Effects of Annealing Temperature on Sensing Properties of Pt/HfO_2/SiC Schottky-Diode Hydrogen Sensor

W.M. Tang, C.H. Leung and P.T. Lai

Abstract - Hafnium oxide (HfO_2) is successfully used as gate insulator for fabricating Metal-Insulator-SiC (MISiC) Schottky-diode hydrogen sensor. Sensors undergone N_2 annealing at different temperatures are fabricated for investigation. The hydrogen-sensing properties of these samples are compared with each other by taking the measurements at high temperature under various hydrogen concentrations using a computer-controlled measurement system. Experimental results show that sensitivity increases with the annealing temperature. Higher annealing temperature can enhance the densification of the HfO_2 film; improve the oxide stoichiometry; and facilitate the growth of a SiO_2 interfacial layer to give better interface quality, thus causing a remarkable reduction of the current of the sensor under air ambient. The effects of hydrogen adsorption on the barrier height and hydrogen-reaction kinetics are also investigated.

I. INTRODUCTION

Hydrogen is widely used in our daily life, e.g. in food processing, cooling in power station and electronic fabrication process. However, hydrogen is a very dangerous gas because it can cause serious explosion when a spark is present. In order to prevent these accidents, hydrogen sensors have become increasingly important in leakage detection. The first SiC Schottky-diode hydrogen sensor was developed by Hunter at NASA Lewis Research Center in 1992 [1]. It was a simple Schottky-diode structure, which had a catalytic metal Pd directly deposited on SiC. The fabrication procedure of this hydrogen sensor is simple. However, its structure is not stable after long-term high-temperature operation because intermixing of materials between layers occurs at high temperatures due to the poor interface properties of this structure. A Metal-Insulator-Semiconductor (MIS) structure involving the use of a gate insulator was then developed to reduce the interfacial diffusion between the electrode and the substrate. The gate insulator can make the structure more stable for gas sensing. HfO_2 is a promising gate insulator for making MISiC Schottky-diode hydrogen sensor because preliminary results showed this high-*k* sensor had much higher sensitivity than its SiO_2 counterpart [2]. Annealing the deposited HfO_2 film can provide better dielectric properties; activate the sensor for higher sensitivity; stabilize high-temperature performance. So, in this study, the effects of the annealing temperature on the sensing properties of the sensor are investigated.

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II. EXPERIMENTS

N-type (0001) Si-face 4H-SiC wafer was used in this study. HfO_2 was deposited at room temperature by DC sputtering of hafnium metal (99.99 % purity) at a power of 17.5 W in a mixed Ar/O_2 ambient (Ar to O_2 ratio 4:1) for 20.9 min. An electrode consisting of 100-nm Pt with a diameter of 0.5 mm was then deposited on the wafer by DC sputtering through a stainless-steel shadow mask. The sample then underwent an annealing at 650 ^{o}C in N_2 (1000 ml/min) for 5 min (denoted as H650 sample). In order to investigate the effects of annealing temperature on the sensor performance, two more hydrogen sensors annealed at 750 ^{o}C and 850 ^{o}C were fabricated (denoted as H750 and H850 samples respectively). The final structure of the hydrogen sensors fabricated is shown in Fig. 1. In order to facilitate taking data, a computer-controlled measurement system was constructed (see Fig. 2)

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for studying the steady-state and transient responses of the sensors.

III. RESULTS AND DISCUSSION

Fig. 3 shows the *I-V* curves of the samples measured in air and in 48-ppm H_2 in N_2 at 450 ^oC. The *I-V* curve shifts to the left upon exposure to hydrogen due to the formation of a polarized layer at the electrode-insulator interface. When hydrogen-containing molecules come to the surface of the front electrode, they dissociate to hydrogen atoms, which then diffuse through the electrode to form a polarized layer at the electrode-insulator interface. This polarized layer provides an extra electric field to lower the potential barrier at the electrode-insulator interface, and hence produce the shift of the *I-V* curve. The inert shows the sensitivity of the samples at different temperatures when the test chamber environment is changed from air to 800-ppm H_2 in N_2. The sensitivity is defined as $(I_{H2}-I_{air})/I_{air}$ where I_{H2} and I_{air} are currents measured under H_2 environment and air respectively. All the samples show a maximum sensitivity at 450 ^oC. When temperature increases, H_2 can decompose faster to H atoms at the surface of the electrode, and more H atoms can more rapidly diffuse through the electrode, thus increasing the device sensitivity. At very high temperature (> 450 ^oC), the reaction rate of the H atoms with oxygen at the surface of the electrode increases rapidly, and so the sensitivity decreases. The *I-t* curves of the samples at 450 ^oC (bias voltage V = 2.5 V) are shown in Fig. 4, and can be used to obtain the current shift (I_{H2} – I_{air}) and thus sensitivity of each sample. The measured data show that the H850 sample has the highest sensitivity while the H650 sample has the lowest.

