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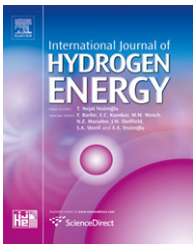

Sensing mechanism of hydrogen gas sensor based on RF-sputtered ZnO thin films

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ABSTRACT

The mechanism of hydrogen (H_2) gas sensing in the range of 200–1000 ppm of RF-sputtered ZnO films was studied. The *I–V* characteristics as a function of operating temperature proved the ohmic behaviour of the contacts to the sensor. The complex impedance spectrum (IS) of the ZnO films showed a single semicircle with shrinkage in the diameter as the temperature increased. The best fitting of these data proved that the device structure can be modelled as a single resistance-capacitance equivalent circuit. It was suggested that the conductivity mechanism in the ZnO sensor is controlled by surface reaction. The impedance spectrum also exhibited a decreased in semicircle radius as the hydrogen concentration was increased in the range from 200 ppm to 1000 ppm.

1. Introduction

Hydrogen becomes one of the resources of clean energy, since the burning of the H_2 is water, which is decomposed again into hydrogen and oxygen. It has a wide range of flammability in air, which is about 4–75% by volume and the lowest limit of H_2 concentration in air to cause explosion is 4.65% [1,2]. This makes it more flammable than other fuels. Therefore there is a need for a device which is capable of detecting low levels of H_2 [3]. Semiconductive metal-oxide (MO_x) sensors were studied and used extensively for hydrogen detections for their simplicity, reliable, low-cost and easily mass produced [4], and among them were tungsten oxide (WO_3) [5], tin oxide (SnO_2) [6] and zinc oxide (ZnO) [7]. Nanostructure ZnO is a promising material for chemical gas sensors due to its large surface-to-volume ratio [7,8]. High sensitivity gas sensor of nanostructure ZnO has been prepared using different methods, such as radio frequency (RF) sputtering [9], sol–gel [10], and oxidation of Zn metal [11].

Many published reports on the application of ZnO as gas sensors have used the technique of RF sputtering for the material deposition, since this method of preparation is among the standard process in the IC technology. Nevertheless, more effort is needed to clarify the sensing mechanism of the ZnO gas sensors. In the present work the current–voltage (*I–V*) behaviour and the impedance spectroscopy of nanostructure ZnO prepared by RF reactive sputtering was studied. The measurements were carried out at different temperatures ranging from room temperature (RT ~26 °C) up to 500 °C. The effects of hydrogen concentrations on the impedance behaviour are also presented.

2. Experimental details

An *n*-type silicon (Si) with a coated thin layer of silicon dioxide (SiO_2) of about 1.0 μm thickness was used as a substrate for the device. Suitable electrodes and heating element were patterned after the deposition of platinum metal (Pt) (thickness

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of 0.12 μm), on tantalum (Ta). Both metals were deposited using A500 Edwards RF magnetron sputtering equipment.

The same sputtering unit was used to prepare ZnO with a thickness of 0.25 μm and a total area of $2 \times 2\ mm^2$ by reactive sputtering with a power of 230 W at room temperature through a lift-off mask. The base pressure was 1×10^{-6} mbar, which was raised to 2.3×10^{-2} mbar by purging the chamber with high-purity argon and 80% oxygen gases, through separate gas flow controllers. The high-purity Zn metal target was initially exposed to continuance plasma to clean the surface prior to the coating process. A quartz crystal monitor (FTM-7) was used to monitor the thickness and to control the sputtering rate. The films were then heat-treated at 500 °C in air atmosphere for 6 h in order to stabilise the baseline resistance.

The current–voltage (*I–V*) characteristics of the Pt/ZnO/Pt device structure were measured with the DC voltage sweep from −5 V to 5 V at 50 mV increment employing the Keithley 237 source measure unit (SMU).

The complex impedance measurement was carried out using Agilent 4294A Impedance analyzer in the frequency range of 100 Hz–2 MHz, with 0.5 V ac signal amplitude. The effects of the cabling and electrode assembly on the impedance data were nulled with a suitable calibration. Both units are controlled by a PC through a GPIB interface, and Lab View v8.5 software was employed for data acquisition. Fig. 1 presents the schematic of the measurement system setup and the top view of the device with the total dimensions of $12 \times 12\ mm^2$.

All the measurements were performed at temperatures in the range from RT (~26 °C) to 500 °C, in a dark cylindrical chamber with a volume of 550 cm^3. The temperature was varied and controlled by changing the applied voltage to the heating element using GW INSTEK GPS 3030 DC power supply, while the temperature was measured by Pt – 100 RTD (with a ceramic envelope) that was attached to a Keithley 2100 DMM. The accuracy of measured temperatures was around ±3 °C. High-resolution XRD and field emission SEM were used to study the microstructure of the prepared ZnO films.

