Pd/Cr Gates for a MIS Type Hydrogen Sensor

Linfeng Zhang[1], Erik F. McCullen[1], M.H. Rahman[2], Ron J. Baird[1], Ratna Naik[3], Lajos Rimai[1], Greg W. Auner[1], K. Y. Simon Ng[2*]
[1]Department of Electrical and Computer Engineering
[2]Department of Chemical Engineering and Materials Science
[3]Department of Physics and Astronomy
Wayne State University, Detroit, MI 48202

Abstract

Instead of the pure Pd gates in MIS type hydrogen sensor, Pd-Cr alloy gates with different composition and structure were used to improve the sensor's performance. The use of Pd-Cr alloy not only extended the dynamic range from 100 ppm to 50,000 ppm of hydrogen, but also showed quick response. The dynamic range and sensitivity were related to the nature of metal outer surface and the metal/insulator interface respectively.

Introduction

As documented in earlier publications [1], the Pd/AlN/Si structure behaves as a voltage dependent capacitor. This type of sensor showed high sensitivity and selectivity to hydrogen down to 1 ppm. However it showed saturation around 60 ppm, as well as a long response time and baseline drift. After exposure to high hydrogen concentration, the Pd gate could be easily separated from the insulator surface, and the morphology of the Pd gate would change significantly [2, 3]. To make a more stable catalytic metal gate, other elements, such as Ag, Cr and Ni, could be added to the Pd to make the gate more stable.

In this paper, four samples with different Pd-Cr gate structure were prepared. Their morphology, dynamic range, sensitivity and stability were compared to the corresponding properties of sensors with pure Pd gates. These results would provide a better understanding of the relationship of the metal gate structure and composition to the sensor's response, and would shed light on the design of a MIS type sensor with better performance.

Experimental

AlN (500 Å) was prepared in the plasma source molecular-beam epitaxy (PSMBE) chamber. The Al back contact (3000 Å), and Pd or Pd-Cr alloy gates of 1.0 mm diameter were deposited in magnetron sputtering chamber. The composition and chemical state of the gates were studied by X-ray Photoelectron Spectrometry (XPS). The morphology of the gate surface was investigated through atomic force microscopy (AFM). The electrical response measurements were performed in a separate gas flow chamber and are described in detail elsewhere [1].

* Corresponding author. Phone: +1 313 577 3805. Fax: +1 313 578 5814. Email: sng@wayne.edu

Results and discussions

In order to investigate the effect of the surface composition of the gate and the role of the gate/insulator interface, four sets of capacitors with different gates structures were prepared: Pd/AlN/n-Si, $Pd_{0.96}Cr_{0.04}$/AlN/n-Si, Pd/$Pd_{0.96}Cr_{0.04}$/AlN/n-Si, and $Pd_{0.96}Cr_{0.04}$/Pd/AlN/n-Si (Fig. 1)

The morphology changes of the Pd and Pd alloy gates due to hydrogen exposure were studied with AFM. Compared the surface of the pure Pd gate before and after exposure to 50,000 ppm hydrogen, the morphology changes dramatically from many small grains to some large aggregates. The root mean square roughness (RMS) increased from 1.243 nm to 2.039 nm. However, on the $Pd_{0.96}Cr_{0.04}$ gate, there is no significant morphology change on the alloy surface. The RMS increases from 0.374 to 0.508 nm. Comparing these two samples, the surface of the Pd-Cr alloy gate would be more stable and smooth.

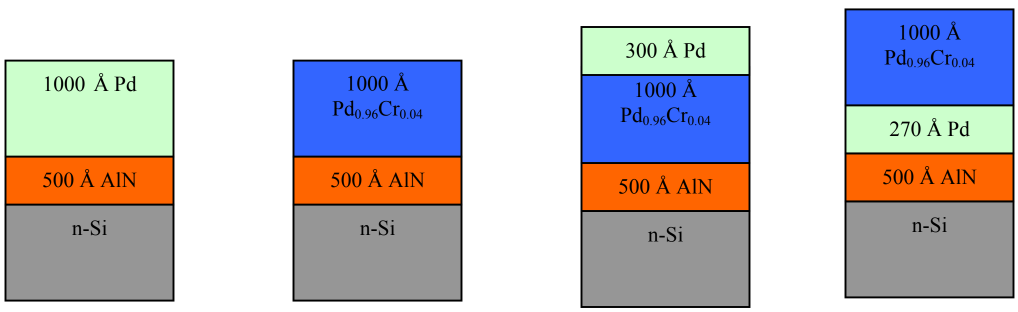

Fig. 1 Schematics of the four samples with different metal gate structures: Pd, $Pd_{0.96}Cr_{0.04}$, Pd/$Pd_{0.96}Cr_{0.04}$, and $Pd_{0.96}Cr_{0.04}$/Pd, to illustrate the effect of the metal/insulator interface and metal outer surface on the hydrogen sensing

Fig. 2 shows a part of the response from the $Pd_{0.96}Cr_{0.04}$ gated sample at 80 ^{o}C. This sample could be used to measure hydrogen concentration up to 50,000 ppm, its dynamic range is 1,000 times wider that of the Pd-gated sample. This sample is found to be stable even after more than 20 hours of testing and there was no response baseline drift. Thus, there is a direct correlation of the absolute voltage value to a hydrogen concentration. In practice, such type of sensor would be more useful because the sensor could measure the true hydrogen concentration continuously.

