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Hydrogen gas sensing properties of Pt/Ta_2O_5 Schottky diodes based on Si and SiC substrates

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Abstract

In this paper, we fabricated Pt/tantalum oxide (Ta_2O_5) Schottky diodes for hydrogen sensing applications. Thin (4 nm) layer of Ta_2O_5 was deposited on silicon (Si) and silicon carbide (SiC) substrates by radio frequency (RF) sputtering technique. We compared the performance of these sensors at different elevated temperatures of 100°C and 150°C. At these temperatures, the sensor based on SiC exhibited a larger sensitivity while the sensor based on Si exhibited a faster response toward hydrogen gas. We discussed herein, the responses exhibited by the Pt/Ta_2O_5 based Schottky diodes demonstrated a promising potential for hydrogen sensing applications.

Keywords: tantalum oxide; RF sputtering; Schottky diode; gas sensor; hydrogen

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1. Introduction

Tantalum (V) pentoxide (Ta_2O_5), otherwise known as tantalum oxide has been an attractive material in applications such as coatings, [1] catalysts, [2] electronic circuitry [3] and is best utilized in capacitors [4, 5] due to its high-k dielectric property. The material has also been reported as promising for electrochromic applications. [6] There are many different methods for the deposition of tantalum oxide as a film such as: RF sputtering, [7-9] sol-gel, [6] chemical vapor deposition (CVD) [10] and pulsed laser deposition (PLD). [11, 12]

The Schottky diode has been reported as a small and effective device that as a gas sensitive layer is deposited between the metal and the substrate, the sensitivity is increased towards sensing a particular gas species. [13-15] Previously, Comini et al. [16] utilized tantalum and its oxide as a dopant on titania based films. Mohammadi et al. [17] also deposited tantalum oxide in hybrid TiO_2-Ta_2O_5 type gas sensors. Their work demonstrated the potential of the material and herein, we study the performance of Pt/Ta_2O_5 Schottky diode based hydrogen (H_2) sensors as Ta_2O_5 is deposited on two different types of substrates.

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2. Experimental

Two types of substrates were chosen for comparative study of gas sensing towards hydrogen in this paper. Si wafers were purchased (Silicon Quest International, USA) with an orientation of <100> and were diced into 10×10 mm^2 square substrates. SiC wafers (Tankeblue semiconductor Co., China) with orientation <1100> were purchased and diced into 3×3 mm^2 square substrates. The Si and SiC substrates were prepared by initially washing in semiconductor grade acetone for 5 min to remove any artifacts and impurities from both the polished and unpolished surfaces. The substrates were rinsed in isopropanol and DI water for 2 min to remove excess oils and acetone remaining on the surface. The native oxide layer on both the polished and unpolished surface of the substrates were removed by etching in 5% HF in H_2O for 10 s and blown dry with N_2 after rinsing in DI water. The deposition of 40 nm Ti and 100 nm Pt layers onto the unpolished backside of the substrates also performed by sputtering.[18] The ohmic contact was then formed by annealing on a hotplate at 500°C for 30 min. Electron beam evaporation method was utilized to deposit the same thicknesses of Ti and Pt onto the unpolished side of SiC substrates and the ohmic contact was formed by annealing at 500°C for 30 min in a pure N_2 gas carrier.

A 99.99% pure tantalum (Ta) target was used for deposition of Ta_2O_5 thin film via denton vacuum discovery sputtering technique. The chamber was pumped to an operating pressure of 10^{-7} Torr. The substrates were heated to a temperature of approximately 300°C in an atmosphere of 20% O_2 in 80% Ar. RF Sputtering of Ta was performed for 600 s using a RF power of 25 W whilst the substrates were rotated at 3 rpm to encourage uniformity during the deposition process. After the deposition process, the sputtered film was annealed by heating the surface face down on a hotplate at 500°C for 10 min. Subsequently, a circular catalytic Pt layer was deposited on the Ta_2O_5 thin films by DC sputtering (set at 0.2 A for 10 min) using a stainless steel mask to form the Schottky contact with diameter of 1 mm and thickness of 30 nm.

3. Results and Discussion

The morphological surface of the RF sputtered Ta_2O_5 layer on Si and SiC substrates is characterized by AFM as shown in Fig. 1a and 1b, respectively. The AFM images clearly show that the surface morphology of the deposited Ta_2O_5 layer on Si is far smoother than deposited on SiC. The mean surface roughness of the sputtered layer is 0.223 nm and 0.392 nm for the sputtered Ta_2O_5 films on Si and SiC substrates, respectively. The thickness of the Ta_2O_5 layer was measured by a profilometer as approximately 4 nm.

