

Performance of a MIS Type Pd-Cr/AlN/Si Hydrogen Sensor

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ABSTRACT

An MIS Hydrogen sensor with a Pd_{0.96}Cr_{0.04}/AlN/Si structure was fabricated, exhibiting the dynamic range considerably wider than that of analogous devices with pure Pd gates. A useful response could be obtained for Hydrogen concentrations as large as 50,000 ppm. Although the response amplitude was much reduced at the lower concentrations, satisfactory signal to noise down to 50 ppm could be obtained. The saturating magnitude of the electrical response is in the range of 0.1 to 0.5 V, which is the same as that for the pure Pd gated devices, inspite of the 3 orders of magnitude difference in the saturation hydrogen concentration. This result will be discussed in terms of the response mechanism of these devices.

INTRODUCTION

When biased in depletion the Pd/AlN/Si metal/insulator/semiconductor (MIS) structure behaves as a voltage dependent capacitor [1, 2]. At constant capacitance, the presence of hydrogen in the surrounding gas causes a voltage shift, which increases in magnitude with increasing hydrogen concentration. This type of sensor shows high sensitivity and selectivity to hydrogen down to 1 ppm. However it saturates at around 60 ppm [3]. It also has a very slow response time and exhibits baseline drift. Such a sensor may present a problem to quantify hydrogen in high concentrations. Moreover, it is known that at high hydrogen concentrations (>1%), Pd goes through a phase transition from α to β . The Pd gate could be easily separated from the insulator surface, and the morphology of the Pd gate would change significantly, possibly negatively affecting the sensors performance [4, 5]. To make a more stable catalytic metal gate, other elements could be added to the Pd to suppress the phase transition and increase the dynamic range.

In our study, Pd-Cr alloy was used as the metal gate. Aluminum nitride (AlN) was used as insulator since its band gap (6.2 eV) is much wider than the band gap of Si (1.2 eV). Furthermore, AlN has high chemical durability and its thermal expansion coefficient matches well that of Si(111) substrates thus improving the stability of the sensor

This paper, describes the preparation of devices with Pd-Cr gates. Their morphology, dynamic range, sensitivity and stability were compared to the corresponding properties of sensors with pure Pd gates. These results might provide a better understanding the effect of Cr on the sensor's response, and guidance towards the design of a MIS type sensor with improved performance.

EXPERIMENTAL

Pd-Cr/AlN/n-Si thin film devices (1 mm diameter gates) were fabricated by a combination of plasma source molecular-beam epitaxy (PSMBE) and magnetron sputtering. The composition of the Pd-Cr was controlled by the power on the Pd and Cr sputtering targets. The electrical measurements were performed in a separate gas flow chamber and are discussed in detail elsewhere [6].

RESULTS

Initially devices with Pd_{0.90}Cr_{0.1} gates were prepared but showed no observable sensitivity to hydrogen. The probable reason was the presence of a sufficiently large surface concentration of oxidized Cr to block all active sites on the gate. Therefore the concentration of Cr was decreased to 4% and the results reported below were obtained on Pd_{0.96}Cr_{0.04} gated devices .

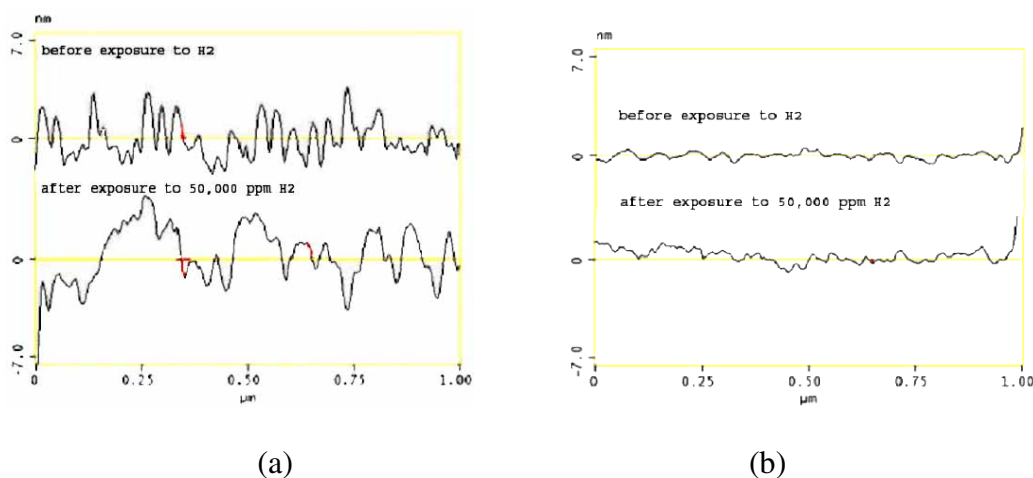


Fig. 1 Cross sections of AFM images of Pd (a) and Pd_{0.96}Cr_{0.04} (b) gate surfaces before and after exposure 5% of hydrogen