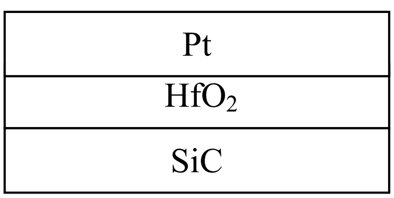

Fig. 1 Structure of the hydrogen sensor.

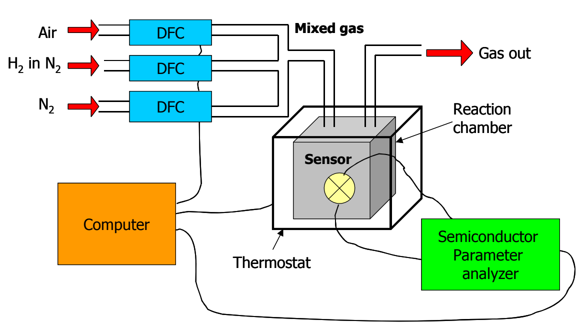

Fig. 2 Computer-controlled measurement system.

Fig. 5 shows the variation of physical oxide thickness and leakage current in air (I_{air}) of the sensors. The oxide thickness of the as-deposited HfO_2 film is 9.76 nm and is reduced to 5.51 nm after annealing in N_2 at 650 ^oC for 5 min due to densification of the high-*k* film at high temperature. As the annealing temperature further increases, it does not have much effect on the physical oxide thickness, implying that the annealing at 650 ^oC can basically complete the densification. The graph also shows that sensors annealed at higher temperatures have smaller I_{air}. Possible reasons are (1) better stoichiometry and dielectric properties of bulk HfO_2; (2) thicker SiO_2 interfacial layer grown between HfO_2 and

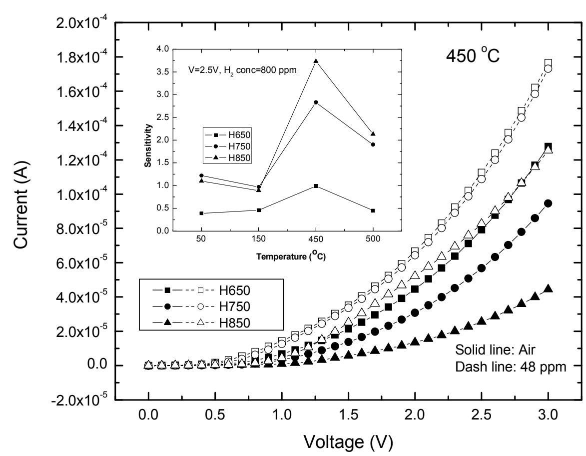

Fig. 3 *I-V* curves of the samples in air and in 48-ppm H_2 at 450 ^oC. The insert shows the sensitivity of the samples at different temperatures.

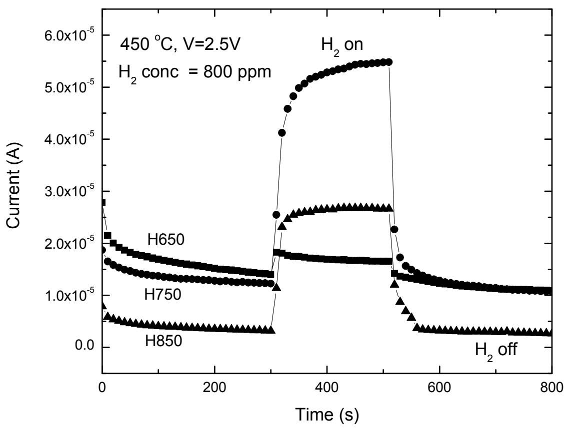

Fig. 4 Current-time (*I-t*) characteristics of the samples at 450 ^{o}C under a fixed bias voltage of 2.5 V.

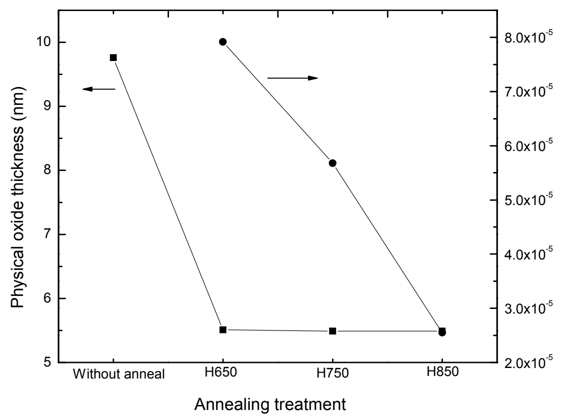

Fig. 5 Variation of physical oxide thickness and leakage current in air (I_{air}) of the H_2 sensors annealed at different temperatures in N_2 ambient.

the SiC substrate for blocking the injection of electrons from the substrate into the high-*k* dielectric more effectively [3, 4]; (3) fewer interface traps and oxide charges [5].

In Fig. 6, the sensitivities of the samples upon exposure to different H_2 concentrations are compared at 450 ^{o}C and a forward bias of 2.5 V. The sensitivities of all samples increase with hydrogen concentration. It is found that the sensitivity of the devices strongly relies on the annealing temperature. Sensitivity increases with annealing temperature because the samples annealed at higher temperatures have smaller I_{air} and larger change in barrier height (see Fig. 7).

