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Plasma Oxidized W-WO_x Sensor for Sub-ppm H_2S Detection †

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Abstract: In this work we have fabricated W-WO_x core-shell nanowire structure using plasma oxidation, a CMOS compatible process, for sensing H_2S gas. For comparison, the sputtered stack structure of W-WO_x with different thickness ratios of W to WO_x is fabricated and characterized for H_2S sensing. The sensor fabricated using plasma oxidation process is found to be significantly better in sensing performance compared to the sensing results obtained from sensor fabricated using sputtering. The response of plasma oxidized sensor is 90.4% for 1 ppm H_2S with response and recovery time of 4 s and 46 s respectively. In contrast, the sensor fabricated with sputtered film shows a response of 30.6% at 1 ppm with response and recovery times of 19 s and 84 s respectively. This study clearly indicates that plasma oxidation is an efficient method for development of stable sensors.

Keywords: plasma oxidation; core-shell nanowire; RF sputtering

1. Introduction

Semiconducting metal oxides play a vital role in smart sensors due to their ease of fabrication, low cost and small size. Heterostructures with metal cores and semiconductor shells prove to be good gas sensors due to the controllable chemical and thermal stabilities of the shell [1]. Core-shell nanoparticles are typically synthesized in two steps; first the core is synthesized following which the shell is formed around it. The main disadvantage of these processes is incompatibility with existing CMOS technology and difficulty in reproducibility. So, there is a need to develop sensor fabrication process using CMOS compatible processes for scalability [2].

In this work, W-WO_x core-shell nanowire based sensor is fabricated by using plasma oxidation for H_2S sensing. We describe the effect of oxygen plasma process on the tungsten nanowire to form W-WO_x. The same device architecture is adopted for fabrication of sputtered sensor device. The sensing response of sputtered W-WO_x stack structure towards H_2S is also investigated. The comparison of sensing results of the sensors fabricated using the two process shows better sensing capabilities of plasma oxidized devices.

2. Fabrication

The fabrication flow is as shown in Figure 1. The suspended W nanowire structures are exposed to oxygen plasma process in RIE to yield W-WO_x core-shell structure at optimum RIE power and pressure. The fabrication of sputtered stack of W-WO_x uses RF sputtering to form W-WO_x film. The plasma processed and RF sputtered sensors are named S_a and S_b hereafter.

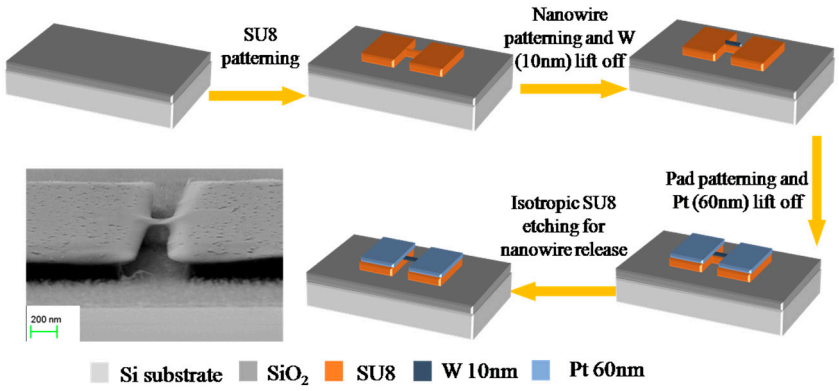

Figure 1. Fabrication flow with SEM micrograph of the final sensor device.

