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Electro-deposited PdNi-Si Schottky barrier hydrogen sensors with improved time response

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Abstract

Hydrogen sensor based on electrodeposited PdNi-Si Schottky barriers have been fabricated with a gradient structure in the PdNi concentration in a single electrodeposition run through variation of the deposition potential. By varying the electrodeposition potential after a fixed amount of charge, we are able to create various Schottky barrier structures. The resulting sensors in the back to back diode configuration show very low idle leakage current and high sensitivity to hydrogen. The structure with increased Ni concentration at the PdNi-Si interface shows dramatically improved time response as compared to the sample with uniform PdNi concentration .

Keywords: Schottky barrier; low power consumption; improved time response

1. Introduction

Hydrogen sensors are crucial in enhancing safety in Hydrogen production, storage, transport and use [1]. Leak detection and monitoring is vital in Hydrogen applications especially as Hydrogen can embrittle storage containers and cause explosive leaks.

Solid state hydrogen sensors are of interest due to their simplicity and their compatibility with allied electronic systems. The basic operating principle of Pd or Pt based hydrogen sensors is two-fold. First, the noble metal catalyses the dissociation of Hydrogen molecules into atoms, and secondly, the hydrogen atoms diffuse into the metal leading to a physical and electrical modification. The sensors based on resistivity change in Pd/Pd-alloy films draw currents in the microampere to milliampere range, and are therefore not very power efficient. Those that sense current changes in Pt/Pd-semiconductor Schottky barriers consume significantly lower power. In this paper, we present a method to speed up the response time of PdNi-Si Hydrogen sensors through growth of a gradient in PdNi concentration with depth.

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2. Fabrication

We have previously introduced a hydrogen sensor based on electrodeposited PdNi-Si Schottky barriers. The sensor is small in size and has an extremely low idle current due to its back to back diode configuration (Fig 1) [2]. The Hydrogen sensor was fabricated on a 1.0-2.0 Ω.cm, <100> n-type silicon wafer. The process flow is shown in Fig 2. To grow the thermal oxide on the Silicon surface, the Silicon wafer was initially rinsed in fuming nitride to remove organic residues, followed by dehydration and transfer of the wafer to a furnace for a 50nm thermal oxide growth, which act as the insulating layer for the second metal layer in the device. Next a 300nm layer of Aluminium was deposited on the back side of wafer by evaporation. The oxide layer was then patterned using photolithography and the exposed layer was etched away by 20:1 Hydrofluoric acid. Subsequently, the wafer was immersed in the PdNi electrochemical solution and a 50nm PdNi film is deposited into the area that was etched away in the previous step. The PdNi film on the exposed Silicon surface will form the Schottky diode. A second photolithography was utilised to pattern the substrate for contact pads and wires made by evaporation of 100nm Al. The redundant Al on the Silicon wafer was lifted off using Acetone which acted as well as a final clean stage.

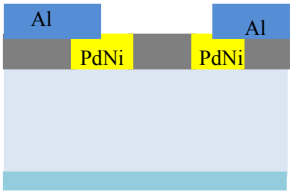


Fig.1. Cross section of back to back Schottky barrier Hydrogen sensor

Pd and Ni were co-deposited from the solution to create an alloy with 30% Ni which suppresses an irreversible phase change at higher Hydrogen concentrations that occurs in pure Pd. The sensors exhibit large change (factor of 100) in current on exposure to gaseous Hydrogen. Despite this large change, the current was observed to be less than 500 nA over the measured Hydrogen pressure range of 25 mbar. The sole significant drawback of the sensor was the slow response time of the order of 10s of minute, which we address here using method to speed up the response time through growth of a gradient in PdNi concentration with depth.

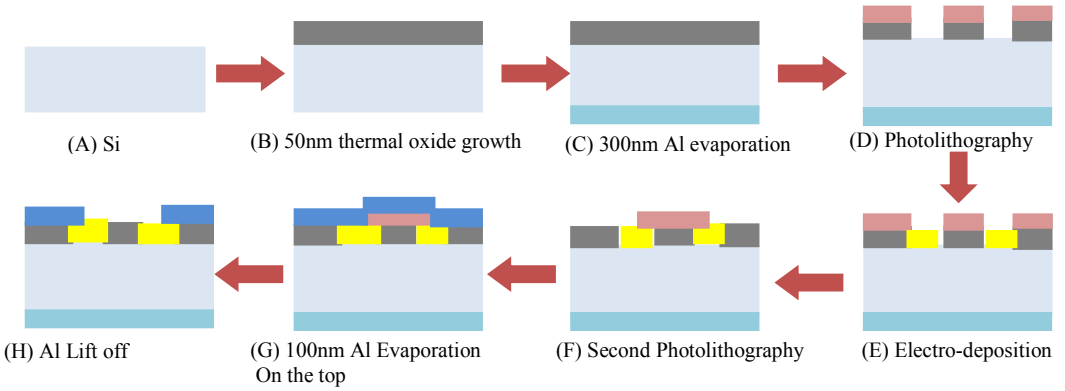


Fig.2. Fabrication Process of Hydrogen sensor

3. Experiment and results

Fig 3(a) shows that a wide range of Ni concentrations can be achieved from a PdNi solution simply by varying the deposition potentials. The concentration ratios of the elements are determined by the electro-deposition potential with larger negative voltages leading to higher Pd concentration.