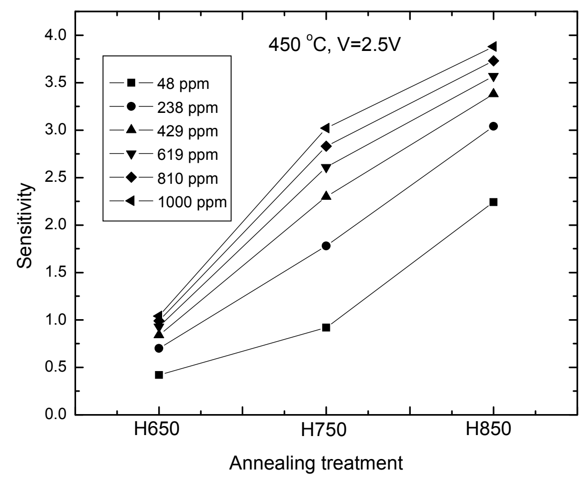

Fig. 6 Sensitivity of the samples upon exposure to different H_2 concentrations at 450 ^{o}C (bias voltage V = 2.5 V).

The sensitivity of the H850 sample is much higher than those of the H750 and H650 samples. When a 1000-ppm H_2 in N_2 gas is introduced, the H850 sample exhibits a high sensitivity of 388 %, which is about 3.7 and 1.3 times higher than those of the H750 and H650 samples respectively. Fig. 7 shows the change in barrier height of the samples upon exposure to different H_2 concentrations. When H_2 concentration increases, the barrier height of the sensors decreases. This is because when more hydrogen-containing molecules reach the front electrode, more dissociated H atoms can be absorbed at the electrode-insulator interface to fo-

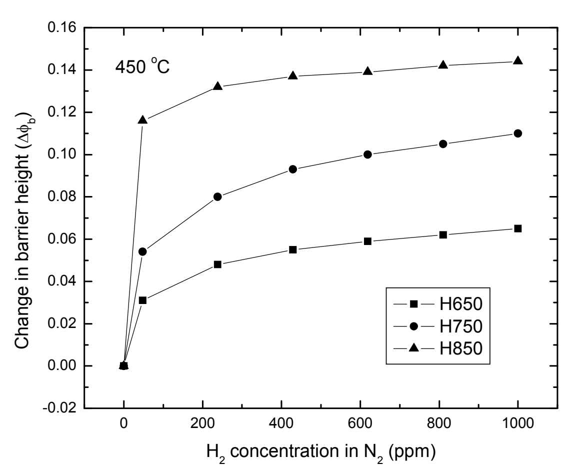

Fig.7 Barrier height of the samples upon exposure to different H_2 concentrations at 450 ^{o}C.

rm a stronger polarized layer, causing a larger barrier-lowering effect. Interface traps and oxide charges may screen the effect of the polarized layer [4]. The samples annealed at higher temperatures have better HfO_2/SiC interface properties and hence give a larger $\Delta\phi_b$. The plot of $1/\ln(I_{og}/I_o)$ vs $(1/P_{H2})^{1/2}$ of the samples at 450 ^oC is shown in Fig. 8, where I_o and I_{og} are the saturation currents in air and in H_2 respectively; P_{H2} is the hydrogen partial pressure. The graph shows good linearity, which confirms the hydrogen-reaction kinetics of the sensors.

IV. CONCLUSION

Pt/HfO_2/SiC Schottky-diode hydrogen sensors annealed at different temperatures have been fabricated and studied. Experimental results show that the sensors demonstrate high sensitivity, rapid and stable response at high temperature. These properties indicate promising applications for detecting hydrogen leakage in harsh environments. The study has also found that raising the annealing temperature can increase the sensitivity of the hydrogen sensors. It is because high-temperature annealing can increase the thickness of the SiO_2 interlayer and densify the high-k film, resulting in fewer interface states, oxide charges and better film stoichiometry to give smaller I_{air} and hence higher sensitivity.

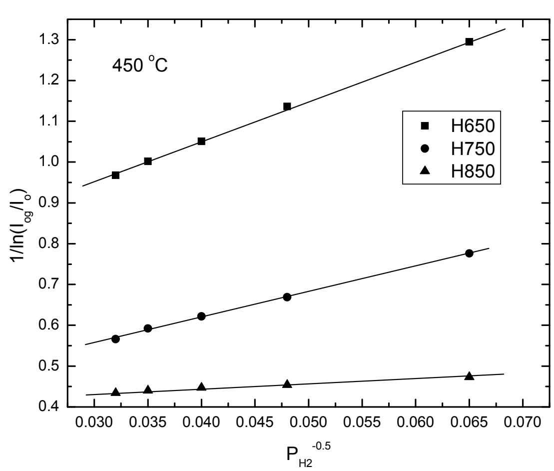

Fig. 8 Steady-state reaction kinetic analysis for hydrogen absorption of the samples at 450 ^oC.

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