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Palladium decorated silicon carbide nanocauliflowers for hydrogen gas sensing application

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ABSTRACT

Silicon carbide (SiC) nanostructures have attracted significant attention for device applications due to their unique structural, electronic and catalytic properties. Here, the efficiency of three dimensional SiC nano-cauliflowers (NCs) for hydrogen gas sensing application has been investigated. We have deposited a vertically aligned, ordered Pd decorated SiC NCs directly on a silver (Ag) coated porous anodic alumina (AAO) substrate by DC magnetron cosputtering and then it used as a gas sensor without additional processing. The sensor shows remarkably high and selective responses to hydrogen gas with low detection range 2–500 ppm at relatively high temperature range (30–500 °C). Our results demonstrate the potential application of Pd decorated SiC NCs for fabricating highly sensitive and selective hydrogen gas sensors.

1. Introduction

Recent energy demands and growing levels of greenhouse gases have directed towards the hydrogen as a clean energy resource [1–4]. Hydrogen is odorless energy fuel producing water as secondary product [5,6]. But its low ignition energy (0.02 mJ) and wide flammability range (4–75% in air) cause intense explosion [7,8]. Moreover, most of the previous reports were focused on the low temperature hydrogen gas sensors [9,10], but these hydrogen sensors cannot fulfill the demands to detect the hydrogen leakage in combustion emission, aeronautical and commercial applications at high operating temperature [11–16]. Hence, it is today's requirement to develop a hydrogen gas sensor capable of long term operations and withstanding aforementioned harsh environments.

In recent time, SiC based gas sensors have been extensively investigated due to their high electron mobility, wide band gap energy, saturation velocity, high frequency characteristics, high thermal conductivity, Young's modulus, excellent thermal and chemical stability in harsh environments such as high temperatures, organic solvents, acids, alkalis, mechanical stress, and corrosion [17–22]. The sensitivity and response time of sensors can be achieved by controlling the microstructure, working temperature, exposed surface area and catalyst. The gas diffusivity can be controlled by the surface microstructure. Therefore, to achieve high sensitivity and selectivity, a favourable way is to construct hierarchical structures, which can facilitate the more diffusion of analyte gas molecules for better interaction with the detection material [23]. For this reason, hierarchical nanostructures like SiC NCs can be used as an ideal solid-state gas sensing material under harsh conditions. Although many methods such as sol-gel, chemical vapour deposition, plasma, microwave and laser synthesis have been used to synthesize the SiC nanostructures, however physical vapour deposition (PVD) techniques, particularly sputtering has been considered as an effective way to fabricate high-quality contamination free three dimensional nanostructures [24,25].

Here, three dimensional SiC NCs were grown on Ag/AAO substrate via DC magnetron cosputtering. The hydrogen gas sensing performance of fabricated sensor have been investigated at H_2 concentrations 2–500 ppm for an operating temperature range of 30–500° C. Furthermore, we have studied the variations in sensor response in different humidity conditions for hydrogen gas. This work shows a simple approach to design a high performance gas sensor which can be functional in harsh environments.

2. Methods

2.1. Materials and chemicals

Silicon (Si), carbon (graphite, C) and silver (Ag) targets (2" diameter) of high purity (99.99%) were purchased from Testbourne Ltd.

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UK. Argon (Ar) gas cylinder of high purity (99.9%) was purchased from Sigma Gases, India. Oxalic acid ($H_2C_2O_4$), and aluminium foil (0.3 mm thick) were obtained from Merck, India. Deionized water was used for electrochemical anodization.

2.2. Sensor fabrication

Synthesis of porous alumina was already discussed in previous study [26]. The AAO template is electrically insulator. However, the structural features of the AAO membrane provide a hint for the design of nanostructured electrode for sensing applications. After anodization, deionized water rinsed porous AAO substrate was kept in the sputtering chamber at a distance of 5 cm from the Ag target. The sputtering chamber was initially evacuated to a base pressure of 2×10^{-6} Torr. Thereafter working pressure of sputtering chamber was kept constant at 10 mTorr by constant flow of Ar gas using mass flow controller (MKS). The deposition of Ag was carried out for a period of 5 s by applying 30W sputtering power at room temperature. The resistance of Ag/AAO substrate was found to be 1 Ω. i.e., good for electric contact with the sensing layer.

SiC NCs were deposited directly on the Ag/AAO substrate by reactive DC cosputtering technique (Fig. 2). The distance between targets (Si & C) and substrate was kept at 7 cm. Prior to deposition, the sputtering chamber was initially evacuated to a base pressure of 2×10^{-6} Torr. The working pressure was kept constant at 10 mTorr by constant flow of Ar gas using mass flow controller. The deposition of SiC was carried out for a period of 1 h by applying 85 W and 80 W sputtering power at room temperature, respectively.