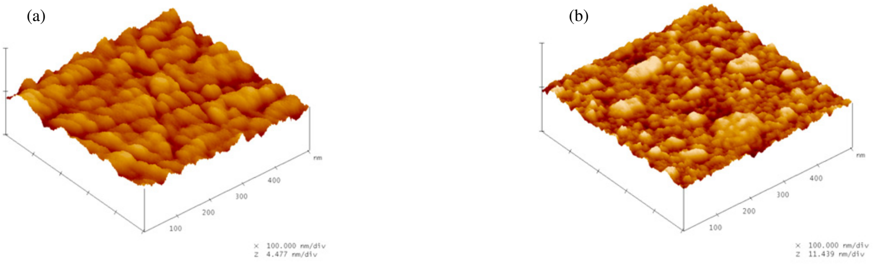
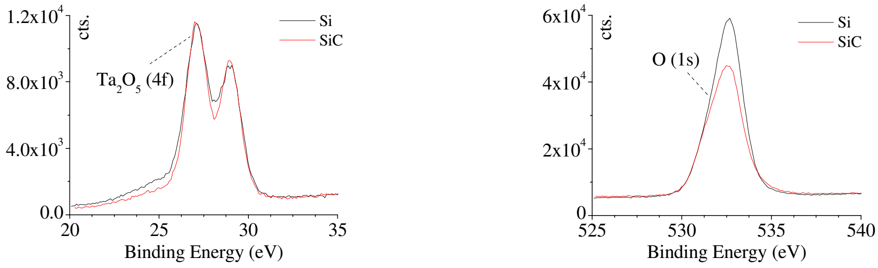


Fig. 1. AFM images of RF sputtered Ta_2O_5 on (a) Si and (b) SiC substrates.

The elemental composition of the Ta_2O_5 layer deposited on both the Si and SiC substrates was determined by X-Ray Photoelectron Spectroscopy (XPS) in a Thermo K-Alpha spectrometer using a Al-Kα source with a spot size of 400 μm. Charging was minimized using a low energy electron and ion flood gun. Individual peaks were scanned at 50 eV pass energy. For the Ta_2O_5 layer sputtered on Si substrates, the atomic percentages for the Ta(4f) and O(1s) peaks were 3% and 39%. The other elements present in the sample were Si(2p), C(1s) and F(1s) with 45%, 12% and 1%. The shape and position of the Ta4f peak correspond to that of Ta_2O_5.[19] However, the ratio of Ta:O of 1:13 is in stark contrast to the expected stoichiometric value of 1:2.5. This discrepancy is explained by the presence of the Si surface signal. It shows that the substrate is not uniformly covered with a tantalum oxide layer and that gaps exist in the oxide over-layer. It may therefore be deduced that the tantalum oxide coverage is more island-like than a uniform 4 nm thin layer with the gaps filled with a silicon oxide. The oxygen signal therefore consists of two contributions – tantalum oxide as well as silicon oxide. The slight asymmetry of the oxygen 1s peak is indicative of more than one oxide species. The silicon peak (not shown) also clearly shows an oxide as well as the silicon elemental peak.

The same result is obtained for tantalum oxide grown on SiC. For the Ta_2O_5 layer sputtered on SiC substrates, the atomic percentages for the Ta(4f) and O(1s) were 2% and 27%. The other elements present in the sample were Si(2p) and C(1s) with 36% and 35%.

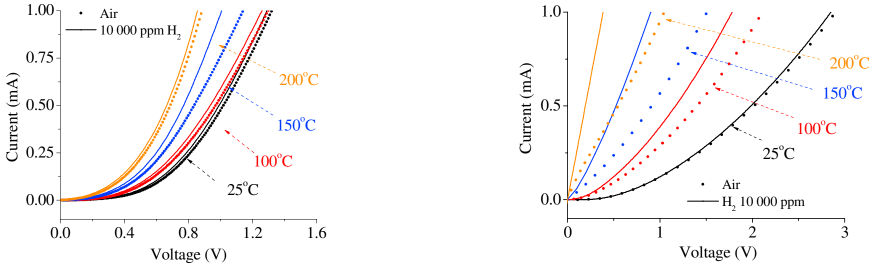


(a) (b)

Fig. 2. XPS plots of binding energy peaks of (a) Ta_2O_5 (4f) and (b) O (1s) deposited on Si and SiC substrates.

The gas sensitivity measurements of the sensors were performed in the same test chamber as previous investigations. [14, 18] The current-voltage (*I-V*) characteristics of Pt/Ta_2O_5 Schottky diodes based on Si and SiC substrates were measured towards 10 000 ppm H_2 balanced in synthetic air at different temperatures from 25°C to 200°C and are shown in Fig. 3a and 3b, respectively.

It can be seen that the sensors based on SiC exhibited a larger voltage shift than the sensors based on Si at temperatures between 100°C and 200°C. However for a comparative study, the author selected the two largest lateral voltage shifts for the sensors based on Si at temperatures which was at approximately 150°C and 100°C.



(a) (b)

Fig. 3. *I-V* characteristics of (a) $Pt/Ta_2O_5/Si$ and (b) $Pt/Ta_2O_5/SiC$ sensors towards 10,000 ppm H_2 gas in synthetic air at temperatures from 25°C to 200°C.

