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Performance of Cr-doped ZnO for acetone sensing

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ABSTRACT

Zinc oxide (ZnO) doped with chromium (Cr) was synthesized by reactive co-sputtering for gas sensing applications. The effect of varying the contents of Cr (from 1 to 4 at%) on the ZnO gas sensor response was studied. X-ray diffraction analysis reveals the high orientation of *c*-axis of the prepared films. The optimum operating temperature of the undoped ZnO was 400 °C and shifted to 300 °C for the Cr-doped ZnO under the acetone vapour. The 1% Cr doping ZnO gas sensor was most sensitive for the acetone vapour. The ability of the 1% Cr-doped ZnO to produce repeatable results under different acetone vapour concentrations was tested. The timing properties of the doped Cr ZnO gas sensor were 70 and 95 s for the rise and recovery time respectively.

1. Introduction

Many advanced technology applications of zinc oxide (ZnO) has been published in the past two decades, such as thin film transistor (TFT), transparent conductive layer in solar cells [1,2], ultraviolet (UV) and blue LEDs [2], LASER diodes [3,4] and UV sensors [5]. Recently, gas sensing application based on nanostructure ZnO received significant attention, in which the surface-to-volume ratio of the sensing element was increased and as consequences, the response to different gases was improved [6,7].

ZnO properties are highly dependent on the method of preparation as well as preparation conditions. ZnO had been prepared through sputtering deposition, chemical vapour deposition (CVD), pulse laser deposition, and molecular-beam epitaxial [8]. Among these methods, RF sputtering deposition of ZnO has attracted considerable attention as the produced films are highly repeatable with controllable properties. Nonetheless, ZnO is not a preferred gas sensor material due to its low response and high operating temperature.

A substantial number of studies have shown the ability of ZnO doping, especially for the n-type. Aluminium (Al), indium (In) [9], and gallium (Ga) [10] doped ZnO proved to be highly transparent and highly conducting, suitable for various applications. Furthermore, ZnO doped with different transition metals (TM) have shown ferromagnetic behaviour at room temperature [2]. Metals such as cobalt (Co) [11], chromium (Cr) [12–14], and manganese (Mn) [15] have been studied for this purpose. Doping ZnO with various elements showed a significant improvement on the sensing behaviour of ZnO gas sensors [16,17]. Recently, chromium-doped ZnO gas sensor was demonstrated for oxygen sensing application at relatively low operating temperature [18].

Volatile organic compound (VOC) vapours are the primary sources of indoor environmental pollutants and are considered seriously harmful to the human body [19,20]. Notable correlations between VOC emissions and different kinds of cancers were reported [21]. Due to these pressing issues related to health and environment, more work is needed concerning the detection of VOC vapours, [21–25]. Among the VOCs, acetone is widely used in many applications; such as a solvent and an extracting regent. High acetone concentration (>10,000 ppm) in the air may cause cephalalgia and nausea [26]. Moreover, acetone is used as biomarker for diabetes since it can be found in the exhaled breath of the diabetes patient [27].

Previous work of the undoped ZnO gas sensor [22] showed a measurable response towards different VOCs concentrations. However, the prepared undoped ZnO gas sensor showed high operating temperature of 400 °C. In this work, we report the ability of Cr-doped ZnO prepared by RF sputtering as gas sensors for reducing gases such as acetone vapours. The use of sputtered Cr- doped ZnO for sensing applications has not been studied extensively before. The Cr concentration in this study was varied from 1 to 4 at% and the effect of Cr concentration on the operating temperature as well as its response was investigated.

2. Experimental details

Prior to the growth of ZnO, n-type silicon (Si) wafer with (1 0 0) orientation was cleaned by RCA (Radio Corporation of America)

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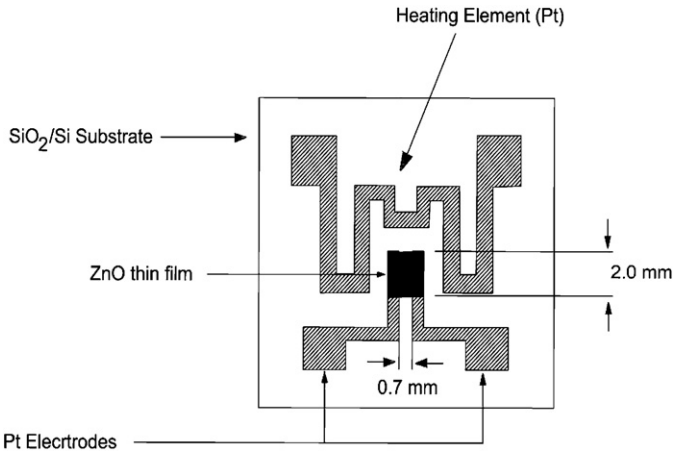

Fig. 1. Layout structure of ZnO gas sensor with the sensing element's dimension of 2 mm × 2 mm.

