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Investigation on a novel SiC Schottky barrier diode hydrogen sensor with trench-insulator structure

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Abstract

A novel SiC Schottky barrier diode (SBD) hydrogen gas sensor with trench-insulator structure was proposed in this paper. A physical model is built for this hydrogen sensor based on 4H-SiC SBD thermionic emission theory, tunneling effect of carriers, adsorption/desorption principle of hydrogen and modulation effects of Schottky barrier height. Use Silvaco TCAD, the semiconductor simulation software, to analyze SBDs with trench-insulator layer and to compute current-voltage characteristics at different temperature, hydrogen concentration and trench width under forward bias. The temperature and hydrogen concentration affect the I–V characteristics of the devices by changing the Schottky barrier height. Compared with normal metal–silicon carbide and metal–insulator–silicon carbide devices at 573 K in terms of on–off voltage, current resolution, response speed, and stability, the trench-insulator hydrogen sensor showed good performance. Relationship between device characteristics and trench width was researched using the above model. Trench width has an opposite effect on sensor resolution and sensitivity.

1. Introduction

With the environmental pollution problem affecting the human development process, the application of new energy is imminent [1]. As a clean energy, hydrogen is expected to replace petroleum in the future [2, 3]. However, during the storage of hydrogen, hydrogen leakage may occur unexpectedly due to aged equipment, insufficient connection, etc. If any leakage of hydrogen is not found in time or handled improperly, it will seriously endanger the safety of life and property. For one thing, since hydrogen is flammable, common fire sources (collisions, friction, naked light, static electricity, etc.) can ignite the hydrogen-air mixture and even lead to explosion [4–6]. For another, when the hydrogen concentration is too high, the very low partial pressure of oxygen in the air can cause suffocation. Therefore, the detection of hydrogen leaks has become a crucial issue [7, 8]. In particular, hydrogen concentration monitoring at high temperatures has been a prerequisite in almost all fields of hydrogen industry.

Different materials and structures have been studied for hydrogen sensor applications. On the one hand, silicon carbide material has been applied to hydrogen sensor. Compared with silicon material, SiC material has many advantages such as high thermal conductivity, high breakdown field strength, and wide band gap [9, 10]. On the other hand, the SBDs based on SiC semiconductor have become the focus of research in the field of sensors owing to their extensive array of industrial applications and fast response [11]. Typically, the SiC-SBD structures mainly include metal–SiC (MSiC) [12] and metal-insulator–SiC (MISiC) with an insulation layer intervening.

Gas sensors based on SBD with Pd gates were presented in 1992 [13]. G.W. Hunter et al showed that Pd/SiC had poor stability compared with Pd/SnO2/SiC at 350°C for several weeks in 1998 [14]. Since then, research on gas sensors has focused principally on the MISiC structures. As an important part of MISiC sensors, the insulation layer has been widely studied, mainly concentrating on the use of metal oxide, among them are Ga2O3 [6], ZnO [2], WO3-ZnO [7], Ta2O5 [11], SiO2 [15], HfON [16], and TiO2 [17]. However, due to the poor
interface quality between SiC and these insulators, the properties of MISiC devices are intensively limited [1]. The film tends to fall off at high temperatures and eventually the device fails. Therefore, AlN material becomes an excellent dielectric layer in semiconductor sensor due to good lattice matching with SiC. In addition, as a high thermal conductivity, good dielectric property, and wide band gap semiconductor material, it has a similar thermal expansion coefficient with SiC material [18]. Therefore, the interfacial defects are minimized due to the involvement of the AlN layer. This film does not fall off easily at high temperatures, which makes the device work stably for a long time. By inserting AlN material between the catalytic metal Pt and SiC substrate, the stability and sensitivity of Pt/AlN/SiC device are improved, but the current of the device is reduced and the on-off voltage is increased [19].

In this paper, we have investigated the new trench-insulator SBD hydrogen sensor which has a regular arrangement of AlN layers. Use theoretical analysis and software simulation to gain the I–V characteristics of the trench-insulator SBD device. Compared with the normal Pt/AlN/SiC and Pt/SiC SBD devices, the trench-insulator device has many advantages, such as low switching loss, high sensing response speed, high current and resolution. The effects of different trench widths on device characteristics were studied. And the response results of the trench-insulator device under different hydrogen concentration and temperature conditions were obtained.

2. The trench-insulator SBD device model and sensing theory

Figure 1 shows the cross-sectional view of the trench-insulator SBD device. The substrate and the 5 μm epitaxial layer are n-type nitrogen-doped SiC material with doping concentration of $1 \times 19 \text{ cm}^{-3}$ and $4 \times 15 \text{ cm}^{-3}$, respectively. The anode catalytic metal is platinum, which is capable of catalyzing hydrogen. The cathode is replaced by an ohmic contact in simulation. Considering the influence of insulation layer thickness on device sensitivity, resolution and other performance, the thickness of AlN layer in simulation was determined to be 2 nm [15].

