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Enhancement in alcohol vapor sensitivity of Cr doped ZnO gas sensor

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ABSTRACT

In this work, we have demonstrated that Cr doping enhances the ethanol sensitivity of ZnO thin film based gas sensor. Cr (0 and 5 wt%) substituted ZnO thin films have been grown on Al_2O_3 substrate using pre-doped target through RF magnetron sputtering technique. XRD and Raman analyses confirm single phase wurtzite structure of the films and average crystallite size reduces on Cr substitution . SEM images exhibit particles of Cr doped ZnO are more uniform and smaller than the undoped thin film. EDS and XPS spectra revealed successful doping of Cr^{3+} ions and formation of oxygen vacancy on the surface of ZnO film. Moreover, the doping effect enhances the sensitivity of ZnO sensor almost two times and an improvement in the response time/recovery time was also observed. This may be due to increase in surface to volume ratio which leads adsorption of more numbers of ethanol gas molecules at the surface.

1. Introduction

Nowadays, gas sensors are extensively demanded for a wide variety of domestic and industrial applications to monitor exhaust harmful, flammable and toxic gases [1]. The gas sensing study of various metal oxides like ZnO, SnO_2, WO_3, TiO_2 and others [2–6], has been already reported in literature. Among all, ZnO with a wide band gap (3.37 eV) and high excitonic energy (60 meV) is a promising material being the advantages of nontoxic, abundant, inexpensive, easy to prepare and numerous structures [7]. Because of diverse applications in modern electronic and optoelectronic devices, ZnO in thin film structure is most demanded and already used in heat mirrors, UV light emitters, transparent conductive layer in solar cells, light emitting diodes (LED), lasers, thin film transistors (TFT), piezoelectric transducers, liquid crystal display (LCD) and other devices [8–12]. Due to larger exposed surface area, ZnO thin film nanostructure is expected to improve the gas sensing response at low operating temperature. The sensing studies of undoped and doped ZnO thin films have been already tested for different gases like ammonia (NH_3), carbon monoxide (CO), nitrogen dioxide (NO_2), methane (CH_4), alcohol, and others [13–15]. Ethanol vapour has been one of the most extensively studied gas for the metal oxide gas sensors. Ethanol gas sensors can be used in many fields such as biomedical, chemical, the control of fermentation processes, leaks in industrial distribution lines, wine quality monitoring, safety testing of food packaging and also to monitor drunken driving [16,17]. Current research on ethanol gas sensing has been focused on the development of sensors based on low cost, quick response and high sensing information to meet all the demand for fast, incessant and trace detection. But, traditional ZnO gas sensors suffer from high operating temperature, poor selectivity, and relatively low response, which limit their applications in real-time gas sensing, often in favor of more expensive approaches [18]. As most of the ZnO thin film based gas sensors are operated at the temperatures above 200 °C, which makes it necessary to implement heating structure in sensor device. The life time and long term stability of these sensors are found to decrease after operating at elevated temperature [19]. Several techniques, such as surface functionalization, hetero-structure formation and doping have been utilized to overcome the above stated drawbacks [20]. In this direction, doping is one of the most effective way to improve the gas sensing response because dopants could alter the energy band structure, mending the morphology and surface-to-volume ratio, creating more active center at the grain boundaries, producing defects and vacancies. Aluminium (Al), indium (In), gallium (Ga) and transition metals, such as titanium (Ti), cobalt (Co), iron (Fe), nickel (Ni), manganese (Mn) and vanadium (V) already proved as successful dopants for ZnO in various applications [21,22]. Compared with above stated elements, Cr has often doped into ZnO matrix to modify its optical,

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electrical and ferromagnetic properties [20,23] and until now, it does not apply widely in gas sensing application. In addition, as Cr^{3+} and Zn^{2+} have closely ionic radius, Cr^{3+} can easily replace to occupy Zn^{2+} position into the ZnO crystal lattice. So, Cr doped ZnO might be a hopeful option to enhance the gas sensors sensitivity. It is known that the undoped and doped ZnO thin films can be grown by different chemical/physical techniques, such as, sol- gel, thermal evaporation, sputtering, chemical vapor deposition, pulse laser deposition, and molecular beam epitaxy [24,25]. Among all, sputtering is our first choice due to its adequate advantages, like growth of thin film at relatively low temperature, good interfacial adhesion to the substrate, control the preferred crystalline orientation and high packing density of the grown film.

In this research work, we have deposited undoped and 5 wt% Cr doped ZnO thin films on Al_2O_3 substrate by RF magnetron sputtering and studied their ethanol gas sensing performance at a temperature of 100 °C, which to the best of our knowledge has not been reported earlier.

2. Experiment and characterizations

2.1. Thin films preparation

ZnO and 5 wt% Cr doped ZnO thin films were grown on Al_2O_3 (0001) (10 mm × 10 mm) substrates via RF magnetron sputtering technique at room temperature. Both films were deposited from the synthesized Cr doped (0% and 5%) ZnO targets, however Zn and Zn–Cr metal target were used in earlier reported studies [1,8,25,26]. These targets (50 mm diameter and 3 mm thickness) were prepared through simple sol-gel method and sintered at 500 °C for 4 h. In the starting, Al_2O_3 substrate was cleaned very carefully through various cleaning steps. The target to substrate distance was fixed at 70 mm. The chamber pressure was fixed around 4×10^{-3} mbar by starting diffusion pump. The ultimate pressure was created 1×10^{-6} mbar through high vacuum system. The chamber pressure was further raised to 3×10^{-2} mbar by adding high purity argon (Ar) gas. Before starting deposition on substrate, the target was pre-sputtered for 15 min keeping the substrate covered to remove the contamination of target surface. Both films were deposited at a fixed RF power of 100 W and deposition time of 1 h by keeping the Ar flow rate unchanged. After completing sputtering, each of the deposited thin film was taken out of the sputtering chamber and then moved in a furnace for annealing in the presence of air for 2 h at 500 °C.