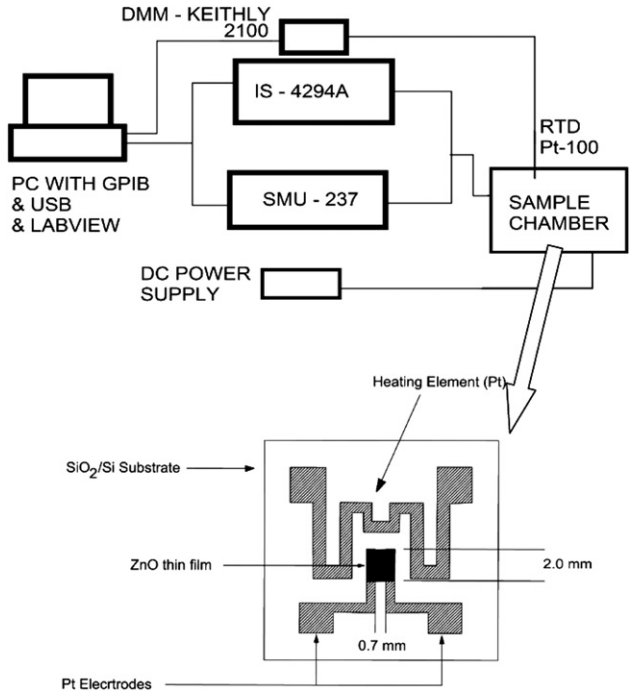

Fig. 1 – The measurement system used in the experiment with the sensor.

3. Results and discussion

The prepared ZnO thin films were observed to be highly transparent, with thickness of about (250 ± 20) nm, as measured by FTM-7 and confirmed using the filmmetric unit. The XRD diffraction pattern proved that the prepared ZnO on thermally oxidized *n* – Si substrate was highly c-axis oriented, giving a peak at Bragg angle equal to 34.02°, which belong to the (0 0 2) phase of wurtzite structure (Fig. 2).

The d-spacing of the prepared ZnO phase obtained was 0.2629 nm, which was higher than that of the published values of 0.2604 nm (with reference to JCPDS No. 36–1451), suggesting an elongation of unit cell along the c-axis. The increase of d-spacing may be related to the generation of oxygen or zinc vacancies [12,13]. The SEM image of the device is posted in Fig. 3, which shows the ZnO thin films and the Pt electrodes on SiO_2/Si substrate.

Fig. 4 depicts the image of FE-SEM of the ZnO film on a thermally oxidized Si, which shows a uniform distribution of nanostructure grains with a diameter of about 20 nm.

Fig. 5 depicts the *I–V* characteristics of the device measured at room temperature before and after annealing at 500 °C for 6 h, from which a linear relationship has been observed. Such behaviour indicates the ohmic nature of the Pt contacts which might be the consequence of high carrier concentration of the prepared ZnO, where the tunnelling barrier becomes small and a quasi-ohmic contact may be created [14].

The effect of the annealing process is obvious whereby the current of the annealed device has been enhanced indicating a decrease in the resistance of the annealed ZnO. The decrease is a result of the enhancement in the grain size of the ZnO that caused the reduction in the grain boundaries, which subsequently improved the crystal lattice deficiencies of the film.

The effect of temperature on the *I–V* characteristics is depicted in Fig. 6. It shows the enhancement of the current

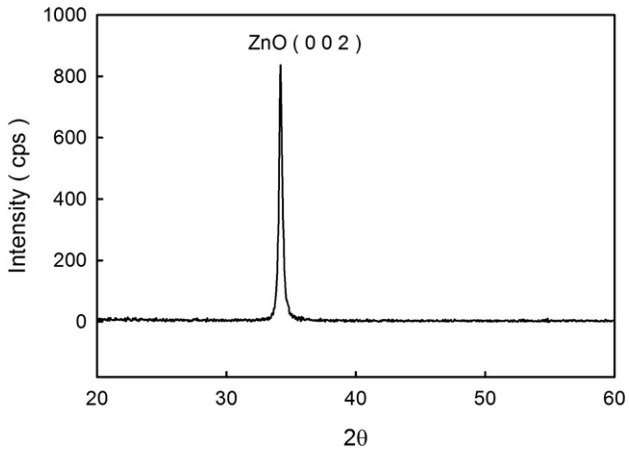

Fig. 2 – HR-XRD of RF-sputtered ZnO thin films on thermally oxidized Si substrate.