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ZnO thin film prepared by a sol-gel spin coating technique for NO_2 detection

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ABSTRACT

The ZnO thin film sensor is developed by a low-cost sol–gel spin coating technique on a glass substrate. The structural, morphological, surface compositional, optical and electrical properties of the ZnO thin film were studied using XRD, FESEM, XPS, HRTEM, FTIR and UV–VIS techniques. The gas sensing performance of ZnO thin film is studied at different operating temperature for various gases like NO_2, NH_3, CH_3OH, Cl_2 and H_2S. The ZnO thin film sensor was highly selective towards NO_2 gas with a maximum response of 12.3 at 100 ppm concentration at 200 °C operating temperature. ZnO film sensor can also detect low concentration of NO_2 gas up to 5 ppm with the response of 4.1. The ZnO thin film sensor shows excellent repeatability, high stability and moderate response and recovery time, for NO_2 gas in the 5–100 ppm concentration range.

1. Introduction

Nanocrystalline metal oxide including SnO_2, ZnO, TiO_2, CuO, Fe_2O_3, WO_3, Ga_2O_3 and V_2O_5 in the form of thin films and nanostructures are promising candidates for high-performance gas sensors for their excellent gas sensing properties towards various toxic and pollutant gases [1]. Among these, ZnO has been most attractive material because of its structural diversity, high detection sensitivity and stability towards most of the oxidizing as well as reducing gases [2]. ZnO gas sensors have been widely studied towards various gases like acetone, CO, ethanol, H_2, H_2S, LPG, NH_3, and NO_2 [3–10].

The detection of toxic gases (CO, SO_x, NO_x, NH_3, and ethanol) plays a vital role to conserve our environment unpolluted and personal safety because of their enormous effects on human health and environment [11]. Nitrogen dioxide (NO_2) is produced from natural as well as anthropogenic sources; natural sources like emission from bacteria, volcanic activity, lightning and anthropogenic sources like power generation, heating, internal combustion engines in automobile and naval applications [12]. NO_2 is highly toxic and most harmful gas which affects on human's nervous system and could cause to lose consciousness at a very low concentration [13]. According to WHO's 2005 air quality guidelines, NO_2 is a free radical, it could reduce tissue antioxidant defences due to causes injury and inflammation [14]. During the controlled NO_2 exposures, more than 1 ppm concentrations are enough to induce changes in pulmonary function in healthy adults. On repeated exposure to high concentrations of NO_2 gas (1–5 ppm) disturbs breathing and ventilatory function, like increase in breathing frequency and reduced lung gas exchange [12,14]. Thus, there are strong demands for highly sensitive and selective NO_2 gas sensor, which can detect NO_2 gas at a low concentration (10–100) [13]. Therefore, we make an attempt to fabricate a gas sensor based on ZnO thin film, which detects NO_2 gas at lower concentrations.

In the present study, we proposed here a new route to develop ZnO thin film sensor by the sol–gel spin coating technique. Sol-gel spin coating technique have various advantages for synthesis ZnO thin film, like low cost, low annealing temperature, growth of large area film, simple working principle and compositional modifications [15,16]. The synthesized film was characterized by using X-ray powder diffraction (XRD), Field emission scanning electron microscope (FESEM) with EDS, X-ray photoelectron spectroscopy (XPS), High-resolution transmission electron microcopy (HRTEM), Fourier transform infrared spectroscopy (FTIR) and Uv–vis spectroscopy. The gas response of the film was investigated towards NO_2, NH_3, CH_3OH, Cl_2 and H_2S gases at different operating temperature. Also, different gas sensing parameters were studied such as gas response, selectivity, response/recovery time, reproducibility and stability.

2. Experimental procedure

2.1. Fabrication of ZnO thin film

The ZnO thin film was prepared by the sol-gel spin coating technique onto a glass substrate using zinc acetate dihydrate [Zn $(CH_3COO)_2 2H_2O$] as a source of Zn. The precursor solution (0.2 M) was

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prepared by dissolving required amount of zinc acetate (99.99%, A.R. Grade Thomas Baker) in absolute ethanol and m-cresol (99.99%, A.R. Grade, Merck) and the mixture were vigorously stirred at 70 °C for 90 min until a clear and homogeneous solution. To improve the homogeneity of the prepared solution, it was kept in an air tight beaker for 24 h at room temperature and then prepared to deposition. The precursor gel preparation method adopted from Nimbalkar et al. and makes some changes in that method [17]. The solution was deposited onto a pre-cleaned glass substrate by a single wafer spin coater (APEX Instruments, Model spin NXG-P1). After setting the substrate on the substrate holder of the spin coater, 0.5 ml of coating solution was dropped and spin-coated at 2000 rpm for 40 s in an air and dried on a hot plate at 200 °C for 5 min. To attain desired thickness of ZnO film, the above procedure repeated 10 times. At last, to obtain nanocrystalline ZnO thin film, prepared film was annealed at 400 °C for 2 h in air ambient.

2.2. Characterization techniques

The structural properties of the ZnO thin film were carried out using a Bruker D2 phaser X-ray diffractometer with Cu Kα radiation (1.54056 Å) in a 2θ range from 20 to 90°. The surface morphological study of the ZnO thin film was investigated using field emission scanning electron microscopy (Zeiss Ultra 55 FE-SEM with Oxford EDX system). The elemental compositions and valence states of ZnO thin film were determined by using X-ray photoelectron spectroscopy (XPSPHI 5000 Versa Probe II USA). High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images were obtained using Tecnai G2 F30, FEI. To investigate the chemical species in ZnO thin film fourier transform infrared spectroscopy (FTIR) measurement was carried out using FT/IR-4600 Jasco, Japan. The absorption spectra of the ZnO thin film were measured using UV–Vis-NIR V-770 Jasco, Japan in the 300–1000 nm wavelength range. The thickness of ZnO thin film was measured by using Bruker Dektakxt profilometer and is found to be 151 nm (± 10 nm). The DC electrical conductivity of the ZnO thin film was measured by using a locally fabricated two-probe technique in the temperature range 300–573 K.

