Variation Resistance of different operation temperature of NO₂ and NH₃ gases for the Ag-doped SiC gas sensor

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Abstract. A pure and Ag-doped silicon carbide (SiC) films on the p-type silicon (110) wafers were prepared with various dopant ratios (1, 3, 5 and 7%) using pulsed laser deposition technique (PLD) with the Nd: YAG laser (λ= 1064 nm, 500 mJ, 6 Hz). The samples were deposited under high pressure up to (10⁻⁴ mbar) at a substrate temperature of 250 °C. The thin films have been examined for (NO₂ and NH₃) sensing at different operating temperatures. The maximum sensitivity of pure SiC of NH₃ gas about (12%) at 200 °C and (14.42%) for NO₂ gas at 100°C while the maximum sensitivity of Ag-doped samples about (24.39%) of NH₃ gas at 200°C for (1%wt) and (62.98%) of NO₂ gas at 25°C for (3%wt). For the pure sample, we found that the fastest response time was (18.9 s, 22.5 s ) for NH₃ and NO₂ gases at (300 °C,100 °C), respectively, while for impure samples (3% wt) about (12.6 s, 13.5 s) of NH₃ and NO₂ at 100°C. The results also showed that the lowest recovery time for the pure film was 33.3 s for NH₃ gas at 100°C, while for NO₂ gas its value was (30.6 s) at 200 °C. Also for the SiC: Ag (3% wt, 5%), it was found that the fastest recovery time was about (45 s) for NH₃ gas at 25 °C and (41.4 s) for NO₂ gas at 100°C.

Keywords: Silicon carbide; Thin film; silver-doped; Gas sensor;

1. Introduction

Silicon carbide has been promising physical, electrical, and mechanical properties such as its wide band gap, high strength, high melting point, and high hardness. SiC possesses excellent resistance to chemical and thermal environments as well as having thermodynamically stable. The unique properties of SiC material make it attractive for a wide of applications in high-frequency, high-power and high-temperature optoelectronic devices as well as that the fast response time and wide bandgap offered by SiC promise to enhance the performance of sensors [1-4]. Many techniques such as reactive evaporation, reactive sputtering and sputtering can be used for making SiC films but the most popular method is chemical vapour deposition (CVD) [5].

A gas sensor is a device that provides information about the composition of its surrounding environment. The physicochemical features of the metal oxide sensitive layer (like electrical resistance, temperature and mass) change reversibly as it interacts with chemical species (absorption, chemical reaction, and charge transfer). These changes are converted into an electrical signal, as voltage, current, conductance or frequency which is then read and subject to additional data processing. The electric conductivity measurements of several metal oxides can be used to identify explosive, reducing, or oxidizing gases [6].

Due to the increased requirements for the stability of sensors under the influence of intense radiation and electromagnetic fields, there is a great problem of search for new functional semiconductor materials for the creation of highly sensitive gas sensors that slightly change their
properties over time under hard external influences. Materials based on SiC are one of the most promising materials in terms of chemical inertia, time stability of properties and resistance to radiation impacts.

In recent years, SiC has attracted significant interest as a possible material for sensor devices. Gas sensors based on SiC have significant potential in aerospace applications including fire detection fuel leak detection, and emission monitoring [7].

The pulsed laser deposition technique can be used to prepare both polycrystalline, crystalline and amorphous films at relatively lower temperatures depending on the process parameters [8]. Thin-film formation by PLD technique includes ablation of target materials by short (ns), intense and focused laser pulses. Ablated particles with kinetic energies ranging from (a few to 100 eVs) are expelled in a small angular region perpendicular to the target surface and condense on the substrate to form the film. [9].

PLD has proven itself as a flexible method for growing thin films of a wide range of materials, including metals, semiconductors, insulators, and high-temperature superconductors. Aside from stoichiometric transition between the deposited film and the target, PLD has the advantages of a strong adhesion at low temperatures, epitaxial layer growth and high deposition rate. [10-16]. The chemical composition of the substrate, laser fluence, laser wavelength, substrate temperature, the distance between the substrate and target and background atmospheric gas all play a role in the quality of the films fabricated by the PLD technique [17].

