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Graphene decorated Pd-Ag nanoparticles for H_2 sensing

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ABSTRACT

Hydrogen sensor based on graphene nano-composite with Pd-Ag nanoparticles was fabricated by MEMS process. Structural and morphological properties of the sensing film were studied by an energy dispersive spectroscopy (EDS) and field emission scanning electron microscopy (FESEM), respectively. The H_2 sensing properties of as-formed sensor were investigated by measuring the resistance changes at different H_2 concentrations. The maximum gas response was 16.2% at 1000 ppm of H_2 gas. The gas sensitivity of the as-formed H_2 sensor showed linear behavior with the hydrogen concentration. Experimental results showed that the coupling of graphene with Pd/Ag alloy enhanced significantly hydrogen sensing performance.

Introduction

Hydrogen (H_2) is an ideal fuel due to high energy efficiency, eco-friendly resource and can be obtained from different renewable sources [1,2]. As a major drawback for using H_2 gas is its explosive nature, applications of H^2 sensor technologies raised as an important field which solves safety problems including the specific detection of explosive concentration of H_2 gas [3]. Micro electromechanical systems (MEMS) technology is momentous for a lot of reasons that includes numerous processing technologies that are related with the fabrication of integrated circuits with small sizes, low power consumption, and that are operated at room temperature. The MEMS-based resistive sensors have attracted considerable attention due to their ease of fabrication, low cost, fast response, high sensitivity, fast recovery time and high stability [4,5]. The working principle of the MEMS based resistive sensors is that electrical resistance of the sensing film is changed under an exposure of reducing gas. H_2 sensitive materials are the key portion of H_2 sensors, whose operation is dependent on the repeatability, sensitivity, response and recovery behaviors with H_2 species. Palladium (Pd) is one of potential catalytic metals due to its high selectivity for the adsorption of H_2 molecules for H_2 sensing [6]. At high H_2 concentration, the pure palladium membranes suffer from hydrogen embrittlement [7]. To solve the problem, palladium alloys such as Pd-Ag are used that allows higher permeation along with mechanical and chemical stability and therefore lowering the total cost of the raw material [8]. Pd/Ag alloy nanoparticles show the improved resistance and electrocatalytic ability due to the high synergistic interaction between Ag and Pd [9].

Graphene, a two-dimensional (2-D) atomic material, with the maximum surface area to volume ratio, has a lot of

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potential applications in diverse fields [10]. For hydrogen detection, the surface modification of graphene is considered as an effective way such as decorating with noble metal nanoparticles. Johnson et al. studied the hydrogen sensing properties of graphene nanoribbon porous films decorated with palladium (Pd) which showed fast recovery and response time at room temperature [11]. Mubeen et al. studied the application of hydrogen sensing with porous carbon nanotubes (CNTs) doped with palladium [12]. The above studies reveal that the incorporation of metal nanoparticles with graphene plays a major role in detection of gases. Thus, the nano-composite of graphene with Pd-Ag nanoparticles would be a good combination for H_2 sensing due to its high electrical conductivity and large surface area for H_2 molecular adsorption [13].

In this study, a graphene_Pd-Ag nanocomposite based H_2 sensor has been fabricated by a simple MEMS process and its sensing properties were investigated. It was expected that a decoration of graphene with Pd-Ag nanoparticles would improve the hydrogen adsorption due to large number of active sites from Pd/Ag alloy nanoparticles and high carrier mobility of bottom layer graphene. The changes in electrical resistance of the graphene_Pd-Ag nanocomposite upon exposure to different H_2 concentration and operating temperature were analyzed.

Experimental

In present work, the micro-heater sensor platform was fabricated using a conventional MEMS process reported by B. Sharma et al. [14,15]. The H_2 sensor was designed with a chip and the membrane dimensions of the platform and sensing area were 5.0 mm × 4.0 mm and 2.1 mm × 1.5 mm, respectively, as shown in Fig. 1. Commercially available graphene (Sigma Aldrich) was dispersed in a isopropanol solution having a concentration of 0.1 wt%. The graphene was deposited on the sensing area by spin coating. After then, dual sputtering of Pd and Ag were employed and the etching with HNO_3 for 10 min to deposit the Graphene_Pd-Ag nanocomposite thin film on the sensing area.

