Applied Surface Science 256 (2010) 3468–3471

Contents lists available at ScienceDirect

Applied Surface Science

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

Low operating temperature of oxygen gas sensor based on undoped and Cr-doped ZnO films

N. Al-Hardan *, M.J. Abdullah, A. Abdul Aziz, H. Ahmad

School of Physics, Universiti Sains Malaysia (USM), 11800 Penang, Malaysia

ARTICLE INFO

Article history:
Received 30 September 2009
Received in revised form 14 December 2009
Accepted 15 December 2009
Available online 24 December 2009

Keywords:
Gas sensor
Zinc oxide
Oxygen sensors

ABSTRACT

Undoped and doped ZnO with 1 at.% (atomic percentage) chromium (Cr) was synthesized by RF reactive co-sputtering for oxygen gas sensing applications. The prepared films showed a highly c-oriented phase with a dominant (0 0 2) peak at a Bragg angle of around 34.2°. The operating temperature of the prepared ZnO sensor was around 350 °C and shifted to around 250 °C for the doped ZnO sensor which is lower than that of previously reported work. The sensitivity of the sensor toward oxygen gas was enhanced by doping ZnO with 1 at.% Cr. Good stability and repeatability of the sensor were demonstrated when tested under different concentration of oxygen atmosphere.

1. Introduction

Zinc oxide-based material shows attractive properties for different modern technological applications [1]. With a wide band gap of 3.37 eV and a high excitonic energy (60 meV), ZnO is a good candidate for optoelectronic applications such as light-emitting diodes (LEDs), especially in the UV and blue regions of the electromagnetic spectrum, as well as for laser applications [2,3]. In gas sensing, ZnO has been tested for harmful and toxic gases [4–6]. However, it was found that one of the disadvantages of ZnO gas sensor is its high operating temperature and low sensitivity [7].

Transition metals have been used as successful doping materials for ZnO. Many reports showed ferromagnetism properties of ZnO above room temperature when doped with chromium (Cr), manganese (Mn) and vanadium (V) [8]. It was also observed that the resistivity of the ZnO:Cr is increased due to the depressed carrier concentrations which resulted in the increased of the electrical resistivity of the films. Such high resistivity effect has been shown to enhance the sensitivity of the metal oxide gas sensors [6]. Thus doping ZnO with Cr might be a promising choice to enhance the gas sensors sensitivity.

In this work we report the fabrication of undoped ZnO and Cr-doped ZnO by reactive RF co-sputtering. The effect of Cr doping on the operating temperature and the response of the ZnO gas sensor to oxygen (O_2) gas is presented, which to our knowledge has not been reported before.

2. Experimental details

N-type silicon wafer with (1 0 0) orientation was chosen as a substrate since it is being used extensively in microelectronic industry. The wafer was cleaned using RCA process, and then inserted into a tube furnace at 1100 °C for growing a thick film of SiO_2 as an insulator layer by dry and wet oxidation process. The thickness of SiO_2 layer as measured by spectral reflectance using Filmetric unit was approximately 1.2 μm. The substrate was then cut into a square geometry with dimension of 12 mm × 12 mm. The insulating layer of SiO_2 blocks charge transport between the active layer and the substrate, thus providing a good protection of radiation and high temperature environments [9,10].

A positive photoresist was used to pattern the heating element and the electrodes. Tantalum (Ta) as an adhesive layer (with 20 nm thickness) and followed by platinum (Pt) (with 120 nm thickness) were deposited using A500 Edwards RF magnetron sputtering unit with the power of 150 W. The distance between the Pt electrodes was about 0.7 mm. The whole layout of the device structure is shown in Fig. 1. Undoped and Cr-doped ZnO with a thickness of 250 ± 30 nm and total area of 2 mm × 2 mm was coated by RF reactive co-sputtering with the power of 230 and 90 W for the Zn and the Cr, respectively. Since the sputtering yield of the Cr was higher than that of the Zn, this setting of process parameter resulted in 1 atomic percentage (1 at.%) Cr (as confirmed by the EDS measurement). The samples were fixed on a rotating substrate holder at a distance of 100 mm above the target and the substrate temperature was kept at ambient temperature. The ultimate chamber pressure was 1×10^{-6} mbar, which was raised to 2×10^{-2} mbar by purging the chamber with high-purity argon (Ar) and 80% O_2 through two

* Corresponding author. Tel.: +60 17 4961778; fax: +60 4 6579150.
E-mail address: naif.zd06@student.usm.my (N. Al-Hardan).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.12.055

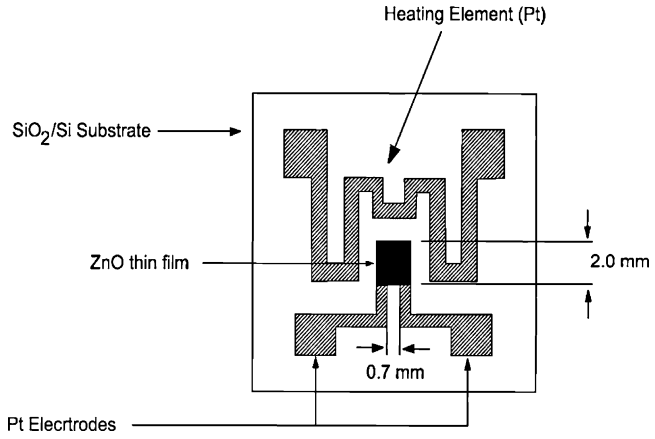

Fig. 1. Layout structure of ZnO gas sensor with the sensing element's dimension of 2 mm × 2 mm.

separate gas flow controllers. The Zn and Cr targets were initially exposed to Ar plasma for surface cleaning prior to the coating process.