2.3. Characterization

XRD patterns of the SiC NCs working electrode were recorded using Bruker AXS D8 Advance diffractometer. The morphologies and chemical composition of the samples were characterized by FE-SEM & EDAX (Carl Zeiss Ultra plus, and OXFORD Instruments), and Raman spectroscopy (Renishaw, United Kingdom). The gas sensing measurements were carried out in a custom made sensing setup equipped with PID controlled electric heater. The details of sensing setup were given in authors' previous study [26]. Before sensing test, the sensing chamber was evacuated to 5×10^{-2} Torr with a rotary pump. Thereafter, mixed ratio of high purity H_2 gas (99.99%) and synthetic air (99.99%) were introduced at a rate of 50 cm^3/min controlled by mass flow controller (MKS, USA) in different humidity conditions. The volume of the chamber is approximately 300 cm^3. The electrical response of sensor was monitored using source-meter (Keithley 6221) and nanovoltmeter (Keithley 2182A). The sensor response is defined in Eq. (1)

$$Response\,(\%) = \left(\frac{R_a - R_g}{R_a}\right) \times 100 \quad (1)$$

where R_a is resistance of sensor in air, and R_g is resistance of sensor in analyte gas.

3. Results and discussion

3.1. Structural properties

As shown in Fig. 1a, XRD analysis of sensing electrode shows the sensing material SiC in amorphous form. The sensing electrode also consists of two characteristic peaks at 38.05°, and 44.29° corresponding to (111), and (220) planes of cubic phase of Ag (JCPDS ICDD no. 11164) along with two characteristics peaks at 31.91°, and 33.59° corresponding to (110), and (107) planes of hexagonal phase of Al_2O_3 (JCPDS ICDD no. 20921). No XRD peak of Pd was observed due to small thickness of Pd layer in comparison to SiC layer [8]. In addition, as shown in Fig. 1b, the Raman spectrum of the sensing material shows the five characteristics peaks of SiC NCs at 462, 620, 990, 1373, and 1566 cm^{-1}. The broad peak at 462 cm^{-1}, corresponds to a—Si clusters (Si—Si) and the weak band at 620 cm^{-1} is assigned to Si—Si vibration modes [27]. The weak band at 990 cm^{-1} corresponds to longitudinal optical (LO) vibration of Si—C bond [28,29]. The band centered at 1373 cm^{-1} is due to disorder (D band) in the graphitic clusters sp^2 C—C bonds of amorphous carbon and the band at 1566 cm^{-1} (G band) is assigned to graphitic bonds (C:C) vibration modes [30].

SEM images of the cross-section and top surface of sensing layer are shown in Fig. 2a-b, respectively. The thickness of SiC layer on substrate is around 1000 (±3) nm. Fig. 2c-d shows the elemental distribution and mapping on the sensing layer. All elements are uniformly distributed on the sensing electrode surface. The EDX measurements show that sensing layer contains about 26.75 atomic% Si, and 25.78 atomic% C, and 0.88 atomic% Pd alongwith Al, Ag and O from the AAO substrate.

3.2. Sensing properties

The sensing response of the sensor exposed to 100 ppm H_2 in dry air as a function of time at 300 °C is plotted in Fig. 3(a-b). A very fast response within 7 s was achieved with the recovery time of 13 s with almost constant signal upto 30th cycles. Here, response/recovery time were defined as the elapsed time to reach 90% of the final equilibrium value [31]. The response curve of the gas sensor exposed to various concentration of H_2 gas at 300 °C is shown in Fig. 3(c). This result indicates that the gas sensor is able to detect concentration of H_2 down to 2 ppm and has a good response in the range of 2–500 ppm at 300 °C. Fig. 3(d) shows the response and recovery time characteristics at different H_2 gas concentrations. Here, high surface area of SiC NCs provide the large number of catalytically enhanced surface reaction sites for hydrogen gas, which accounted for the fast detection of hydrogen gas [21,32,33]. The observation of longer response times with decreasing gas concentrations can be attributed to diffusion-limited kinetics at low H_2 concentration [34]. The sensing response of the sensor exposed to 100 ppm H_2 in dry air as the function of temperature is plotted in Fig. 3(e). It can be seen that the gas sensor exhibits pronounced increase in response with increasing the temperature. Small response at low temperatures was observed due to slow chemical activation between adsorbed gas molecules and sensing layer [35]. Here, the wide band gap of SiC minimize the possibility of recombination between electron-hole pairs, reducing the effects of noise and enabling fabricated sensor to be operated at high temperature with high stability [18–20]. The elevated temperature promotes the interaction between oxygen ion and hydrogen atoms, which thus greatly improves the sensitivity of the sensor [19].

Fig. 4(a) shows the I–V characteristics of the sensor in absence/presence of hydrogen gas (100 ppm) at 300 °C in dry air. During hydrogen exposure, the conductance of the sensor increases (shift towards low voltage) due to the increase in free charge carriers (i.e. electrons). The influence of moisture on the sensor response to H_2 gas was investigated with 100 ppm H_2 in air with different relative humidity (0–80%) conditions at 300 °C (Fig. 4(b)). An increase in the response of approximately 4.6% was observed for SiC NCs sensor under the high humidity (60% RH) conditions and then a decrease to initial response was observed upto 80% RH. This abrupt change in response under humidity causes due to the hydroxyl ions (OH^-) adsorption on sensing layer. The selectivity of H_2 gas with respect to other potentially interfering gases such as ammonia (NH_3), hydrogen sulfide (H_2S) and carbon monoxide (CO) at 300 °C for 100 ppm concentration was investigated (Fig. 4(c)). The sensor showed a remarkably high H_2 response (~41%) with a weak