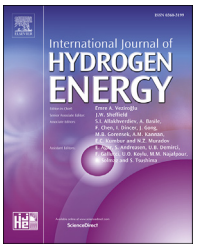
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–7

Available online at www.sciencedirect.com

ScienceDirect

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



Pd/Ag alloy as an application for hydrogen sensing

Bharat Sharma, Jung-Sik Kim *

Department of Materials Science and Engineering, University of Seoul, Seoul 02504, North Korea

ARTICLE INFO

Article history:
Received 24 June 2017
Received in revised form
18 August 2017
Accepted 21 August 2017
Available online xxx

Keywords:
Pd/Ag
MEMS
Microheater
Hydrogen sensors
Sensor response

ABSTRACT

A highly sensitive H_2 gas sensor was fabricated using a Micro Electromechanical Systems (MEMS) procedure having an embedded micro-heater. The palladium-silver (Pd/Ag having stoichiometric ratios 77:23) thin film was deposited by the RF/DC magnetron sputtering and used as the hydrogen sensing layer designed as a zig-zag pattern. Morphological and structural properties of the Pd/Ag thin film was studied by Field emission scanning electron microscope (FESEM), Atomic force microscopy (AFM) and Energy Dispersive Analysis of X-rays respectively. The working temperature of the micro heater showed a linear relation with variations of the heater voltage. The electro thermal properties of the H_2 sensor were studied by finite element method (FEM). The sensing properties of the fabricated H_2 sensor as the change of electrical resistance were studied with respect to hydrogen concentration and temperature. Experimental results showed high sensor response and response time after application of the heater voltage. The sensing properties of the alloyed Pd/Ag thin film were more improved than those of pure palladium. The maximum sensor response (R_s) of the fabricated H_2 sensor was 14.26% for 1000 ppm H_2. The sensor response of the fabricated H_2 sensor showed linear behavior with the heater voltage (operating temperature) and positively corresponded with the hydrogen concentration.

Introduction

Hydrogen sensitive materials are the key portion of hydrogen sensors, whose operation is dependent on the sensor response, repeatability, response time and recovery behaviors with hydrogen species [1,2]. Among various hydrogen sensing materials, palladium (Pd) is one of potential catalytic metals due to its high selectivity for the adsorption of H_2 molecules [3–5]. The exposure of pure palladium on the high H_2 concentration can results in losing the sensor ability due to the H_2 embrittlement. However, hydrogen sensors based on Pd films show some shortages such as mechanical and topographical instability caused from severe lattice expansion and contraction during hydrogenation and dehydrogenation with repeated on–off cycles of exposure to H_2. One of methods solving such mechanical instability of Pd is to be alloying with other elements [6,7]. E. Lee et al. fabricated the novel H_2 sensor that uses the change in electrical resistance for palladium thin films with nanometer (nm) thicknesses [8]. C. Lo. Et. al. proposed the zig-zag Pd–SiO2 thin film H_2 sensors having high relative sensor response (7.7%–9%), a faster response time (10s-30s), and a lower detection concentration limit (50ppm-100 ppm) [9]. M. Kandyla et al. studied the nanocomposite of NiO:Pd H_2 sensors that can detect H_2 concentrations as low as 300 ppb in air and working temperature in the115–145 °C range [10].

Addition of silver to palladium would stabilize the H_2-palladium alloy by avoiding the phase transition from α to β phase [11,12]. Pd–Ag based alloy has great selectivity and

* *Corresponding author.*
E-mail address: jskim@uos.ac.kr (J.-S. Kim).

http://dx.doi.org/10.1016/j.ijhydene.2017.08.142

penetrability towards hydrogen at room temperature, thus becoming an essential wellspring of hydrogen sensitive material for hydrogen sensors that will shape the palladium hydrogen structure which alters the electrical properties. Furthermore, when the hydrogen concentration changes, the detection signal of Pd/Ag alloy is changed. Structural and morphological properties of the Pd–Ag alloy have been found to be an essential for making thin H_2 membranes [13,14]. In addition, alloying Pd with Ag increases hardness, chemical inertness and hydrogen permeability that makes Pd/Ag alloy a vital source for sensitive material of hydrogen sensor. Graham proposed that Pd/Ag alloys have higher H_2 solubility as compared to Pd [15]. Gryaznov as well found that the permeability of H_2 in Pd/Ag is higher than that in Pd [16]. Experiments revealed that 23–30% Ag content in a Pd/Ag alloy has significantly high permeability and solubility as compared to Pd [17]. Addition of Ag decreased the critical temperature of alpha to beta ($\alpha \rightarrow \beta$) phase transformation, and raised the solubility of H_2, while concurrently decreasing its diffusion coefficient, increasing H_2 permeability [18]. T. Lai et al. showed that the higher the surface of Pd/(Pd + Ag) ratio, the higher the hydrogen permeability [19].