The morphology changes of the Pd and Pd alloy gates due to hydrogen exposure were studied with Atomic Force Microscopy (AFM). The samples were incubated under a constant 100 sccm H₂/N₂ flow in the testing chamber at 80°C for 8 hours. The AFM analysis of the surfaces was performed only after a subsequent period of 24 hours outside the testing chamber at room temperature. Fig. 1 a-b shows a comparison of the surface of the pure Pd and Pd-Cr gate before and after exposure to 50,000 ppm hydrogen. Because the AFM tips used here were type NP from Veeco (the tip radius was 20 nm and the front and back angles were 35°), these tips could not effectively probe the bottom of the cracks on the surface. Thus the real depth of the surface could not be measured through AFM.

The above data indicates, first, that the surface of the Pd_{0.96}Cr_{0.04} film appears to be more stable in high hydrogen concentration. Second, the roughness of the Pd-Cr alloy is much lower than of pure Pd, and it is practically unaffected by Hydrogen exposure. Third, the effective surface area of Pd-Cr gate is substantially smaller than that of the Pd. Thus there are less active sites on the Pd-Cr surface to dissociate hydrogen molecules into hydrogen atoms and protons.

Therefore, the morphology of the gate surface can have a direct influence on the sensor's dynamic range and sensitivity.

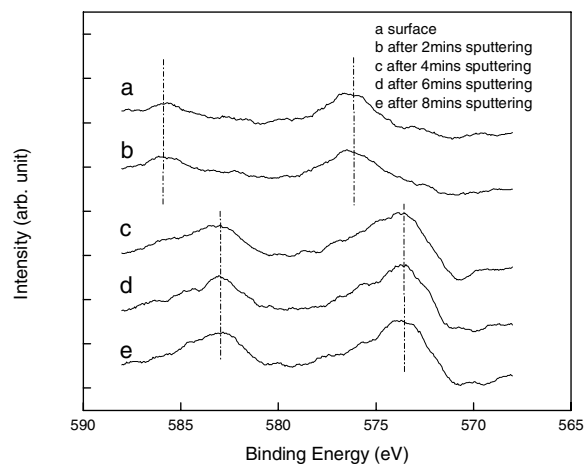


Fig. 2 The main peak of Cr shifts with different sputtering time

From the Ellingham diagram, Cr is very easily oxidized at room temperature even at partial pressure of oxygen as low as 10^{-40} atm. In order to assess the thickness of oxidized chromium layer, XPS was used. Depth profiling was performed using argon ion sputtering. Due to the very small Cr XPS signal in the 4% sample, an identically prepared sample with 10% Cr was used for XPS analysis instead. Fig. 2 shows the XPS results for the Cr 2p peak. This diagram shows the shifting of the peaks to lower binding energy with sputtering, indicating that the surface Cr was oxidized to CrO_2 down to about 80-100 Å.

Response of device to hydrogen

Before the hydrogen testing was performed, the temperature of the samples was maintained at 80 °C for at least 4 hours in 100 sccm nitrogen flow inside the electrical testing chamber. This pretreatment procedure was found to produce more stable and consistent results. For all experiments, the total flow rate was maintained constant at 100 sccm, for different hydrogen concentrations, balanced with nitrogen.

