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Pt/SnO_2 Nanowires/SiC Based Hydrogen Gas Sensor

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Abstract—**Pt/SnO_2 nanowires/SiC based metal-oxide-semiconductor (MOS) devices were fabricated and tested for their gas sensitivity towards hydrogen. Tin oxide (SnO_2) nanowires were grown on SiC substrates by the vapour liquid solid growth process. The material properties of the SnO_2 nanowires such as its formation and dimensions were analyzed using scanning electron microscopy (SEM). The current-voltage (*I-V*) characteristics at different hydrogen concentrations are presented. The effective change in the barrier height for 0.06 and 1% hydrogen were found to be 20.78 and 131.59 meV, respectively. A voltage shift of 310 mV at 530°C for 1% hydrogen was measured.**

I. INTRODUCTION

Recently, the interests in nanostructured materials have been increased because they often show novel physical and chemical properties which are different from those displayed by their bulk counterparts [1-3]. They are more stable when they operate at high temperatures for a long time. The electrical properties of the polycrystalline materials alters due to grain coalescence, porosity modification and grain-boundary alteration [1]. In 1991, Yamazoe [2] reported that the reduction in size of the crystallite caused a huge enhancement in gas sensor performance. Nanostructured materials such as semiconducting metal oxide nanoparticles, nanowires and nanorods have been widely used for gas sensing applications because of their large surface to volume ratio [3, 4]. Examples of such materials include: SnO_2 nanobelts for CO and NO_2 [5], In_2O_3 nanowires for NO_2 [6], WO_3 nanowires for NO_2 [7], and TiO_2 nanotubes for H_2 [8]. The increase in the surface of nanostructured materials also causes surface effects which leads to increase in catalytic activity or surface adsorption. Therefore, the extension of the surface exposed to gas adsorption makes improvement in the sensitivity of the materials.

SnO_2 is an n-type semiconductor with a wide band gap (3.6 eV) and is extensively used for applications including gas sensing, electrochemical or photoelectrochemical-based energy conversion [9, 10], anti-static films and anti-reflecting coatings in solar cells [11]. SnO_2 has been widely utilized for gas sensing applications due to its suitable physicochemical properties including high stability and reactivity to reducing gases such as hydrogen [12]. When SnO_2 is exposed to different gas species, the material's resistance changes because of the charge carrier exchange between the adsorbed gas and the oxide surface [13]. Hence, the gas sensing properties of SnO_2 depend on its surface structure.

There are a number of reports in literature dealing with the gas sensing applications of nanostructured SnO_2. Zhang et al. [14] has conducted experiments with SnO_2 single nanowires sensor in a FET structure for different gases including oxygen and CO. Room temperature sensing properties of a single crystalline SnO_2 nanowire sensor towards nitrogen dioxide has also been investigated by Law et al. [9]. Other experiments were carried out by Lou et al. [15] on nanostructured SnO_2-based gas sensors. They prepared SnO_2 nanomaterials by three different methods: chemical precipitation, sol-gel and dissolution-pyrolysis. They also conducted gas sensing measurements and reported that the SnO_2-based sensor prepared by dissolution-pyrolysis method has high sensitivity, quick response and recovery to different gases. Li et al. [16] also have developed SnO_2 nanoparticles gas sensors. They reported that the SnO_2 nanoparticles have high sensitivities towards reducing gases.

SiC is a semiconducting material with a wide band gap of 3.2 eV which is suitable for high temperature gas sensing [17]. To date, gas sensors based on metal-oxide-SiC have been investigated [18-20]. By using metal oxide in between the substrate and the catalytic metal, selectivity, sensitivity and stability of the such sensors can be increased [21].

In this paper, we present gas sensing properties of the devices combining transition metals such as platinum and nanostructured metal oxide (SnO_2) with SiC operating at high temperatures. The microstructural characteristics and development of the sensor using the vapour liquid solid growth method to grow SnO_2 nanowires have been demonstrated. We have investigated the hydrogen gas sensing performance for an operating temperature in the range of 300-650°C. We have also studied the barrier height changes for different concentrations of hydrogen gas obtained from the *I-V* measurements.