3. Results and Discussion

Sensing Characterization

The devices are tested for H_2S. The reaction is as shown below.

$$H_2S + \ 3O^- \overset{T°C}{\Leftrightarrow} H_2O + SO_2 + \ e^-$$

Synthetic Air (80% Nitrogen and 20% oxygen) is used as the reference gas. The reactions are allowed to stabilize by monitoring the current, after which H_2S of the required concentration is introduced which causes a change in the conductivity which is monitored. The sensitivity is calculated using the formula

$$Sensitivity \ = \frac{\text{Ra} \sim \text{Rg}}{\text{Ra}} \times 100\%$$

The device S_a is tested for H_2S to obtain the optimum operating temperature by exposing the device to fixed 1 ppm concentration at different temperatures and recording the response. The optimum temperature is found to be 150 °C. The sensor is also capable of room temperature operation. It is then tested for varying concentrations of H_2S, from 10 ppb to 1 ppm at 150 °C at 0.1 V applied voltage, as shown in Figure 2a. The observed sensitivity is 90.4% at 1 ppm with response and recovery of 4 s and 46 s respectively and LOD of 10 ppb. Similarly the optimum sputtered device S_b (W of 2 nm and WO_3 of 10 nm) is tested for H_2S (Figure 2b).The optimum temperature is found to be 200 °C with no response at room temperature. It shows sensitivity of 30.6% at 1 ppm with response and recovery times of 19 s and 84 s respectively with LOD of 10 ppb at the optimum temperature. Figure 3 compares the response of sensors fabricated using plasma oxidation and sputtering. The plasma processed sensors are better in sensing performance compared to sputter deposited sensors.

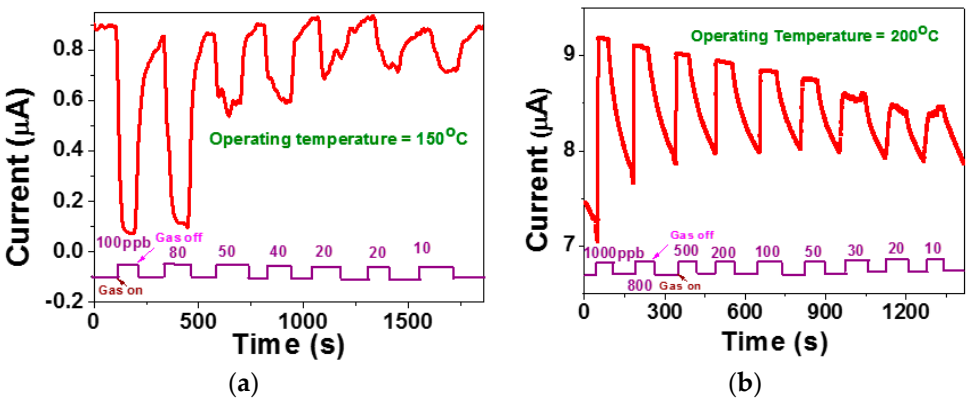

Figure 2. Transient response of devices towards H_2S (**a**) plasma oxidized and (**b**) sputtered stack.

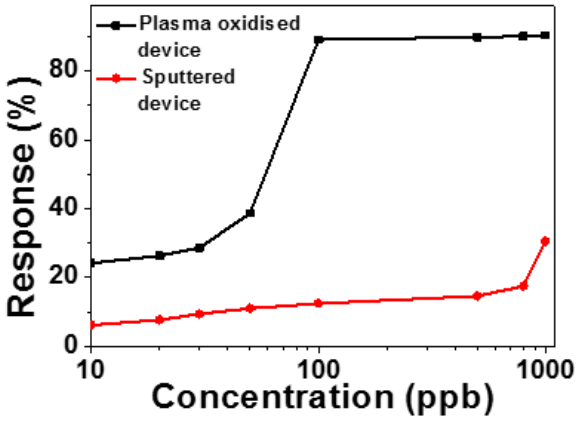

Figure 3. Sensitivity comparison of plasma oxidized and sputtered device.

4. Conclusions

We have fabricated W-WO_x core shell structure using plasma oxidation of metallic tungsten. The better sensing capabilities of the plasma oxidized device is shown by fabricating W-WO_x stack using RF sputtering with comparable thicknesses and sensing for H_2S. The plasma oxidized device gives response of 90.4% at 1 ppm at 150 °C with LOD of 10 ppb. The response of the plasma oxidized device is higher by 195.4% than the sputtered device (200 °C). The device also shows excellent response and recovery times of 4 s and 46 s respectively making it suitable for H_2S leak detection.

Conflicts of Interest: The authors declare no conflicts of interest.

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