Fig. 3 shows the response from the $\text{Pd}_{0.96}\text{Cr}_{0.04}$ gated sample at 80 °C. The maximum voltage shift is 0.12 V, which is one third of the maximum response from a device with pure Pd gate. The results clearly show that this type of device could be used to measure hydrogen concentration up to 50,000 ppm, corresponding to a dynamic range that is 1,000 times wider than that of the Pd-gated sensor. Moreover, the two absolute voltage values corresponding to 25,000 ppm (Fig. 3a) are the same (0.515 V), even though the hydrogen was turned on for the second 25,000 ppm response before the signal went back to the baseline. Fig. 3(b) shows this behavior more clearly at 100 ppm, 500 ppm and 1000 ppm hydrogen concentrations. This device remains stable even after more than 20 hours of testing with no apparent response baseline drift. Thus, there is a direct correlation of the absolute voltage value to hydrogen concentration. This is an important practical advantage of this sensing structure, as it yields a single device capable of

measuring Hydrogen concentration over such a wide range without need of frequent base line monitoring.

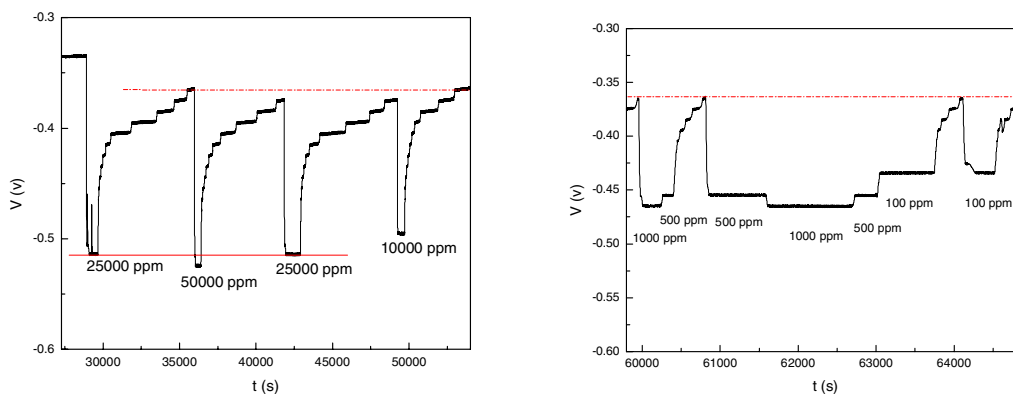


Fig. 3 The response to hydrogen from Pd_{0.96}Cr_{0.04}/AlN/Si at 80 °C

DISCUSSION

These experimental results can be understood if one assumes that the number of the sites that can be occupied by protons in the AlN near its interface with the gate limited. If protons occupied all these sites, the sensor would show saturation. Because there is equilibration between the outer surface and the metal/insulator interface, if the hydrogen molecule/atom concentration absorbed through outer surface could be decreased for the same hydrogen concentration in the gas phase, the number of sites occupied by protons would decrease at the metal/insulator interface. Thus, one approach to improve the dynamic range is the modification of the metal outer surface to lower the concentration of adsorbed hydrogen. In our experiments, the adding of the Cr would decrease the number of active sites by blocking some of the active sites on the surface as well as by making the gate surface smooth (Fig. 1). 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 to 50,000 ppm.

From the capacitance-voltage curve, the maximum capacitance (C_0) due to AlN could be obtained at low frequency without the consideration of the series resistance effect. For the present devices C_0 in the order of 2000 pF. Assuming that the charges causing the response (i.e. the induced voltage drop across the AlN layer) remain near the metal/insulator interface, the number of protons can be calculated based on the voltage, $Q = C_0 \Delta V$. From Fig. 3, when the in saturation number of protons is 2.0×10^9 for the Pd_{0.96}Cr_{0.04} gates, half of that for the pure Pd gate (5.4×10^9). It is possible for these protons to form monolayer on the metal/AlN interface. Furthermore, the number of protons in pure Pd film is far less than the calculation from Sievert's law (4.6×10^{14}) or from hydrogen solubility testing using the electrochemical "stripping" method (1.2×10^{14}).

It is well known that the addition of Cr would decrease the solubility of hydrogen in Pd-Cr alloy, thus 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 AFM study has shown that the pure Pd gate suffers more drastic morphological changes upon exposure to high hydrogen concentrations, and therefore could affect the sensors performance over the long term. Adding Cr tends to suppress the change of the surface morphology and maintain a stable and smooth metal alloy film surface. Also, with this alloy, the sensor could measure the hydrogen in a much higher concentration range and the response to hydrogen was much more reproducible. Moreover, adding 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.

Considering the performance of the sensor at high hydrogen concentration, Pd-Cr metal film seems to be a very promising gate material for hydrogen sensor.

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