II. EXPERIMENTAL

The Pt/SnO_2 nanowires/SiC based MOS devices were fabricated using n-type 6H-SiC wafer. The SiC wafers were diced into 3 mm×3 mm squares. The thickness of the SiC wafer was approximately 250 µm. A circular pad of Pt and Ti metal layers with 1 mm diameter was deposited on the unpolished side of the wafer by sputtering. This side forms the ohmic contact after high temperature annealing. The thickness of the Pt and Ti are 100 nm each. Consequently, the SnO_2 nanowires were deposited by the vapour liquid solid growth mechanism on the polished side of the SiC samples. Platinum was used as a growth catalyst. Small platinum clusters were dispersed on the SiC substrate by sputtering and the as prepared substrates were placed in the tubular furnace together with the source SnO_2 powder. The oxide is placed at 1370°C while the SiC substrates at temperatures between 450 and 500°C. The deposition takes place at 100 mbar with a flux of 75 sccm of Ar as gas carrier. A circular pad of platinum with diameter of 1 mm was deposited on the nanostructured metal oxide by sputtering to form a Schottky contact. After fabricating the devices, they were annealed in air at 450ºC for 4 hours and at 600°C for 2 hours.

The sensor was placed in the chamber with an alumina micro-heater in close contact, to control its operating temperature. The gas sensing measurements were conducted in a computerized multi channel gas calibration system, which allows different concentrations of the analyte gas including hydrogen and propene to be exposed to the sensor. Concentrations in the range of 0.06 to 1% of hydrogen and propene were introduced in the test chamber at constant volumetric gas flow rate of 200 ml/min.

The *I-V* measurements were carried out using a Keithley 2602 current sourcemeter to investigate the effective change in the barrier height due to exposure to the different concentrations of hydrogen. Since the change in the Schottky barrier height results in the alteration of the voltage-current characteristics, the response of the sensor was measured as the shift in voltage when the sensor was biased at a constant current. The voltage shift was recorded using an Agilent 34410A multimeter.

III. RESULT AND DISCUSSION

A. *Material Characterization*

The nanowires have a very high aspect ratio as the length exceeds several microns and the width is smaller than 100 nm, and they are uniformly dispersed on the substrate. A SEM image of SnO_2 nanowires is shown in Fig. 1.

High resolution TEM and electron diffraction showed that the wire is single crystalline, with atomically-sharp termination of lateral sides. Bragg reflections and the whole symmetry of the ED pattern agree with the cassiterite tetragonal SnO_2 phase (P42/mnm-SG 136). The direction of the electron beam is parallel to the [010] zone-axis of the reciprocal lattice and the nanowire grows along to the [100] direction [22] .

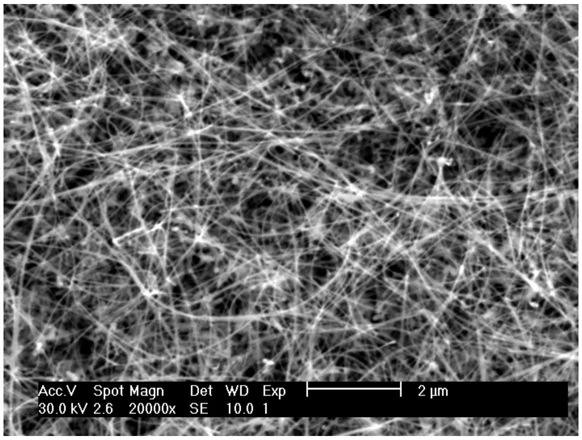

Figure 1. SEM image of SnO_2 nanowires

B. *Electrical Properties*

From Fig. 2 the sensor shows the highest sensitivity towards different hydrogen concentrations at 530˚C (e.g. the voltage shifts for 0.5% hydrogen were 145, 189 and 150 mV at 420, 530 and 620˚C, respectively). Therefore, 530˚C was chosen as an operating temperature. The forward and reverse *I-V* characteristics of the device towards different hydrogen concentrations (0.06, 0.125, 0.25, 0.5, and 1%) at 530˚C are highlighted in Fig. 3. Information regarding the change in the barrier heights is extracted from these *I-V* curves. The lateral shift in the *I-V* characteristics is due to changes in barrier height. The changes in slope in the linear portion of the characteristics are because of the change in the series resistance resulting from a decrease in the metal oxide resistance.

