary, the pH was adjusted using 0.1 M NaOH. Various concentrations of phenyl hydrazine (0.05–12.5 mM) as a target analyte were prepared by dilution. The current–voltage response (*I–V*) was then recorded from 0.5 to 1.9 V, whereas the delaying and response times were respectively 1 and 10 s. All measurements were conducted at RT under stagnant conditions. The sensitivity of the sensor for phenyl hydrazine was estimated from the slope of the calibration curve of current versus concentration divided by the surface area of the working electrode.

3. Results and discussion

Fig. 1 shows X-ray diffraction spectra of the nanocomposite ZnO:SiO_2 thin films prepared by sol–gel technique on Si substrates and annealed at different temperatures. It can be seen that the diffraction patterns of ZnO:SiO_2 samples are mainly composed of ZnO phase. As seen in Fig. 1, a strong Si(111) peak at 28.3° is observed for the as-prepared film, the annealed films at 200 °C and 400 °C. Then this peak disappears, and three peaks located at 32.1°, 34.2° (weak), and 35.7° (weak) appear, corresponding to ZnO(100), ZnO(002), and ZnO(101), respectively, for films annealed at 600 °C, 800 °C, and 1100 °C. Moreover, as shown in Fig. 1, the relative intensity of the ZnO(100) diffraction peak compared to the (002) peak increases gradually by increasing the T_a. It is observed that the *c*-axis orientation of ZnO films increases by increasing the T_a. Therefore, it is suggested that the ZnO:SiO_2 thin films are nanocrystalline and well matched with the hexagonal crystal structure having preferred orientation along the (100) plane. It is well known that ZnO usually grows along the (002) direction (*c*-axis perpendicular to the substrate) due to the lower surface free energy of the (002) plane. It has been reported that the structure of ZnO films evolves from (002) crystal plane growth mode to (100) mode, i.e., (002)–(110)–(100)–(101) crystal plane, which is related to the different surface free energies associated with different planes [14] in good agreement with the present work. In addition, the substrate temperature activates the ZnO film growth from relative lower surface free energy to higher surface free energy. Singh et al. [15] reported that the orientation was found to depend on the substrate temperature and the type of the substrate. The films deposited on Si show predominant (100) orientation, while those deposited on glass show a strong *c*-axis oriented crystal structure with (002) preferred orientation. Moreover, the latter authors found that the (100) peak dominates when the substrate temperature gradually increased [15], which is consistent with the present XRD results. Lu et al. [16] synthesized ZnO films by CVD with (100) preferred orientation on Si(100) and α-Al_2O_3 (0001) substrates. They suggested that in this type of texture of the deposition at a non-equilibrium state (e.g., low temperature and/or high deposition rate), the surface free energy of the (002) plane is not necessarily smaller than those of other planes. A large density of defects (e.g., vacancies and/or the interstitials), impurities in the films, or the deposition at a non-equilibrium state can all result in another orientation. The preferred orientations (like the (100) orientation) should be investigated since they could possess different properties and contribute to promising applications. Chao et al. [17] synthesized ZnO films that exhibited a single diffraction peak of (100). The films were obtained by CVD on Si(111) heated to 460 °C. It was stated that (100) ZnO films might find special applications in non-linear optics [17]. In the present study, it is shown that ZnO:SiO_2 nanocomposite films that possess ZnO particles exhibiting a (100) orientation can be prepared by the sol–gel technique. Moreover, the positions of the diffraction peaks for each phase do

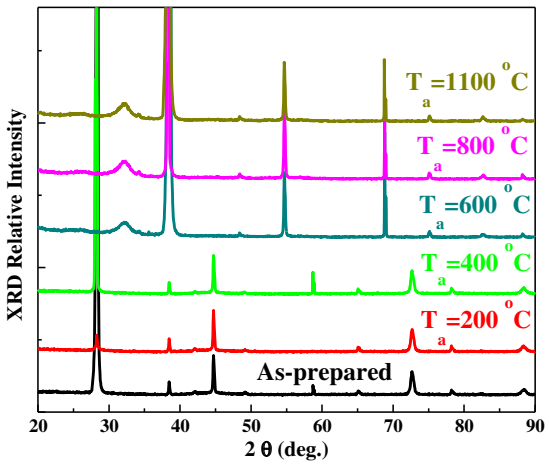

Fig. 1. X-ray diffraction spectra for nanocomposite ZnO:SiO_2 thin films annealed at different temperatures.