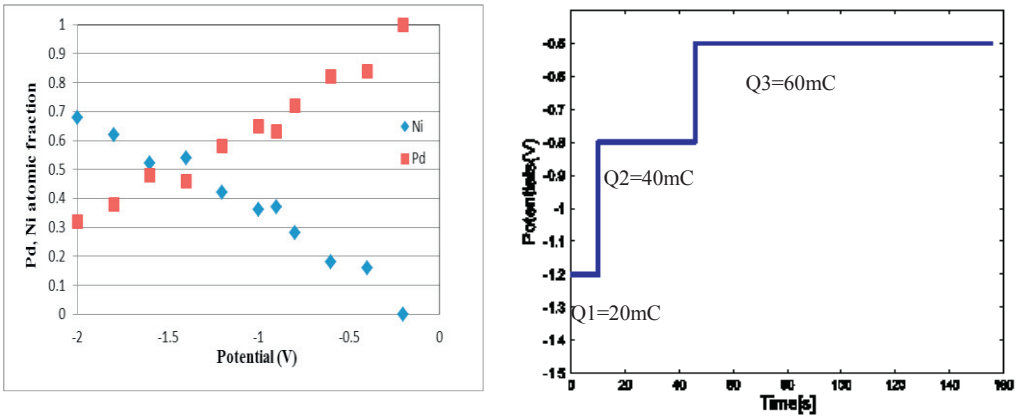


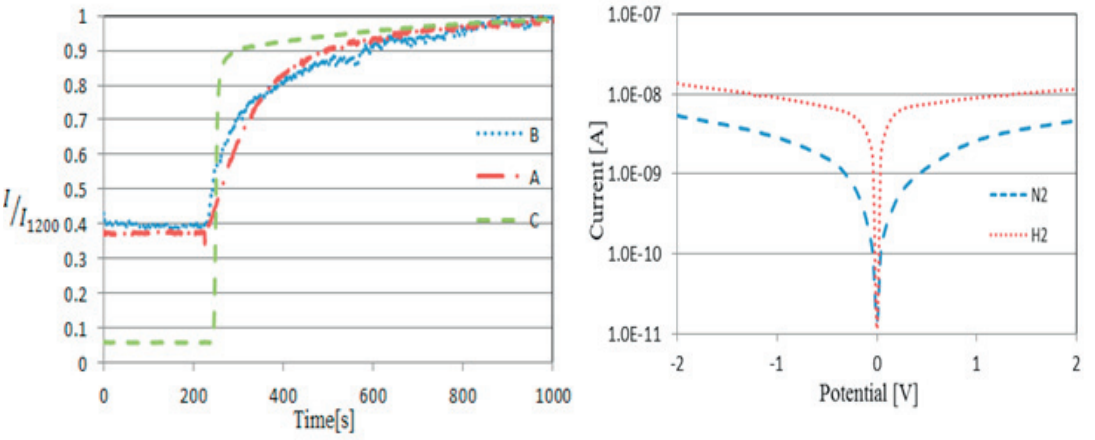
Fig.3. (a) Energy dispersive x-ray analysis Pd, Ni atomic fraction in films deposited at different potentials from a PdNi solution. (b) The potential variation during the electro-deposition with three steps. Each step corresponds to 20mC of charge.

Based on results displayed in Figure 3, by varying the electro-deposition potential after a fixed amount of charge, we are able to create various Schottky barrier structures (Fig 4). Structure A has uniform concentration, structure B has an increased Pd concentration at the top surface to speed up H2 dissociation and structure C has as well an increased Ni concentration at the Si interface to improve the interface dynamics.

(A) (B) (C)

Fig.4. Three structures of PdNi Schottky barrier,(A) uniform concentration, (B) increased Pd concentration at the top surface, (C) increased Ni concentration at the Si interface.

When applying an electrodeposition potential of -0.8V, the EDX data show that the alloy film contains nearly 30% Ni. The higher the deposition potential applied, the lower the Ni concentration and vice versa. The PdNi-Si Schottky barriers have been fabricated with a gradient structure in the PdNi concentration in a single electrodeposition run through variation of the deposition potential as Fig 3 (b) shows. The total deposition process was divided into three steps for the 50nm PdNi structure variation. Initially, the electrodeposition potential was set to be -1.2V to create the bottom layer of the PdNi alloy film with Ni concentration 40%. The total applied charge was set to equal 20mC which corresponds to 7 seconds of electrodeposition. The potential was then set to -0.8V for 30% Ni in the middle layer film. Finally, a voltage of 0.5V was selected to create a 10% Ni concentration on the top layer of the film. The process ends with the total charge of 60mC, which corresponds to a PdNi film thickness PdNi of 50nm.



(a) (b)

Fig .5.(a) Normalized time response of structures A, B, C three devices time response after the exposure to 0.1bar of Hydrogen. . (b). Electrical characteristic of hydrogen sensor with structure for Nitrogen and 0.1bar Hydrogen

Fig 5 (a) shows the time response of the devices after exposure to 0.1bar of hydrogen. The response of the structure C has improved dramatically with a response time of less than a minute while structure B remains similar to structure A. This clearly indicates that hydrogen dissociation is not the limiting factor and that larger Ni concentration at the Si interface speeds up hydrogen capture. Fig 5 (b) illustrates the I-V characteristics of the structure C Schottky barrier hydrogen sensor in Nitrogen and Hydrogen ambient. The sensor exhibits a low current in the Nitrogen ambient over the entire potential range. While under the hydrogen exposure, the modification of the PdNi work function changes the Schottky barrier at the interface leading to a strong current increase in the sensor.

4. Conclusion

The fabrication and characterization of three different structure PdNi-Si Schottky barrier hydrogen sensors is presented. The new gradient structure sensor has a low idle current in Nitrogen ambient and exhibits a sensitive current change on exposure to 0.1 bar Hydrogen. The improvement of response time (less than one minute) with increased Ni concentration at the surface indicates that hydrogen dissociation is not the limiting factor for the time response. The time response characteristic reveals that the higher Ni concentration at the Si interface will speed up hydrogen capture.

Acknowledgements

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