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NO_2 Breath Sensor Based on InGaN@GaN Core-Shell Nanowires for Early Detection of Metabolic Disorders

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Metabolic disorders such as diabetes, liver and lung disease can be detected early through the analysis of chemicals present in a human's breath. NO_2, a volatile organic compound, has been identified as a potential biomarker for these conditions. Over the years, several breathe sensors have been proposed for the detection of NO_2 in the human breathe. However, the detection of NO_2 in the complex environments such as high humidity and in the presence of several interfering gases and at low operating temperature is extremely difficult. Herein, we propose, indium-doped gallium nitride@ gallium nitride core-shell nanowires (InGaN@GaN) to detect NO_2 levels in breath and diagnose metabolic disorders with high accuracy and sensitivity. The sensor based on InGaN@GaN exhibits 4-fold increase in sensitivity compared to the sensors based on bare GaN. These sensors offer a non-invasive and convenient method for early detection of metabolic disorders, facilitating timely treatment and improved patient outcomes.

I. Introduction

The early detection and treatment of metabolic disorders is imperative in mitigating the progression of the disease and its related consequences. Breath sensing analysis can play a significant role in the detection of metabolic disorders, one of which is diabetes, which can result in alterations of NO_2 levels in a human's breath. Breath sensing devices, such as breathalyzers, can detect these alterations and provide non-invasive, real-time measurements of NO_2 levels [1]. NO_2 breath sensing is a non-invasive diagnostic method for identifying metabolic disorders, including diabetes and lung disease. This method has gained considerable attention in the biomedical application due to its ease of use, convenience, and ability to provide real-time results with just a simple breath test [2, 3].

Over the years, various breath analyzers have been proposed for the detection of NO_2 in human breath, including those based on infrared spectroscopy, gas chromatography, mass spectroscopy, and metal oxide-based gas sensors. Among these, metal oxide-based gas sensors have gained significant attention due to their remarkable sensitivity, durability, broad detection range, and low production costs. To date, several metal oxide-based sensors, such as SnO_2, In_2O_3, WO_3, ZnO, and GaN have been proposed for the detection of NO_2 [4]. GaN, in particular, has been considered a promising material for gas sensing due to its superior physical, chemical, and optical properties. Through years of research, our understanding of the essential control parameters and material modification techniques in semiconductor-based gas sensors has progressed. To improve the sensitivity, selectivity, and repeatability of these sensors, various approaches have been identified, such as doping, alloying, surface functionalization, size reduction, morphology, and phase control. With this research objective several exotic GaN nanostructures were proposed with improved sensitivity toward NO_2. To improve the sensitivity and reduce the operating temperature several catalytic materials such as gold, platinum, and silver. However, using precious metals is not advantageous in terms of economic perspective owing to their high cost. The incorporation of rGO into the GaN has been considered as an effective approach to improve the sensitivity. However, sensing NO_2 at the parts per billion (ppb) level remains a significant challenge for GaN-based gas sensors. Herein, we proposed facile metal organic chemical vapor deposition (MOCVD) preparation method for the preparation of InGaN@GaN for the detection of NO_2 in the human breathe. The fabricated sensors based on InGaN@GaN and GaN nanowires were investigated for its NO_2 sensing as a function of temperature and concentration. The proposed InGaN@GaN sensor exhibit excellent sensitivity as low as 50 ppb at 25 °C.

II. Results and Discussion

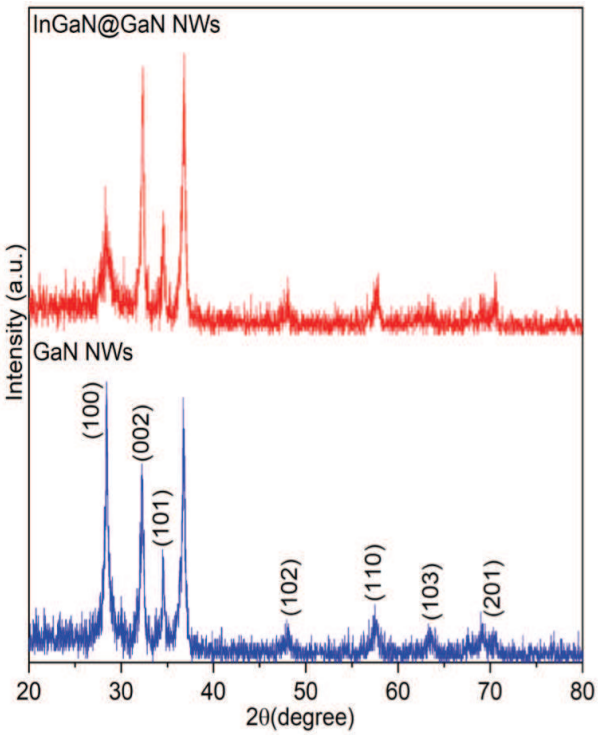

Figure 1. Powder X-ray diffraction pattern of the as-prepared GaN nanowires and InGaN@GaN nanowires.