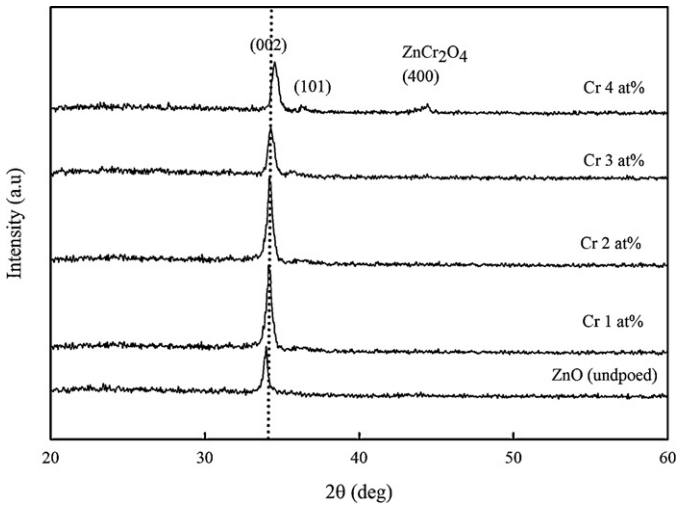

Fig. 2. XRD patterns of the pure and Cr doped ZnO, with different Cr doping contents.

procedure and then thermally oxidized to form ~1.0 μm of silicon dioxide (SiO_2). A photoresist was used to pattern the heating element and electrodes. Tantalum (Ta) as an adhesive layer (50 nm thickness) and platinum (Pt) (120 nm thickness) were deposited using A500 Edwards dual RF magnetron sputtering unit at RF power of 180 and 150 W respectively. The distance between the Pt electrodes was approximately 0.7 mm.

ZnO and Cr-doped ZnO films were synthesized by reactive RF co-sputtering using the same unit. The thickness of the prepared films, measured by a calibrated quartz crystal monitor, was approximately (250 ± 30) nm and later confirmed by a Filmetrics F20 optical reflectometer (based on the optical interference method). The total area of the sensing element was 2 mm × 2 mm (Fig. 1). The substrate temperature during deposition increased to 60 °C as a result of the plasma bombardment. The samples were fixed on a rotating substrate holder at a distance of 100 mm above the targets. The ultimate pressure was about 1×10^{-6} mbar, and was raised to 2.2×10^{-2} mbar by purging the chamber with high-purity 20% Ar and 80% O_2 through two separate gas flow controllers. Metals of high purity Zn and Cr targets were used to prepare the films. Prior to the deposition, process, both Zn and Cr targets were initially exposed to continuance plasma to clean the surfaces. The RF power was maintained at 230 W for the Zn target. For the Cr target, the power was adjusted accordingly to control the doping contents in the range of 1–4 at%. The films were then heat treated at 500 °C for 6 h at ambient atmosphere to stabilize their baseline resistance.

The electrical properties were measured at temperatures ranging from 50 to 450 °C in a dark cylindrical chamber with a total volume of 550 cm^3. The temperature of the heating element was changed and controlled by varying the applied voltage using INSTEK GPS 3030 DC power supply. The temperature was measured by Pt – 100 RTD (with a ceramic envelope) at the surface of the device with a stability of measured temperatures around ±2 °C. The measured resistance was then collected using a programmable electrometer (Keithley – 196), and the collected data were stored for further analysis using LABVIEW via a GPIB interface of the PC. Information regarding the acetone vapour supply can be seen in Ref. [22].

The prepared undoped and Cr doped ZnO films were characterized using X'PertPro from PANalytical High resolution X-ray diffractometer (HR-XRD) for phase identification. The X-ray tube target was copper that emitted X-ray wave length of (Cu Kα (λ = 0.15418 nm)) with diffraction angles in the range of 20–80°. The surface topography was imaged using an atomic force microscope (AFM) in non-contact mode.

3. Results and discussion

3.1. Structure and surface properties

ZnO doped with Cr in the range of 1–4 at% was successfully prepared through co-doped reactive RF sputtering. Quantitative energy-dispersive X-ray spectroscopy (EDX) analysis reveals that the atomic ratio of Cr was in the range of about 1.18–4.1 ± 0.2 at%. Statistical analysis of EDX measurements over several samples of Cr-doped ZnO films, demonstrates that the variation of Cr content is minimal, and the composition of Cr dopant may consider being uniform throughout the sample.

Fig. 2 depicts the HR-XRD spectra of the undoped and Cr doped ZnO prepared films. The data are shown on a linear scale but are displaced vertically for clarity. Initially, all the prepared films were highly oriented towards the *c*- axis phase of the ZnO and the only peak observed was (0 0 2) at a Bragg angle of approximately 34° which belongs to the wurtzite structure of the ZnO (JCPDF 36-1451). Although EDX analysis reveals the successful doping of Cr into the host ZnO, no peaks belongs to Cr metal or Cr oxides were found (within the sensitivity limitation of XRD), indicating that the dopant are incorporated into the host lattice [28]. However, the (1 0 1) phase at Bragg angle of 35.9° of the ZnO began to grow at 3 and 4 at% Cr doping, and the (0 0 4) phase of the $ZnCr_2O_4$ at Bragg angle of 44.3° was also observed with 4 at% Cr doping [29–31]. This shows that the doping limit for the chromium is around 3 at%, in agreement with previous studies [14,32].

The enhancement of (0 0 2) peak at 1 and 2 at% Cr doping should be noted. Several studies have found the same behaviour resulting from the low dopant concentration of ZnO [33,34]. This could be attributed to the decrease of the oxygen defects in the lattice due to the lower ionization energy of Cr (compared with Zn [35]) that would readily combine with O atoms in a form that lead to better crystallinity with enhanced preferred orientation of the film.

The Bragg angle (0 0 2) peak at 34.13° of the undoped ZnO films is lower than the standard position of the ZnO powder (34.42°, with reference to JCPDS no. 36-1451), which indicated that the prepared films by reactive RF sputtering exhibit some kind of strain. The lattice strain along the *c*-axis, ε_s is given by the following equation [36]:

$$\varepsilon_s = \left(\frac{c - c_o}{c_o}\right) \times 100\% \quad (1)$$

where *c* is the lattice parameter of the strained ZnO films calculated from XRD data and $c_o \approx 0.52065$ nm is the unstrained lattice