2. Experimental details
Pure and Ag-doped SiC targets were formed via pressing high-purity powder (99%) under a pressure (5×10^9 psi) using the hydraulic press for (10-15 min) to form a pellet with a diameter of about (3 cm) and thickness (5 mm). Thin layers of pure and Ag-doped silicon carbide material have been deposited on a substrate of p-type silicon (110) with various dopant ratios (1, 3, 5 and 7%) using the PLD technique. The deposition technique was carried out using a second harmonic Nd:YAG laser with (wavelength= 1064 nm, pulse energy=500 mJ, laser repetition rate= 6 Hz). The substrates were cleaned with ethanol and Deionized water before deposition. The samples were deposited under high pressure up to (10^-4 mbar) at a temperature of (250°C) while a target-to-substrate distance was (30mm). A quartz lens had been used to focus the laser beam that falls with an angle of 45 on the rotating SiC target inside the deposition chamber. The sensitivity, recovery time, and response time of the thin films were measured using a gas sensor device.

3. Results and Discussion
The following formula was used to calculate the gas sensitivity ($S$):

$$ S = \left(\frac{R_g - R_a}{R_a}\right) \times 100\% $$

where $R_g$ and $R_a$ are the electrical resistance of film in the gas and air, respectively. The effect of changing doping ratios (1, 2, 3, and 7)% and operating temperature (25, 60, 100, 200 and 300°C) on improving sensor characteristics (sensitivity, response time, and recovery time) was studied. The response and recovery times are determined through the time that it takes for the sensor to experience 10–90% of the steady-state resistance when target gas/air is introduced [18, 19].

Figures 1 and 2 exhibit the sensitivity of pure SiC and Ag-doped SiC (0.01, 0.03, 0.05, and 0.07) as a function of operating temperature in the range (25-300°C) with pulse laser deposition which are deposited on Si (110) substrates at 5% NO$_2$; air mixing ratio and 10% NH$_3$; air mixing ratio on the all samples. In order to achieve the lowest possible value of operating temperature, the effect of operating temperature on the sensitivity of thin films was investigated. The temperature at which the sensor's resistance achieves a constant value is referred to as the operating temperature where the presence of a certain amount of some gases of interest may affect changing that resistance [20, 21].

The results show that the sensitivity have slowly increased with increasing operating temperature. The sensitivity samples when work in room temperature to 100°C have regular behave, while, the sensitivity irregular behave when the operation temperature up to 200°C-300°C. For these reason the Ag doped SiC samples cannot record sensing signal up 200°C.
For 0.03Ag doped, the maximum sensitivity of the tested gas sensor to (40 ppm) of NO₂ roughly 62.9% at 25°C, while the 0.07 Ag doped SiC gas sensor have 0.8% lowest sensitivity to NO₂. It’s also worth noting that for Ag-doped SiC gas sensors, the optimal detecting temperature for maximum sensitivity is almost 100°C. When NH₃ (50 ppm) is utilized as the test gas, the best sensing temperature of the Ag-doped SiC (0.01 Ag) gas sensor is at approximately (25-100°C) while the maximum sensitivity may reach 24.38%.

All of the above results have been indicated that the sensitivities of the reducing and oxidizing gases have been substantially improved and the reason for this is due to the presence of nano-sized SiC particles on the Si substrate, as well as an increase in surface adsorbed oxygen amount.

Also, we can notes that, the samples have Ag-doped SiC respect to pure SiC have enhance sensitivity at room temperature for to the reducing NH₃ and oxidizing NO₂ gases as it obvious in figures. This result maybe attributed, that the Ag have lower energy gap respect to SiC have energy band gap.

![Figure 1](image1.png) **Figure 1** Sensitivity vs. operating temperature of SiC doped with using NO₂ as gas sensing technique.

