Studies on GaN HEMT based gas sensors for low concentrations of NO_2 and NH_3.

Abstract

In recent decades, the demand for gas sensors has increased rapidly because of their large scale use in medical instruments, automobiles and laboratories. For example, nitrogen dioxide (NO_2) and ammonia (NH_3) are found to be among the main constituents of exhaust gases and harmful air contaminants. Inhalation and long-term exposure of these gases can cause health issues and sometimes result in life threatening conditions. Hence, there is a need to detect low concentrations of NO_2 and NH_3. Recently, several wide band gap materials have attracted great interest for application in gas sensing to mitigate some of the limitations associated with metal oxide, polymer and electrochemical cell based sensors. The investigated materials include ZnO, diamond, and GaN and its alloys.

GaN based sensors are gaining momentum due to their unique properties, such as high electron mobility, mechanical stability and wide band gap that allows high thermal resistance and the ability to withstand harsh chemicals, gaseous and the corrosive environments. Furthermore, AlGaN/GaN high electron mobility transistors (HEMTs) are

extremely sensitive to the surface charge and variations in the environmental conditions due to the proximity of 2DEG to the sensing surface and their high sheet carrier concentration (on the order of 10^{13} cm^{-2}), thereby enabling sensing of the gases at low concentrations. This thesis presents the fabrication and characterization of GaN HEMT based gas sensors that can detect low concentrations of NO_2 and NH_3 for a large range of concentrations and a wide range of temperatures. The sensing mechanism corresponding to the temperature dependent response of these gases has been explained in detail.

AlGaN/GaN HEMT heterostructure was grown on 100 mm diameter Si (111) substrate using metal organic chemical vapour deposition (MOCVD). The AlGaN/GaN HEMT based sensors were fabricated with interdigitated electrodes using Ti/Al/Ni/Au (20/120/40/50 nm) metal stack, followed by the rapid thermal annealing at 825 ºC under nitrogen ambient for 30 sec. The contact resistance (R_c) value of <1 Ω.mm was achieved, which confirms the good quality of the ohmic contacts. Subsequently, Ti/Au (25/300 nm) pad layer for wire bonding was deposited. It was followed by the deposition of different functionalization layers such as Pt, Pd and Ag in the open gate region. The fabricated devices were wire bonded to a 16-pin dual in-line package (DIP) for the gas sensing applications.

The Pt/AlGaN/GaN HEMT based sensors exhibited a change in current (ΔI) of 0.5 mA with sensitivity of 1.2 % for 10 ppm NO_2 at room temperature (RT) and recovered at an elevated temperature (300 °C). The heating induced gas desorption led to the recovery of the sensor at an elevated temperature. The sensitivity increased with the increase in relative humidity (0 to 90%) at RT. The mechanisms for current decrease during the exposure of the gas and influence of relative humidity on NO_2 sensitivity were investigated. The high sensitivity of 5.5 % with a corresponding ΔI of 1.8 mA was achieved for 10 ppm NO_2 concentration at 300 °C, which is higher than the reported value with Pt/AlGaN/GaN HEMT based sensors under similar measurement conditions. The large surface area of the interdigitated electrodes and the catalytic property of platinum functionalization layer enabled high sensitivity for low NO_2 concentrations of < 10 ppm. A rapid response of less than 2 min. with a recovery time of less than 5 min. was obtained for all the concentrations. The behaviour of various sensor metrics such as sensitivity, response time and recovery time were studied at different temperatures. The activation energy values of 0.33 eV/molecule and 0.64 eV/molecule were obtained for response time (E_a) and recovery time (E_d), respectively. E_a and E_d are the activation energies of adsorption (chemisorption of O^- with adsorption sites at the top surface) and desorption (dissociation of the existing chemical bond), respectively. Arrhenius plot of sensitivity was obtained for 10 ppm NO_2. The activation energy of 0.085 eV/molecule was obtained for NO_2 sensing using AlGaN/GaN HEMT with Pt functionalization layer. This is the energy of the rate-limiting step of chemisorption of O^- ions, in which negative charge is transferred to the metal/semiconductor interface.

NH_3 sensing using AlGaN/GaN HEMT based gas sensors with Pt functionalization layer and other novel functionalization layers such as Pd and Ag was demonstrated over a wide temperature range of 30-275 °C. Pt/AlGaN/GaN HEMT exhibited the sensitivity of 0.51 % and 0.83 % for 50 ppm NH_3 at 30 °C and 275 °C, respectively. A measurable ΔI of 143 µA and sensitivity of 0.19 % were obtained for a low NH_3 concentration of 10 ppm, which is the lowest NH_3 concentration sensed at RT by Pt/AlGaN/GaN HEMT. The current decreased (ΔI is negative) when the sensor was exposed to different concentrations of NH_3 at RT while it increased (ΔI is positive) above 200 °C. At low temperature (30 °C), NH_3 is adsorbed in a molecular form on Pt surface and donates free electrons to produce negative potential at the Pt/AlGaN interface leading to a decrease in the current. However, NH_3 gets dissociated into positively charged hydrogen ions (H^+) at high-temperature (>200 °C). This results in positive surface potential causing an increase in the current. The behaviour of various sensor metrics such as sensitivity, response time and recovery time were compared for Pt, Pd and Ag functionalization layers. The sensor with the Pd functionalization layer exhibited higher sensitivity at 275 °C as compared to the other sensors due to higher hydrogen affinity of Pd. The sensor with the Ag functionalization layer was found to respond quickly to the change in NH_3 concentration and demonstrated faster response time and recovery time (< 3 min) as compared to other sensors using Pt and Pd. This is attributed to the oxidized Ag surface which creates a favourable site for the adsorption of NH_3 gas. After adsorption, charge transfer from NH_3 to Ag occurs quickly leading to faster response and recovery times.

Having optimized the AlGaN/GaN HEMT based sensors, further efforts were made to investigate novel Pt/AlN/GaN/AlN HEMTs for NO_2 and NH_3 sensing. AlN/GaN/AlN HEMT heterostructures were grown on SiC substrate using molecular beam epitaxy (MBE). A sensitivity of 0.76 % with a corresponding ΔI of 472 µA was obtained for 10 ppm NO_2, which is lower than that obtained for Pt/AlGaN/GaN HEMT based sensor. However, the Pt/AlN/GaN/AlN HEMT based sensor was found to respond quickly to the change in the NO_2 concentration. There was an improvement in the response time from 56 sec to 32 sec for 10 ppm NO_2. Since the time taken for the charge transport from the interface to 2DEG is less due to the lower barrier thickness (7 nm), it results in the decreased value of response time.