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The InGaN and GaN nanowires were prepared using a metal organic chemical vapor deposition (MOCVD) technique. The crystal structure and phase purity of the as-prepared materials were characterized by the XRD, micro-Raman, XPS analyses. The XRD pattern of the as-prepared sample is shown in Fig. 1. The diffraction peaks (100), (002), (101), (102), (110), (103), (200), and (201) consistent with the standard card of hexagonal wurtzite GaN with lattice parameters of a = 0.318 nm and c = 0.518 nm. The diffraction peak of the (002) plane is more intense than those of the other crystal planes revealing that most of the GaN nanowires preferentially grow perpendicular to the (002) crystal plane. The data obtained from the micro-Raman; FT-IR, XPS were consistent with each other. The surface area and pore size distribution of the as-prepared materials were characterized by the nitrogen adsorption and desorption isotherm analysis. The morphology of the as-prepared materials was characterized by the FESEM and TEM. The optical properties of the as-prepared InGaN@GaN and GaN nanowires were investigated using UVDRS and PL spectra analyses. The panoramic view of the FESEM images discloses the numerous nearly uniform size and shape InGaN@GaN core-shell nanowires (Fig. 2a-c). TEM images demonstrate the successful formation of the InGaN@GaN core-shell structure (Fig. 2d-f). The lattice fringes with the spacing of 0.269 nm corresponding to the 0001 plane of the hexagonal wurtzite crystal structure (Fig. 2g). The SAED pattern can be indexed to the (110), (010), and (100) planes of GaN ((Fig. 2h). Elemental mapping confirms uniform distribution of gallium, nitrogen, and indium in the prepared material (Fig. 2i-l).

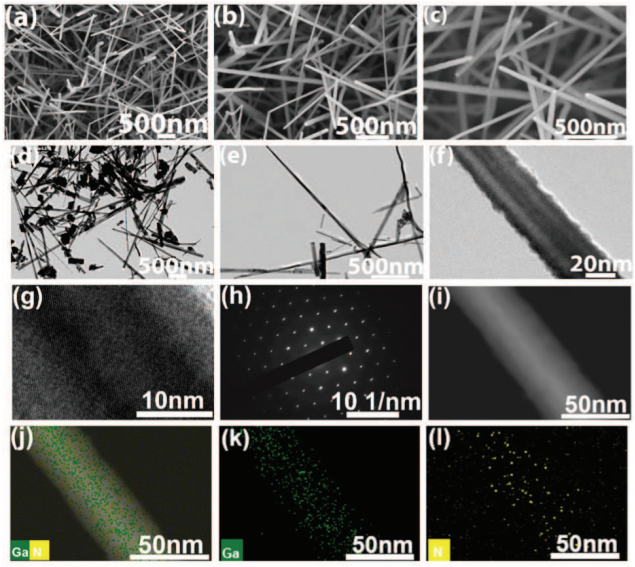

Fig. 2. (a-c) FE-SEM images of the as-prepared InGaN@GaN nanowires at different magnification. (d-f) TEM images of the as-prepared InGaN@GaN nanowires. (g, h) High-resolution transmission electron micrograph and selected area electron diffraction pattern of the as-prepared InGaN@GaN nanowires. (i-l) Elemental mapping of the as-prepared InGaN@GaN nanowires.

The gas sensing characteristics of the sensors based on GaN and InGaN@GaN core-shell nanowires for sensing NO_2-a well-known metabolic disorders biomarkers -in exhaled breath were investigated. To screen for lung disease, exhaled breath NO_2 concentrations up to 50 ppb—twice the level found in healthy individuals—must be detected selectively. All breathe sensing analyses were conducted at a relative humidity of 90% to replicate the environment of exhaled air. All the sensing analyses were performed at 25°C under ultraviolet light illumination to breath-relevant concentrations of 50 ppb to 5 parts per million (ppm) of NO_2. The maximum sensing response of the sensor based GaN and InGaN@GaN core-shell nanowires at 25°C was 85.27 and 355.45, respectively. The sensor based on InGaN@GaN exhibits 4-fold increase in sensitivity compared to the sensors based on bare GaN. The InGaN@GaN sensor showed excellent sensitivity as low as 50 ppb at 25°C. Besides, both the sensors showed excellent selectivity towards to NO_2 compared to the other interfering gases. The performance of the fabricated sensor for breath sensing was evaluated by detecting NO_2. The results demonstrated that the InGaN@GaN-based electronic nose (e-nose) sensor arrays were able to distinguish between healthy and simulated unhealthy breaths without any overlap in the obtained signals. This outcome indicates that the sensor has a high level of precision in differentiating between healthy and unhealthy breaths.

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