Based on the thermionic emission theory [23] the following equation is often used for the *I-V* characteristics of the Schottky diode:

$$I = I_s\{\exp({}^{qV}\!/_{nkT}) - 1\}, \tag{1}$$

where k is Boltzmann's constant, T is the temperature in Kelvin, n is the ideality factor which expresses the effect of a non-ideal Schottky diode and I_s is the saturation current:

$$I_s = SA^{**}T^2 \exp({}^{-q\phi_B}\!/_{kT}), \tag{2}$$

where S is the diode area, A^{**} is the effective Richardson's constant and ϕ_B is the barrier height. The saturation current was obtained from (1) and the barrier height was calculated from (2).

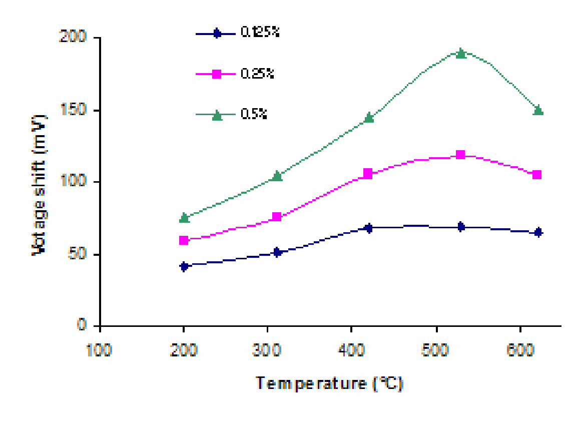

Figure 2. Voltage shifts at different temperatures vs different hydrogen gas concentrations

The effective changes in the barrier heights when the sensor was exposed to different hydrogen concentrations are illustrated in Fig. 4. It was found that in synthetic air at 530˚C, the saturation current and the barrier height were 0.838 nA and 2.04 eV, respectively. When the sensor was exposed to 1% hydrogen, the saturation current and the barrier height changed to 6.84 nA and 1.90 eV, respectively. Obviously, the magnitude of the barrier height shift increases with the increase of hydrogen concentrations. Trinchi et al. [24] have also reported that the barrier height of Pt/Ga_2O_3/SiC based hydrogen gas sensors increases with the increase of hydrogen concentrations.

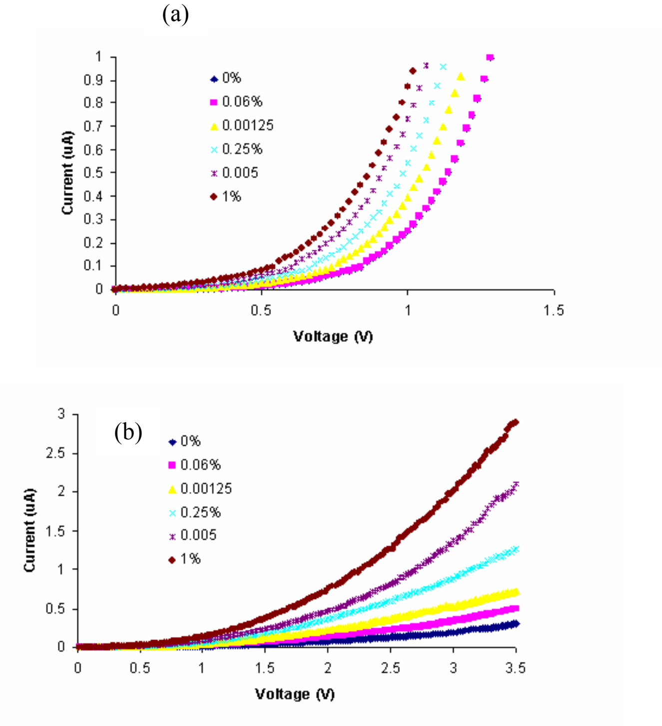

Figure 3. a) Forward *I-V* and b) reverse *I-V* characteristics of the Pt/SnO_2 nanowires/SiC sensor towards different hydrogen gas concentrations at 530˚C.