The prepared films were characterized using X' PertPro from PANalytical High resolution X-ray diffractometer (HR-XRD) for phase identification while energy dispersive spectroscopy (EDS) attached to a scanning electron microscope (SEM) was used to determine the atomic percentage of the Cr in the film.

The sensing properties of the samples were measured at temperatures ranging from 200 to 450 °C, in a dark cylindrical chamber with a total volume of 550 cm^3. The temperature of the heating element was controlled by varying the applied voltage and measured by Pt-100 RTD. The accuracy of the measured temperatures was around ±2 °C. The resistance of the sensor was measured by a two-point probe as a function of operating temperature. The data were collected through a Keithley-196 DMM, which was controlled by a PC using Lab View software via a GPIB interface. High grade O_2 gas (99.99%) and 50% O_2 (balanced with nitrogen) were supplied and certified by MOX-LINDE GASES (Malaysia). The gas flow under test was maintained at 500 sccm (standard cubic centimeter per minute) through a mass flow controller.

3. Results and discussion

The sputtered ZnO thin films showed thickness of about 250 ± 30 nm, as measured by the film thickness monitor (FTM-7) and confirmed by the Filmetrics F20 unit. The XRD diffraction pattern (Fig. 2) for both undoped and doped ZnO with 1 at.% Cr on thermally oxidized Si substrate was measured at Bragg angles range between 20° and 80°. It shows that the prepared undoped and Cr-doped ZnO were highly oriented along the *c*-axis, with a peak at around 34.20°, which belongs to the (0 0 2) phase of the wurtzite structure (with reference to JCPDS No. 36-1451). No peaks that belong to Cr metal or Cr oxide were found, which indicates that the dopant was well incorporated into the host lattice.

The (0 0 2) peak was slightly shifted toward higher angles for Cr-doped ZnO, indicating that the *c*-axis had shrunk in the doped samples. It is well known that the effective ionic radius of Cr^{3+} ions is 0.63 Å, which is smaller than that of Zn^{2+} (0.74 Å). Therefore, when Zn^{2+} ions are substituted by Cr^{3+} ions the *c*-axis became shorter [11–13], which justified the above observation. The enhancement of (0 0 2) peak after doping with 1 at.% Cr should also be noted. Several authors reported the same behavior resulted from the low dopant concentration of ZnO [14–16]. This could be attributed to the decrease of the oxygen defects in the lattice as lower ionization energy of Cr (compared with Zn [17]), would readily combine with O atoms in the form that led to the crystallinity with enhanced preferred orientation of the film.

The EDS measurements on different scanning areas of the film confirmed the Cr concentration of ~1.1 at.% that was uniformly distributed across the whole sample.

The Cr-doped ZnO showed higher resistance as compared to that of the undoped ZnO. Such behavior had been observed by several authors [18–20] which was attributed to the depressed carrier concentrations and hence resulted in the higher resistivity of the films.

The sensitivity S of the sensor is defined as:

$$S(\%) = \frac{Rg - Ra}{Ra} \times 100 \quad (1)$$

where *Rg* and *Ra* represent the resistance of the sensor in the gas and air atmosphere, respectively. Fig. 3 shows the dependence of sensors sensitivity to a fixed oxygen concentration (50%) at different operating temperatures. It can be observed that the Cr-doped ZnO sensor showed higher sensitivity at lower operating temperatures. The enhanced sensitivity at lower operating temperature is attributed to the incorporation of Cr which led to a reduction of the grain size and an increase of the surface area. As a consequence the surface activity is enhanced, and the activation energy of surface chemisorbed O_2 gases is reduced which led to the enhancement of O_2 gas adsorption. Accordingly,

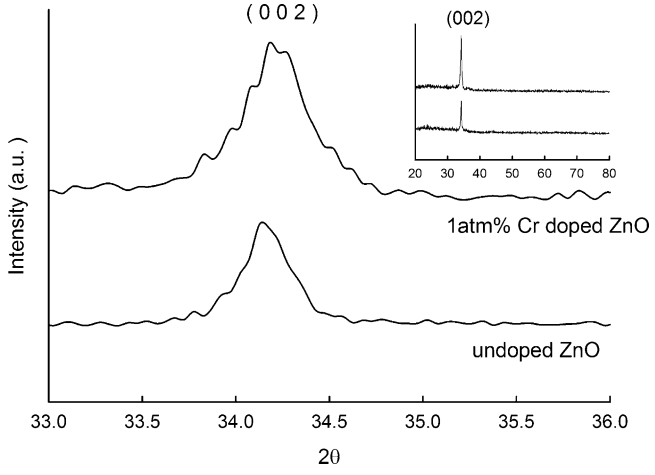

Fig. 2. XRD pattern of undoped and Cr-doped (1%) ZnO.

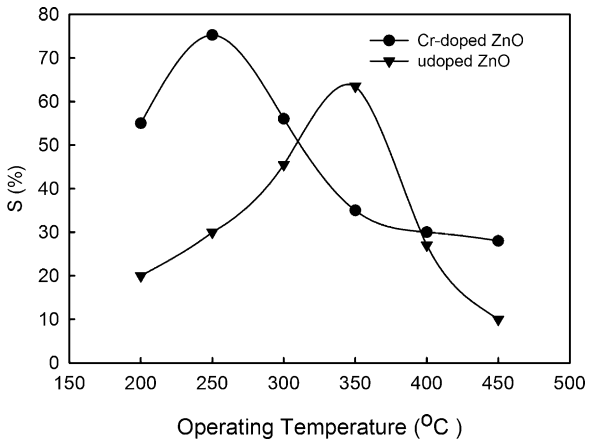

Fig. 3. The dependence of the sensor sensitivity on operating temperatures of doped and undoped ZnO sensor.