Use semiconductor simulation software Silvaco TCAD to gain the I–V curves of the trench-insulator SBD device under different hydrogen concentration and temperature. In this work, we used the newton iteration method to calculate the electron’s drift-diffusion. In the following, the current transport model and Schottky barrier height (SBH) modulation model were analyzed to establish the physical model of device simulation.

2.1. Current transport model

Figure 2 show the equivalent circuit of trench-insulator SBD. The parallel conduction model assumes that each SBD are electrically independent. The equivalent circuit consists of multiple SBDs in parallel and a parasitic resistance $R_s$ in series [20]. The current transport model of each SBD is supported by the theory of thermal electron emission.
For low-doped semiconductors, the current transport model at the Schottky junction is determined by the emission of majority carriers at the barrier. Under forward voltage where $V \gg IR_s$, the current at metal-semiconductor Schottky junction described by the thermionic emission theory is given by [9, 15, 17, 21, 22]

$$I = I_0 \times \exp \left( \frac{qV}{nkT} \right) - 1 = I_0 \times \left[ \exp \left( \frac{V}{n\Phi_T} \right) - 1 \right],$$

where $I_0$ and $v$ are the reverse saturation current and forward bias voltage, respectively, $q$ the unit charge, $n$ the ideality factor, $k$ the Boltzmann constant, $T$ the temperature, $\Phi_T$ the thermal voltage. $I_0$ is expressed as

$$I_0 = AA^* T^2 \times \exp \left( - \frac{\Phi_b}{\Phi_T} \right),$$

$$A^* = \frac{4 \pi q m k^2}{h^3},$$

in which $A$, $A^*$ and $\Phi_b$ are the area of the Schottky junction for Pt/SiC SBD, the effective Richardson constant and the SBH, $m$ and $h$ the electron effective mass and the Planck constant, respectively. $A^*$ is 146 A cm$^{-2}$ K$^{-2}$ for 4H-SiC.

The contact potential difference of Pt and SiC as shown in figure 3(a) falls on the SiC barrier layer, a high resistance area. In figure 3(b), part of the contact potential difference falls in the barrier layer, and the other part falls between the metal Pt and SiC surface, i.e. both surfaces of the AlN layer. Compared with Pt/SiC SBD, the metal-semiconductor direct contact device, Pt/AlN/SiC SBD needs to consider the tunneling effect caused by the AlN layer. According to the tunneling effect, there is a certain probability for electrons with energy lower than the top of barrier across the barrier. The penetration probability is related to barrier thickness and electron energy [23]. The SBD thermionic emission must pass through the AlN layer with the direct tunneling mechanism. The reverse saturation current $I'_0$ of Pt/AlN/SiC SBD is expressed as followed

$$I'_0 = I_0 \times \beta = A' A^* T^2 \times \exp \left( - \frac{\Phi'_b}{\Phi_T} \right) \times \exp \left( \frac{2t_{ox}}{h} (2m^* \chi)^{1/2} \right),$$

where $\beta$ is the transmission coefficient of carriers, $A'$ and $\Phi'_b$ the area of the Schottky junction and SBH for Pt/AlN/SiC SBD, $t_{ox}$ the insulation layer thickness and $\chi$ the effective tunneling barrier.
The equilibrium between metal and semiconductor is broken under forward bias. The number of electrons from the semiconductor to the metal increases, exceeding that from the metal to the semiconductor. A forward current is formed from metal to semiconductor. Due to the above tunneling effect, an inhomogeneous current is generated at the Schottky contacts with different barrier heights. Electron transport at inhomogeneous Schottky contact can be treated with parallel conduction model. These SBDs are able to shunt in parallel due to the positive temperature coefficient (PTC) characteristics of SiC. If the current of the two types of SBDs is extremely uneven, the on-resistance and forward voltage drop of high-current SBDs will increase accordingly, which will promote the redistribution of the current, and finally the current will reach equilibrium.

Obviously, the on-off voltage of Pt/SiC SBD is higher than that of Pt/SiC SBD. When the forward voltage reaches Pt/SiC SBD on-off voltage, Pt/SiC SBD is turned on and the current of Pt/AlN/SiC SBD is very small. Therefore, compared with the normal SBD device, the trench-insulator SBD with diodes parallel structure can achieve lower the on-off voltage. Delfves et al proposed ‘two SBH’ Parallel model. In this model, the total thermionic current is composed of two independent contributions [24, 25]. The forward current consists of the thermionic current provided by each diode given by

\[
I = \sum_{i=1}^{j} I_i = \sum_{i=1}^{j} A_i A^* e^{-\frac{qV}{n\Phi_f}} \times \left[ \exp \left( \frac{\Phi_f}{n\Phi_f} \right) - 1 \right],
\]

where \(I_i\), \(A_i\) and \(\Phi_f\) are the current, area and SBH of the \(i\)th diode, respectively, \(j\) is the total number of parallel diodes. In this current transport equation, a change of SBH in the hydrogen atmosphere results in a current response. Hence, the modulation effect of barrier height is emphatically analyzed below when the device is exposed to hydrogen atmospheres.