In the present work, Pd–Ag based H_2 sensor has been fabricated by a simple Micro Electromechanical Systems (MEMS) process. Since this technology outstands various processing techniques that are correlated with the fabrication of integrated circuited with low power consumption, small sizes and room temperature operation [20]. The main objective of this study is to enhance the thermal capability and sensing performance by depositing Pd–Ag thin film on the sensor platform. Also, the electro-thermal properties of Pt micro-heater embedded MEMS sensor device were studied. The interaction between hydrogen and Pd–Ag alloy was studied by the resistance measurement. The changes in electrical resistance of the Pd–Ag alloy upon exposure to different H_2 concentration and temperature were analyzed.

Experimental

The H_2 sensor was outlined with chip and membrane dimensions of 5.0 mm × 4.0 mm and 2.1 mm × 1.5 mm, respectively as shown in Fig. 1. The dimensions of zig-zag pattern are 1.7 mm × 0.6 mm having the width and spacing of 0.2 mm and 0.1 mm, respectively. The dimension of the Pt resistive-type micro-heater is 1.7 mm × 1.1 mm and the thickness of Pt microheater is 200 nm. The MEMS sensor platform was fabricated as described previously by Yoon et al. [21]. The fabricated sensor platform was used to deposit Pd/Ag sensing layer using dual sputtering technique. Metal mask was placed on the top of sensor platform to deposit the selected area of sensor platform (Fig. 1). The Pd and Ag targets (99.99%) were placed on the left and top side of a chamber and were utilized to deposit films with different compositions of Ag and Pd. The Pd–Ag thin film was deposited by RF/DC magnetron sputtering. The sputtering chamber was cleared to be 1.2×10^{-6} Torr pressure. The argon gas (99.9999%) vacuum was set by adjusting the flow rate and physically controlling the valve used to separate the vacuum pump from the chamber. The Pd–Ag thin film was deposited at a vacuum of 1.2×10^{-2} Torr and an information power of 75 W and 15 W, respectively. A combination of Pd–Ag (77:23) by sputtering system was utilized for the hydrogen sensing material.

The thermal isolation was achieved by backside silicon micromachining process by using KOH (40%, 80 °C) solution. As shown in Fig. 1, MEMS technology has been incorporated in the fabrication process for the formulated H_2 sensor on the sensor platform. After fabrication of microheater, a metal mask was incorporated for the deposition of sensing film. The as-deposited Pd–Ag thin film was patterned by selectively etching using the RIE (Reactive Ion Etching). Finally, the designed H_2 sensor was made through a KOH etching of the back side and lastly, wafer dicing.

The surface morphology and the topology of the Pd/Ag thin film was studied by utilizing a Hitachi S 4300 Field emission scanning electron microscope (FESEM) and Atomic Force Microscopy (AFM) respectively. Elemental analysis was done by using Energy-dispersive spectroscopy (EDS).

As the fabricated H_2 sensor was studied in a flow chamber drafted for gas response testing. The H_2 sensor was situated on the center of the chamber holder. Nitrogen gas (99.9999%) was used as flushing out the test chamber to be inert atmosphere. The sensor was exposed to a flowing hydrogen gas. After sensing response, the hydrogen gas injection was ceased and cleared by nitrogen gas. Mass flow controllers (MFC) were utilized to control the flow rates of hydrogen and nitrogen gases. All data assembled was controlled by a PC furnished with an electronic multimeter (Keithley 2100). The sensor response (R_s) was determined by the equation: $R_s = (Rn-Rg)/Rn \times 100$, 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 200–5000 ppm and 2.5–5.0 V, respectively.

Results and discussions

The core idea for using micro heater is to provide temperature homogeneity for sensing layer. Also, micro heater must operate at fast thermal response time, low thermal mass and less applied voltage so power consumption can be reduced. The heating of microheater is based on joule heating concept [22]. Depending upon the geometry of micro heater the electrical property will be varied. In the present work, we use platinum as the micro heater material due to stable temperature coefficient of resistance (TCR). The temperature of sensing film can affect a variety of factors that includes film resistance, the rate of reaction between the adsorbates on the surface and the quantity of gas absorbed. The temperature of gas sensor is correlated with the sensor response, hence microheater becomes integral part of the gas sensor. To attain acceptable performance of the senor there must be relation between the sensing film and temperatures at which they are operated [23].

Electrothermal properties of the microheater in MEMS platforms were examined using a finite element method (FEM) simulator, COMSOL Multiphysics 3.3. The convection heat coefficients for the bulk silicon and passivation layer are considered for the conventional heat loss. The simulation was performed at an ambient temperature of 25 °C. The effect of

Please cite this article in press as: Sharma B, Kim J-S, Pd/Ag alloy as an application for hydrogen sensing, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.08.142