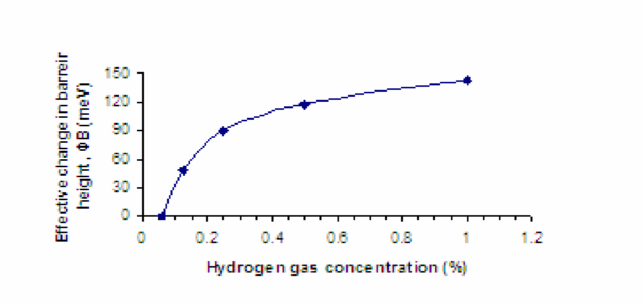

Figure 4. Change in barrier height for different hydrogen concentrations at 530˚C.

C. *Gas Response Performance*

The dynamic response of the device towards different concentrations of hydrogen at 530°C is shown in Fig. 5. Voltage shifts of 95 and 310 mV for 0.25 and 1% hydrogen were recorded at 530˚C, respectively. Kandasamy et al. [19] have reported the voltage shifts of 30 and 80 mV for 0.25 and 1% hydrogen, respectively for Pt/WO_3/SiC devices at 530˚C.

The sensor was also tested towards propene. From Fig. 6 the sensitivity to 0.125% propene at 530˚C was found to be 1.79 times higher than that of hydrogen. Consequently, the sensor is more promising for hydrocarbons gas sensing.

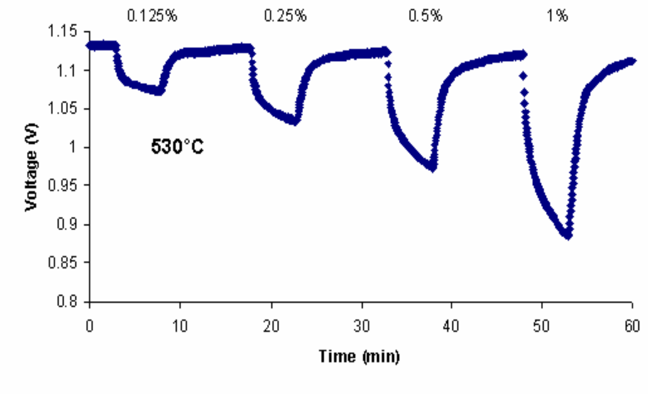

Figure 5. Dynamic response characteristics of the Pt/SnO_2 nanowire/SiC device towards hydrogen (0.12, 0.25, 0.5, and 1%) at 530˚C.

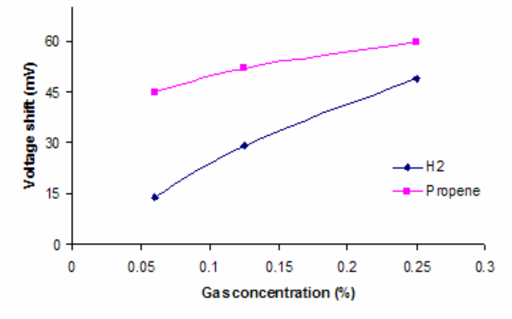

Figure 6. Voltage shifts at different concentrations of hydrogen and propene at 530˚C.

IV. CONCLUSION

We have developed the Pt/SnO_2 nanowires/SiC sensors and tested their sensing properties towards gaseous hydrogen at high temperatures. The morphological characteristics of the nanostructured thin films and electrical characteristics of the devices were investigated. In addition, we have studied the influence of the different gas concentrations and temperatures on the barrier height of the devices. We have also tested the devices' gas sensing towards propene at 530°C. The results show that the sensitivity of the devices towards propene is higher than to hydrogen. Hence, these devices are very promising for hydrocarbons gas sensing.

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