Figure 3. (a) Band diagram of Pt/SiC SBD, (b) Band diagram of Pt/AlN/SiC SBD.
2.2. SBH modulation model

The SBH depends not only on temperature but also on hydrogen concentration. Hydrogen molecules decompose into hydrogen atoms by the catalytic metal Pt. The hydrogen atoms diffuse to the interface under the Pt electrode. With the existence of electric field, the hydrogen atoms form a dipole layer at the interface. The polarization layer reduces the SBH, thus causing the drift of the I–V characteristic curve of the sensor [9, 16, 26]. Therefore, the SBH $\Phi_b$ is given by

$$\Phi_b = \Phi_{b0} - \varepsilon T - \Delta \Phi_b,$$

in which $\Phi_{b0}$ is the SBH at room temperature, $\varepsilon$ the temperature coefficient of the SBH, $\Delta \Phi_b$ the change in the SBH at different hydrogen concentrations. It is found that $\Delta \Phi_b$ is proportional to the hydrogen atom coverage rate ($\theta_i$) at the interface between the metal and the insulator. $\Delta \Phi_b$ is expressed as [14]

$$\Delta \Phi_b = \Delta \Phi_{b, \text{max}} \theta_i,$$

in which

$$\theta_i = \frac{(K_0 C_{H})^{1/2}}{1 + (K_0 C_{H})^{1/2}},$$

where $\Delta \Phi_{b, \text{max}}$, $C_{H}$ and $K_0$ are the maximum change in the SBH, the concentration of hydrogen and the equilibrium constant of the gas-adsorption reaction determined by the interface of the insulation layer, respectively.

In addition to the above physics models, Shockley-Read-Hall (SRH) and Auger recombination model, band gap narrowing model, direct quantum tunneling model, incomplete ionization model and concentration and temperature dependent mobility model are applied to the simulation of the trench-insulator structure devices. The effect of phonon and ionized impurity scattering was consideration in the carrier mobility model. For 4H-SiC material, mobility is assumed to be entirely isotropic in nature.

3. Results and discussion

Using Silvaco TCAD simulator for atlas simulation, the I–V curves of Pt/AlN/SiC, Pt/SiC, and the grooved structure devices were obtained and compared. Finally, the effects of temperature and hydrogen concentration on the trench-insulator device were minutely analyzed.

As shown in figure 4, the I–V curves of the three structures in air at 573 K are simulated due to the SBH reduction by the proposed model. It can be seen that, compared with the Pt/AlN/SiC device, the on-off voltage of the trench-insulator device drops about 0.7 V, and the current is about 8 mA higher at forward voltage of 1.5 V. Compared with the Pt/SiC device, the current of the trench-insulator device increases relatively slowly, and the on-off voltage of the two devices is equivalent. This give a great advantage to the trench device in terms of low on-off voltage and high current. The forward current transport of the trench-insulator device as shown in figure 4 is almost determined by the low barrier region. This result is consistent with the inhomogeneous Schottky barrier model proposed by Fabrizio Roccaforte et al [27].
As one of the most important parameters of SBD sensor, the current resolution, \( \Delta I \), is defined as

\[
\Delta I = I_{H_2} - I_{air}, 
\]

where \( I_{H_2} \) is the SBD current in \( H_2 \), \( I_{air} \) the SBD current in air. The current of three different structure SBDs various with hydrogen concentration as shown in figure 5. The current resolution of the trench-insulator device is about 2.5 mA higher than Pt/AlN/SiC and about 0.1 mA slightly lower than Pt/SiC in 1000 ppm hydrogen concentration. Intervention of AlN layer reduces the current resolution of the device. This shows that the current resolution has a significant connection with the structure of the insulation layer.

