Annealing effect on hydrogen sensitivity of electrodeposited Pd/Porous Si

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Abstract: We study annealing effect on hydrogen sensing properties of porous silicon (PS) samples coated by a continuous Pd layer using electrochemical method. Variation of sample current as sensitivity parameter on Schottky like Pd/PS configuration at room temperature indicate good gas sensitivity but very weak reversibility. Annealing process improve sensitivity and reversibility but increase response time. Based on SEM, XRD and XPS data we conclude that the increase in gas sensitivity is due to Pd crystallization that enhances the number of diffused hydrogen atoms that reach to the Pd/Si/Si interface. Annealing process remove some defects that act as hydrogen traps and results irreversibility in the unannealed samples. On the other hand, heat treatment increases the response time due to formation of thicker oxide and silicide layers.

Keywords: Pd; Electrodeposition; Porous silicon; Hydrogen gas sensor; Schottky like based gas sensor

Introduction

Nowadays, detection and monitoring of hydrogen have been concerned because of its increasing applications. One of the methods for hydrogen sensing is change of the Schottky barrier height between palladium and a semiconductor. Porous Si(PS) as a semiconductor and high surface area has the capability of being a substrate for deposition of palladium and making hydrogen sensor [1-3]. For this rough and porous surface, palladium coating by electrochemical deposition is one of the most suitable methods. In addition, this process is simple and low cost. In this study, we produced porous silicon samples and coated them by palladium using electrodeposition process. Hydrogen sensing properties of the samples and their change after annealing were measured at room temperature. Altering of sensing properties of the samples by annealing was investigated by x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS).

Experimental

Porous layers were prepared by electrochemical etching of silicon in dimethylformamide (DMF) diluted by HF (Merck). Cyclic voltammetry technique with solution of 1.13 mM PdCl_2 (Merck) and 1.2 mM HCl (Merck) in DI water was employed for Pd deposition. Some of the samples were annealed at 300°C for one hour in air ambient. Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were obtained by Philips XL30. The XRD patterns were recorded using a Philips X’pert instrument operating with CuKα radiation (λ = 1.54178Å) at 40 kV/40mA. For the X-ray photoelectron spectroscopy (XPS), an Al anode X-ray source was employed with a concentric hemispherical analyzer (Specs model EA10 plus) to analyze the surface composition. The chamber pressure during the XPS experiment was 10^{-9} mbar.

Hydrogen sensing properties of Pd/Porous Si/p-type Si samples was measured at room temperature. For this purpose, variation of the electrical current due to gas flow in constant bias voltage between two electrodes (one on the palladium surface and the other on the back of silicon) was measured. Schematic drawing of the electrode geometry for sensing measurement is shown in Fig. 1. The detailed descriptions for the hydrogen detection system were presented in our previous works [1].

Results and Discussion

Fig. 2 (a and b) shows a continues layer of granular palladium films covers the top surface and inside the pores. After annealing process we did not observe any change in SEM images (which are not shown here). Hydrogen sensing properties of Pd/porous Si/Si samples were investigated at room temperature before and after annealing process (Fig. 3). We observed weak hydrogen response and irreversible behaviour on the deposited samples using Schottky like configuration. Annealing the samples at 300°C for one hour in air ambient improved hydrogen sensitivity and response time as is shown in Fig 3. In addition, the recovery behaviour was observed after cutting off the hydrogen flow for the annealed samples.
To understand the effect of heat treatment, we studied the changes in structure and surface composition of the samples due to annealing process, by XRD and XPS experiments (Fig. 4). Deconvolution of the spectra was achieved by fitting the data with a Gaussian/Lorentzian combination peak shape (which is not shown here). As illustrated in Fig. 4, we observed Pd and palladium oxide, palladium silicide, Si and silicon oxide in samples. However, the weak Pd peaks in XRD data before annealing demonstrate that there are many irregularity in deposited Pd layer. While after annealing, the Pd layer is crystallized. Also the oxide (palladium and silicon oxide) and silicide layers increase after heat treatment. Granular structure (SEM results, Fig.2) and weak peaks in XRD data before annealing (Fig. 4) indicate presence of many defects and vacancies in the Pd and interface layers. XRD and XPS data of the annealed samples exhibit grain growth and an increase in palladium and silicon oxide peaks as well as silicide formation in the interface. The Pd crystallization results higher sensitivity due to increase in the number of dissolved hydrogen atoms that reach to the PdxSi/Si interface. In addition, the heat treatment eliminates some defects that act as hydrogen traps and results reversibility in the annealed samples. However, the gain in the response time after annealing is due to increasing in the amounts of oxide and silicide layers.

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**References**