![Figure 2](image2.png) **Figure 2** Sensitivity vs. operating temperature of the SiC doped with Ag using NH₃ as gas sensing technique.
The relationship between the response time and the recovery time with operating temperature is exhibited in Figures 3, 4, 5, and 6. This figures 3 and 4 show that the response time with rising operating temperature for NO\textsubscript{2} and NH\textsubscript{3} test gases, the response time decrease with increasing operating temperature. The fast response speed for NO\textsubscript{2} gas (13.5 s) for 0.03 Ag doped SiC sample at 100°C and (13.5s) for 0.07 Ag doped SiC at 100°C for NH\textsubscript{3} gas. While, figures 5 and 6 show that the recovery time with rising operating temperature for NO\textsubscript{2} and NH\textsubscript{3} test gases, the recovery time decrease with increasing operating temperature. The fast recover speed for NO\textsubscript{2} gas (30.6 s) for pure SiC sample at 200°C and (33.3s) for NH\textsubscript{3} gas for pure SiC sample at 100°C.

The decrease in the work function and activation energy of surface reactions may be linked to decreasing grain size and an increase in vacancies created upon SiC lattice [22].

Increased oxygen adsorption on the surface can be lead to removes conduction electrons from the near-surface area, resulting to form an electron-depleted surface layer. a fast response time has been achieved of sensors as results of the increased number of active adsorption sites on the surface. Generally, the response time and recovery time are decreases when increasing the operating temperature as exhibited in the figures. A fast response time, as well as a fast recovery time, are typically necessary for real situations.

**Figure 3** Response time vs. operation temperature of the SiC gas sensor using NO\textsubscript{2} gas.

**Figure 4** Response time vs. operation temperature of the SiC gas sensor using NH\textsubscript{3} gas.
Figure 5 Recovery time vs. operation temperature of the SiC gas sensor using NO$_2$ gas.

Figure 6 Recovery time vs. operation temperature of the SiC gas sensor using NH$_3$ gas.

Figures 7, 8, 9, 10 and 11 illustrate the change in the resistance for SiC pure and Ag-doped SiC sensor with the time as a result exposed to NO$_2$ (5%) and NH$_3$ (10%) in the air ambient supplied into the measuring chamber, with the bias voltage kept at (3V) of each sample at the optimal operating temperature. The sensor resistance is determined directly with time, as it initially reaches a stable state before the gas is opened and at this moment we open the gas to allow mixing with air within the chamber. We turn off the gas once the resistance drops abruptly to a stable state. Then electrical resistance returned to the initial case. The nature of the interaction between the gas molecules and the surface atoms of the sensing film determines a sensor's capacity to detect the presence of gas.

Figure pure SiC shows that the resistance of samples increased with exposed NO$_2$ gas and decreased when exposed to NH$_3$ gas on the surface. The different behavior of samples indicate that pure SiC and 0.07 Ag-doped SiC have higher selectivity beavers for NO$_2$ oxidizing gas and NH$_3$ reducing gas specifically at room temperature.
Figure 7 The variation resistance with time for different operation temperature of NO₂ and NH₃ gases for the pure SiC gas sensor.
Figure 8 The variation resistance with time for different operation temperature of NO₂ and NH₃ gases for the Ag-doped SiC gas sensor (0.01 Ag).
Figure 9 The variation resistance with time for different operation temperature of NO\textsubscript{2} and NH\textsubscript{3} gases for the Ag-doped SiC gas sensor (0.03 Ag).
Figure 10 The variation resistance with time for different operation temperature of NO$_2$ and NH$_3$ gases for the Ag-doped SiC gas sensor (0.05 Ag).

Figure 11 The variation resistance with time for different operation temperature of NO$_2$ and NH$_3$ gases for the Ag-doped SiC gas sensor (0.07 A)
4. Conclusion

Our results indicate that pure and Ag-doped SiC thin films can be used to detect NH3 and NO2 gases at different operating temperature (25-300 °C). The results show that the sensitivity has slowly increased with increasing operating temperature. The maximum sensitivity of the tested gas sensor to 40 ppm of NO2 about 62.9% at 25°C for 0.03Ag doped, while the 0.07 Ag-doped SiC gas sensor have 0.8% lowest sensitivity to NO2. The response and recovery times of samples decrease with increasing operating temperature. The results show that the resistance of samples increased with exposed NO2 gas and decreased when exposed to NH3 gas on the surface. All the above results have shown that the sensitivities to the oxidizing and reducing gases have been greatly enhanced.

5. References

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