The sensitivity, another important parameter of sensor, \( S \), is defined as [8–10]:

\[
S = \frac{I_{H_2} - I_{air}}{I_{air}}. \tag{10}
\]

For the common SBD hydrogen sensors, the response sensitivity is expressed as

\[
S = \frac{I_{H_2} - I_{air}}{I_{air}} = \exp\left(\frac{\Delta \Phi_b}{\Phi_T}\right) \times \frac{\exp\left(\frac{\Delta \Phi_b}{n_{H_2}}\right) - 1}{\exp\left(\frac{\Delta \Phi_b}{n_{air}}\right) - 1}, \tag{11}
\]

where \( n_{H_2} \) and \( n_{air} \) are the ideality factors in \( H_2 \) and air, respectively. The sensitivity changes along with temperature, change of SBH, hydrogen concentration, operation voltage and so on. As the most important parameter that affects sensitivity, \( \Delta \Phi_b \) of common SBDs is determined by \( I-V \) characteristic and equations (1), (2) and (4), as shown in figure 5. As shown in figure 5, the current resolution of the trench-insulator device is about 2.5 mA higher than Pt/AlN/SiC and about 0.1 mA slightly lower than Pt/SiC in 1000 ppm hydrogen concentration. Intervention of AlN layer reduces the current resolution of the device. This shows that the current resolution has a significant connection with the structure of the insulation layer.

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As shown in figures 7 and 8, the response sensitivity for different structure SBDs at 573 K are obtained. The sensitivity of Pt/AlN/SiC is clearly higher than that of Pt/SiC. This confirms that the presence of the AlN layer is conducive to improving the sensitivity of the sensor.

By considering the current resolution, sensitivity and on-off voltage of the three devices, the trench-insulator device becomes the final choice, and its performance was further studied below. Figures 9(a) and (b) show the Ln I–V curves measured under exposure to different concentrations of hydrogen at 573 K and 773 K, respectively. The current of the device increases with the increase of hydrogen concentration and temperature, due to the limited adsorption sites on the device surface and interface [15], which is consistent with equation (7).

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According to the performance requirements of the sensor, the sensitivity should be higher than 20% and the current resolution should be higher than 1 mA at the operation voltage [15]. With the definition in equations (1), (2) and (10), the sensitivity of the sensor decreases with the increase in temperature. Therefore, the operation voltage was determined to be 1.2 V with a sensitivity greater than 20% at 773 K.

Figure 10 shows the current resolution for the trench device at 573 K and 773 K versus hydrogen concentration at 1.2 V forward voltage. It can be seen that the current resolution, \( \Delta I \), meets the requirements of the sensor. Obviously, \( \Delta I \) increases rapidly with hydrogen concentration and then gradually approaches a saturation in high hydrogen concentration. Thus, the maximum current resolution is produced here.
Figure 6. Change in SBH, $\Delta \phi_b$, with hydrogen concentration for Pt/SiC and Pt/AlN/SiC SBDs at 573 K.

Figure 7. The response sensitivity with hydrogen concentration for different structure SBDs at 573 K.

Figure 8. The response sensitivity with hydrogen concentration for Pt/SiC and grooved structure SBDs at 573 K.
Figure 9. I–V curves of the trench-insulator device when exposed to different concentrations of hydrogen. (a) $T = 573$ K and (b) $T = 773$ K.

Figure 10. Change in current versus hydrogen concentration for the trench structure at 573 K and 773 K.
According to the proportion of AlN layer and trench, three different trench-insulator devices were designed and simulated. The proportions of different devices studied were 7:3, 5:5 and 3:7 in air at 573 K. Figure 11 shows the I–V characteristic curves of the three different devices described above. It can be seen that, in a limited range, the magnitude of current is positively correlated with the width of the trench. Figure 12 and figure 13 show the current resolution and sensitivity of the devices with different trench width at 573 K versus hydrogen concentration at 1.2 V forward voltage, respectively.

From figure 12, the device with an AlN material proportion of 3:7 has a high current resolution. The current resolution decreases as the proportion of AlN material increases. Instead, the sensitivity increases as the proportion of AlN material increases as shown in figure 13. If the proportion of the AlN material is reduced, the sensitivity is reduced because the schottky barrier height depends on the trench width, and a larger trench width reduces the device barrier height. Therefore, the structure of the trench insulator layer has a great influence on the performance of the device.

**4. Conclusions**

In this work, a physical model for trench-insulator SBD is analyzed by considering the thermionic theory, the tunneling effect, the parallel SBD effect and the SBH modulation. By using the Silvaco TCAD simulation software, we have obtained the I–V characteristics of the SBDs with different trench-insulator structure in air containing various amounts of hydrogen and temperatures (573 K and 773 K). Analyzed sensitivity and current resolution of the Pt/AlN/ SiC device, the Pt/SiC device and the trench-insulator SBD devices. The trench-
insulator SBD hydrogen sensor exhibits excellent performance relative to the normal Pt/AlN/SiC and Pt/SiC device in terms of on-off voltage, resolution and current. Furthermore, the effect of trench width on device performance was dissected. Trench width has an opposite effect on the resolution and sensitivity of the device. In a word, our research provides a new path to design high-resolution, selective and stable hydrogen sensors based on trench nanostructures.

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Conflicts of interest

The authors declare that there is no conflict of interest.

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Figure 13. Sensitivity with hydrogen concentration for different trench structures at 573 K.
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