H_2 sensing response for Graphene_Pd-Ag nanocomposite based H_2 sensor was studied in gas flow chamber as shown in Fig. 1. The flow velocity of gas, including carrier gas (N_2) and H_2 was precisely measured by the mass flow controllers (MFCs). The working temperatures for the as-formed H_2 sensor can be controlled by micro-heater embedded in sensor platform. The experiments were done at different H_2 concentrations injected into the chamber with the carrier gas. The change in resistance was measured with a digital multimeter (Keithley 2100) connected to a computer. The gas response (Rs) of as-formed sensor was determined by the equation: $Rs = (Rn-Rg)/Rn \times 100$, where Rn and Rg are the H_2 sensor resistances in nitrogen and after hydrogen gas injection, respectively. The hydrogen gas concentration and heater voltage were set to be 100–5000 ppm and 2.0V-5.0 V, respectively. The structure and morphology of the graphene_Pd/Ag nanocomposite thin film were characterized using FE-SEM (S-4700 HITACHI) and energy dispersive X-ray spectrometer (EDX, JEOL, JXA-8500 F).

Results and discussions

The electro-thermal properties of the micro heater in the sensor platform were studied using a finite element method (FEM) simulator, COMSOL Multiphysics 3.3. In the present work, platinum was used as the micro heater material due to stable temperature coefficient of resistance. Fig. 2 presents the temperature distribution in the micro-heater sensor platform at the heater voltage of 4.0 V. The diaphragm area was heated regionally, while the temperature of the substrate silicon region was considerably lower than that of the diaphragm. The formation of a micro hot-plate structure near the sensing area can reduce the significantly power consumption of sensor operation. The lowest and highest temperature in the micro-heater sensor platform were around 29.3 °C and 146.6 °C respectively, when the heater voltage of 4.0 V was applied. The temperature distribution around the area of membrane was consistent and uniform with high temperature, as already confirmed [16]. This is also consistent The FEM simulation reveals that with

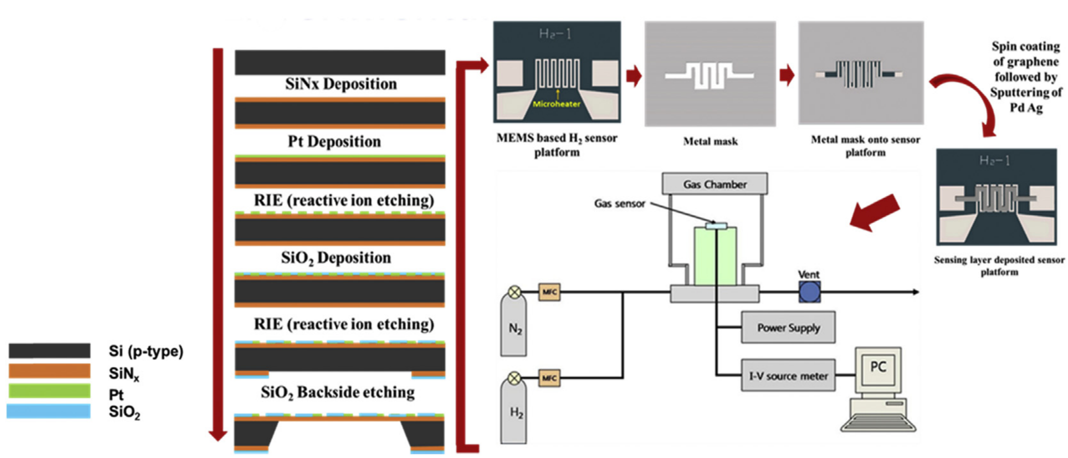

Fig. 1 – Schematic showing the fabrication of as-proposed H_2 sensor and deposition of sensing layer followed by the gas sensing set-up.

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