

Abstract

Rapid industrialization and economic expansion have resulted in the emission of substantial quantities of hazardous gases, including nitrogen oxides (NO_x), carbon monoxide (CO), sulfur dioxide (SO₂), and volatile organic compounds (VOCs), into the atmosphere. Among these, VOCs such as formaldehyde—a known carcinogen and toxic gases like nitrogen dioxide (NO₂) pose serious health risks even at trace concentrations. Consequently, the development of gas sensors that are highly sensitive, selective, stable over a wide operating temperature and voltage range, and cost-effective remains a critical challenge. In this work, chemiresistive gas sensors based on β -Ga₂O₃ were systematically developed through structural engineering strategies involving elemental doping (isoelectronic, donor, and acceptor) and composite formation to selectively detect formaldehyde and NO₂, while addressing the intrinsically poor electrical conductivity and limited selectivity of pristine β -Ga₂O₃. β -Ga₂O₃ nanostructures synthesized via a hydrothermal route were first evaluated for selective formaldehyde detection among common VOCs using the Eley–Rideal reaction model. β -Ga₂O₃ nanorods (~60 nm) exhibited superior selectivity, yielding a response of 30.25% toward 300 ppm formaldehyde at 300 °C. Isoelectronic aluminum (Al) doping was subsequently employed to enhance sensing performance, achieving a maximum response of 48.03% at 300 ppm formaldehyde and 300 °C for 5 wt% Al doping. Temperature-dependent studies revealed phase transformations from GaOOH to α -Ga₂O₃ at 400 °C and from α -Ga₂O₃ to β -Ga₂O₃ at 800 °C, with the β -phase remaining thermally stable up to 1000 °C. Increasing Al concentration resulted in a systematic reduction in lattice volume. Further enhancement was achieved through donor doping with tin (Sn), which significantly improved electrical conductivity and produced a remarkable response of 333.35% toward 300 ppm formaldehyde at 300 °C for 5 wt% Sn doping, attributed to increased carrier concentration without phase segregation. Acceptor doping with zinc (Zn) induced a distinct phase evolution from β -Ga₂O₃ to ZnGa₂O₄ and ZnO composite structures with increasing Zn content, enabling ultra-sensitive formaldehyde detection with a detection limit as low as 0.14 ppb at 300 °C and underscoring the critical role of interface engineering. Finally, a p–n heterojunction composite formed by integrating Sn-doped β -Ga₂O₃ with Li-doped NiO demonstrated exceptional room-temperature NO₂ sensing performance among interfering gases such as CO, NH₃, and VOCs. Both NO₂ and formaldehyde were detected at sub-ppb levels, highlighting the strong potential of the developed sensors for real-time environmental monitoring applications.

Keywords: β -Ga₂O₃; chemiresistive gas sensors; elemental doping; heterojunction composites; formaldehyde sensing; NO₂ detection; volatile organic compounds (VOCs); interface engineering