The forward electrical characteristics follow the Schottky *J-V* equations [20]:

$$J_F = A^{**} \cdot T^2 \cdot \exp\left[-\frac{q \cdot \phi_{B0}}{kT}\right] \cdot \exp\left[\frac{q(\Delta\phi + V)}{kT}\right] \qquad (1)$$

where J_F is the magnitude of the forward current density, A^{**} is the effective Richardson constant, T is the absolute temperature, q is the charge constant, ϕ_{B0} is the barrier height and k is the Boltzmann constant.

The forward barrier height can be calculated using the extrapolation method [20]:

$$\phi_{B(FWD)} = \frac{kT}{q}\ln\left[\frac{A^{**}\cdot T^{2}}{J_{0}}\right] \tag{2}$$

The operation of the Pt/Ta_2O_5 sensors is based on the Schottky barrier height lowering mechanism when they exposed to hydrogen gas. [21] Hydrogen molecules are adsorbed and dissociated into H atoms at the surface of the catalytic Pt transition metal into H atoms. These H atoms then diffuse through the Pt and accumulate at the Pt/Ta_2O_5 interface. As a result, a dipole charge is formed at the barrier and causes the effective lowering of the barrier height.

The change in barrier height with respect to 1% H_2 gas is calculated as 7.24 and 8.01 meV at 100°C and 150°C, respectively for the Schottky diode based on Si substrates. The change in barrier height for the diode based on SiC substrates is 6.98 and 15.77 meV at the same aforementioned temperatures.

The dynamic responses of the sensors towards different concentrations of H_2 under a constant forward bias current of 1mA at 100°C and 150°C are shown in Fig. 4a and 4b, respectively. The sensors based on Si exhibited voltage shifts of 7.38, 9.73, 13.8, 22.2, 41.5 mV and 9.75, 18.2, 31.3, 54.7, 95.7 mV towards 600, 1250, 2500 , 5000 and 10 00 ppm concentrations of H_2 at 100°C and 150°C, respectively. At these operating temperatures and concentrations, the sensors based on SiC exhibited voltage shifts of 4.92, 40.2, 86.7, 126.6, 201.3 mV and 75.7, 183.3, 263.1, 350.4, 489.4 mV, respectively.

The response and recovery times of the sensors at 150°C are shown in Table. 1. The sensors based on SiC substrates showed a larger voltage shift than the sensors based on Si upon exposure to H_2 gas, however the sensors based on Si substrates exhibited a faster saturation over the sensors based on SiC.

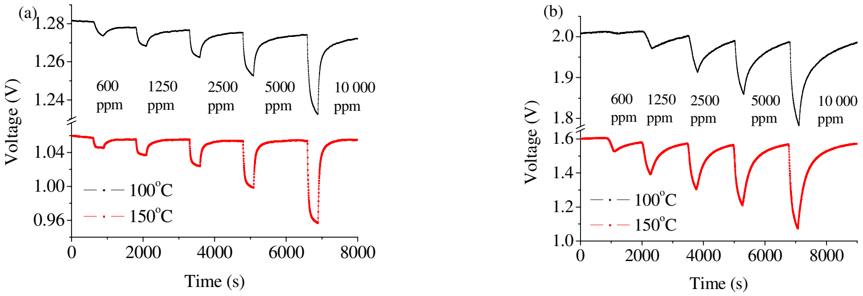


Fig. 4. *Dynamic responses of (a) Pt/Ta_2O_5/Si and (b) Pt/Ta_2O_5/SiC sensors towards different concentrations of H_2 gas at 100°C and 150°C with a constant forward bias current of 1mA.*

Table 1. Response and recovery times of Pt/Ta_2O_5 sensors based on Si and SiC with respect to different concentrations of H_2 gas at 150°C.

H_2 concentration (ppm)	Response time $_{90\%}$ (s)		Recovery time $_{90\%}$ (s)	
	Pt/Ta_2O_5/Si	Pt/Ta_2O_5/SiC	Pt/Ta_2O_5/Si	Pt/Ta_2O_5/SiC
600	102	276	252	702
1 250	108	303	351	774
2 500	153	288	279	711
5 000	141	262	249	807
10 000	141	264	240	939

4. Conclusion

We have fabricated novel Pt/Ta_2O_5 Schottky diodes based on Si and SiC substrates and compared their gas sensing performance towards hydrogen gas. The AFM showed that the roughness of the RF sputtered layer of Ta_2O_5 on SiC was approximately twice of the roughness of that on Si substrates. A comparison of dynamic responses from

Pt/Ta_2O_5 Schottky diodes based on Si and SiC substrates showed a faster response for the sensors based on Si whilst the sensors based on SiC demonstrated a larger sensitivity towards hydrogen gas. The experimental results indicated that by depositing Ta_2O_5 as a gas sensitive layer on both types of substrates can be advantageous for hydrogen gas sensing applications depending on the requirement of high sensitivity or fast response.

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