2.2. Characterizations

The morphological and compositional characterization of undoped and 5% Cr doped ZnO thin films were investigated using x-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM) embedded with energy dispersive x-ray spectroscopy (EDS) and Raman spectroscopy. The phase formation, crystallinity and crystallite size of the thin films were carried out by XRD (Rigaku Miniflex-II) with Cu-K_α radiations (λ = 1.5406 Å) in 2θ range from 30° to 70° operated at a voltage of 30 kV and current of 15 mA. The particle size, shape and elemental composition were evaluated by FESEM (NANO NOVA) equipped with EDS. The Raman spectra for both samples were recorded by a micro-Raman system (Renishaw, UK) in the wavenumber range of 300–800 cm^{-1} using Ar ion laser as an excitation source. X-ray photoemission spectroscopy (XPS) spectra were taken from a PHI 5000 Versa probe II scanning XPS microprobe (ULVAC-PHI, U.S.) at room temperature and at a base pressure better than 6×10^{-10} mbar. All spectra were recorded with monochromatic Al K_α ($h\nu$ = 1486.6 eV) radiations with a total resolution of about 0.7 eV and a beam size of 100 μm.

2.3. Gas sensing performance

The gas sensing study of the thin film based gas sensors was investigated through capacitive response with the gas concentration. Two parallel contacts (approximate size of 2 × 2 mm^2) on the surface of the thin films were made with thermally evaporated aluminium metal through a metal mask on the surface to connect the external wires. The liquid solvent was heated in a vessel of known volume to form ethanol vapour and further exposed to the fabricated sensor placed in a closed chamber using nitrogen as carrier gas at a constant flow rate. The arrangement for studying sensing performance is schematically illustrated elsewhere [27] and fabricated thin film based gas sensor is demonstrated in Fig. 1. The capacitance variations over a range 50–400 ppm concentration of ethanol at 100 °C were recorded through Keithley 590 CV analyzer.

3. Results and discussion

3.1. XRD analysis

Fig. 2 shows the x-ray diffraction patterns of undoped and 5% Cr doped ZnO thin films. The diffraction peaks are identified as the hexagonal wurtzite structure of ZnO. It is also evident from Fig. 2 that the dopant does not change the crystal structure of the host matrix as no any impurity peaks of Cr_2O_3 and $ZnCr_2O_4$ are detected. Additionally, the most intense diffraction peak (002) indicates the preferential growth of c-axis orientation for both ZnO films, because (002) plane corresponds to the lowest surface free energy in the hexagonal wurtzite structure [8]. The average crystallite size (τ) was calculated by the Debye-Scherrer's equation, $\tau = 0.9\lambda/\beta\cos\theta$, using the full-width at half-maximum (FWHM) value of the strongest diffraction peak (002) [28]. It is known that the Debye-Scherrer's formula shows reasonably accurate values for the crystallite size in comparison with the values obtained by other theoretical and experimental methods [8]. The calculated crystallite sizes are 22 nm and 19 nm for undoped and Cr doped ZnO respectively. The variation of crystallite size, lattice parameters and c/a ratio with doping concentration are tabulated in Table 1. It can also be seen from XRD patterns that the intensity of (002) peak decreases and the width increases on Cr doping, which pointed to the degradation of crystallinity and reduction in crystallite size. It is clear from Table 1, that the lattice constant '*c*' is slightly decreasing from 0.5245 nm to 0.5241 nm with Cr incorporation in ZnO matrix. The reason for the change in this lattice parameter may be due to the concentration of foreign atoms and defects, and their difference of ionic radii with respect to the substituted matrix ions. The Cr^{3+} ions can easily replace the Zn^{2+} host ions as the radius of the Cr^{3+} ions (0.63 Å) is much smaller compare to the Zn^{2+} ions (0.74 Å) as well as the Cr—O bond (1.96 Å) in Cr_2O_3 is also shorter than the Zn—O bond (1.98 Å) in ZnO [23]. The broadening of the XRD peaks may also explain on the basis of the effect of microstrain (η). The average microstrain (η) for both the films is calculated by the Williamson-Hall equation, $\beta\cos\theta = (k\lambda/$

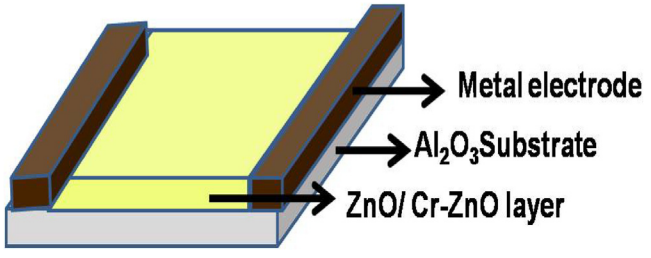

Fig. 1. Schematic illustration of the fabricated thin film based gas sensor.