Fig. 3 is the voltage shift responses as a function of hydrogen concentration from the four types of sensors at 80^{o}C. From the trends of these four type sensor's response, sensor with pure Pd gate could be used to detect or measure hydrogen from 1 ppm to 50 ppm. Sensor with $Pd_{0.96}Cr_{0.04}$ gate could be used when the hydrogen concentration is from 100 ppm to 50,000 ppm. The response amplitudes of the sample with $Pd_{0.96}Cr_{0.04}$/Pd $Pd_{0.96}Cr_{0.04}$ gate, Pd/$Pd_{0.96}Cr_{0.04}$ gate are very similar, they are far less than the response amplitude with pure Pd gate.

Since the number of the sites for protons on the metal/insulator interface is limited, if all these sites are occupied, the sensor would show saturation. In order to widen the dynamic range, the concentration of absorbed hydrogen molecules/protons on the outer surface of the gate must be limited. Thus the number of sites occupied by protons would decrease at the metal/insulator interface. To improve the dynamic range, the metal outer surface was modified to lower the concentration of adsorbed hydrogen. Adding of the Cr would decrease the number of active sites through blocking some of the active sites on the surface and making the gate surface smooth. Thus the number of hydrogen molecules/atoms absorbed on the surface of the Pd-Cr is less than that of pure Pd, and the dynamic range is therefore increased.

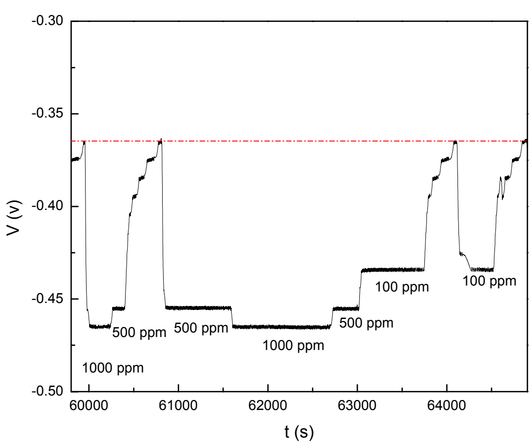

Fig. 2 The bias voltage response of $Pd_{0.06}Cr_{0.04}$/AlN/Si at 80°C with conctant capacitance.

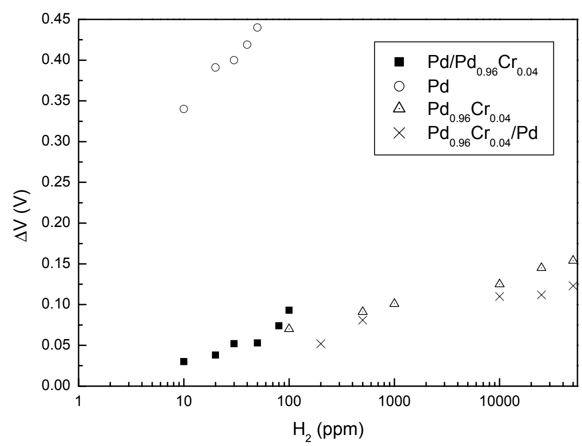

Fig. 3 The voltage shift responses of the four samples with different metal gate structure to hydrogen. Here the sensor with $Pd_{0.96}Cr_{0.04}$ outer surface shows the wider dynamic range than the sensor with pure Pd gate. However the response amplitude decreases in the sensor with $Pd_{0.96}Cr_{0.04}$ layer.

Because the proton layer on the metal/insulator interface determines the thickness of the depletion layer in the semiconductor side, the sensitivity depends on this proton layer. Because the addition of Cr would decrease the solubility of hydrogen in Pd-Cr alloy [4, 5], it is reasonable to suggest that the sensitivity with the Pd/AlN interface is much higher than that of Pd-Cr/AlN interface since the number of protons on the interface of the Pd/AlN is more than that of Pd-Cr/AlN at equilibrium. Also the time needed to arrive at the equilibrium in Pd-Cr is shorter than that in Pd and the turn on response of the Pd/Pd-Cr gated sensor is faster than that of the Pd gated sensor.

Conclusion

The addition of the Cr tends to suppress the change of the surface morphology and maintain a smooth metal alloy film surface. With this alloy, the sensor could measure the hydrogen in a much higher concentration range. Moreover, the addition of Cr would minimize the response baseline drift and make it possible for this sensor to measure the hydrogen concentration continuously. Finally, the turn on response time was dramatically shortened with the adding of Cr. Thus, Pd-Cr metal film seems to be a very promising gate material for hydrogen sensor.

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