2.3. NO_2 sensing properties ZnO thin film

The NO_2 gas sensing performance of ZnO thin film was studied by using a custom fabricated gas sensor unit. In order to study gas sensing performance, the resistance of the ZnO thin film was measured in presence and absence of test gas (NO_2). For gas sensing measurement, two silver electrodes, each 1 mm thick and separated by 10 mm from each other were deposited on ZnO thin film for the superior and constant electrical contacts. The variation in resistance of ZnO film was measured using Keithley 6514 Electrometer data acquisition system (Keithley, USA). To investigate the gas response of the ZnO thin film towards different gases, the film was mounted in air tight test chamber having a volume 250 cm^3 with temperature controller system and the known gas (NO_2, NH_3, CH_3OH, Cl_2 and H_2S) of desirable concentration was injected through a syringe into the test chamber. The gas sensing measurement was carried out in the temperature range 100–300 °C. The electrical resistance of ZnO thin film in the air (R_a) and in the presence of oxidizing test gas (R_g) were measured to calculate the gas response R_s, defined as follows: $R_s = R_g/R_a$ (for reducing gas $R_s = R_a/R_g$).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the X-ray diffraction pattern of the ZnO thin film on glass substrate. The spectra show sharp and well-defined peaks, all diffraction peaks and lattice constants are well matches with the JCPDS card No. 01-079-0205 (a = 3.2417 Å and c = 5.1876 Å). The XRD

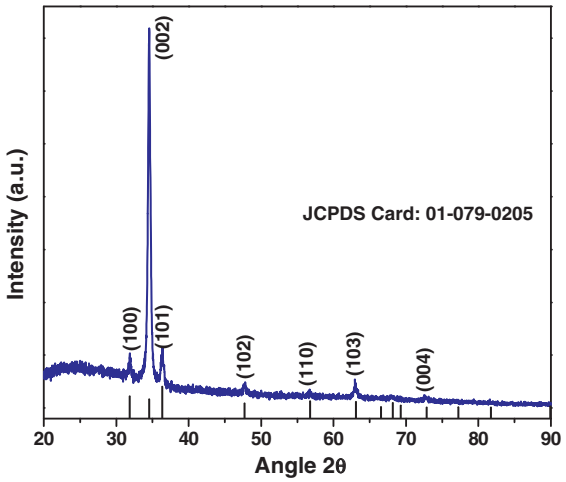

Fig. 1. X-ray diffraction pattern of ZnO thin film.

pattern of ZnO thin film was indexed to a hexagonal wurtzite structure with diffraction peaks of ZnO at 2θ = 31.86°, 34.53°, 36.38°, 47.69°, 56.67°, 62.97°, 72.70° are reflected from (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (0 0 4) in agreement with previously reported values [9,18]. The peak intensity of the (0 0 2) is higher than the other peaks, and which is illustrates that the ZnO nanocrystallites were oriented in their c-axis with hexagonal wurtzite crystal structure and grown along the (0 0 2) plane. The (0 0 2) plane of nanostructured ZnO film is regarded as an energetically stable crystal plane with least amount of surface free energy [19]. The growth of ZnO nanocrystallites along the (0 0 2) plane due to the growth of ZnO film is significantly preferred by the ZnO polar structure, which contains positively Zn^{2+} and a negatively O^{2-} ions, because of this a net dipole moment induces along the c-axis as well as the fastest growing rate as compared to the nucleation of nanocrystallites along the other planes [18–20]. The c-axis preferred orientation confirms a good quality of ZnO film and absence of a secondary phase formation in the synthesized film [19]. The average crystallite size (D) was determined by using Scherrer formula and it was found to be 32 nm.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

where 'D' is crystallite size, 'λ' is the of X-ray wavelength of Cu-K_α line, 'β' is the 'Full width at half maximum' (FWHM) of the peaks, 'θ' is the Bragg angle [21].

3.2. XPS analysis

The X-ray photoelectron spectroscopy (XPS) is a useful technique to investigate the surface composition and valence states of the material. Fig. 2(a) shows the wide region XPS survey spectrum of ZnO thin film. The wide energy spectrum reveals the existence of zinc (Zn), oxygen (O) and carbon (C) elements in the film, illustrate the purity of ZnO thin film. The 283.26 eV, the binding energy of C 1s is used as a charge reference in the spectrum [22] shown in Fig. 2(b). Fig. 2(c) shows narrow scan XPS spectra of ZnO thin film for Zn 2p doublet. The two peaks Zn $2p_{1/2}$ and Zn $2p_{3/2}$ are located at 1044.06 eV and 1021.05 eV respectively with the spin-orbit splitting of 23.01 eV, which confirms the existence of Zn atoms are in the oxidized state [23]. The O 1 s peak shown in Fig. 2(d), the peak exhibited at around 529.79 eV reveals the oxidized metal ions in the nanocrystallites, namely O–Zn in the ZnO lattice [24].

3.3. FESEM, EDX and HRTEM analysis

The surface morphology of ZnO thin film was investigated by using