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AlInN resistive ammonia gas sensors

W.Y. Weng [a], S.J. Chang [a], T.J. Hsueh [b,*], C.L. Hsu [c], M.J. Li [c], W.C. Lai [d]

[a] Institute of Microelectronics and Department of Electrical Engineering, Advanced Optoelectronic Technology Center, Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 70101, Taiwan
[b] National Nano Device Laboratories, Tainan 741, Taiwan
[c] Department of Electronic Engineering, National University of Tainan, Tainan 700, Taiwan
[d] Institute of Electro-Optical Science and Engineering, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT

We report the growth of AlInN epitaxial layer and the fabrication of AlInN resistive NH_3 gas sensor. It was found that surface morphology of the AlInN was rough with quantum dot like nano-islands. It was also found that the conductance of these AlInN nano-islands increased as NH_3 gas was introduced into the test chamber. At 350 °C, it was found that measured incremental currents were around 105, 127, 147 and 157 μA when concentration of the injected NH_3 gas was 500, 1000, 2000 and 4000 ppm, respectively.

1. Introduction

Ammonia (NH_3) is a colorless gas with a special odor. It is commonly used in various industrial sectors [1]. Although NH_3 is extensively used in our daily life, people may develop a burning sensation in eyes, nose and throat when exposed to NH_3. Inhalation of NH_3 vapor could also cause acute poisoning to people. Hence, detecting and measuring NH_3 vapor concentration in the environment is necessary. The most commonly used method to detect gaseous NH_3 was either by potentiometric electrodes [2] or by infrared devices [3]. However, these devices are expensive and bulky. It is also possible to detect NH_3 vapor concentration by semiconducting metal oxide materials [4–9]. It has been shown that near surface conductivity of these materials changes upon exposure to certain gas molecules. Furthermore, it was found that such resistance change is related to various defects such as oxygen vacancy, metal vacancy or others [10,11].

Recently, it was found that III-nitride epitaxial layer can also be used to detect gaseous butane, propane, ethyl alcohol and carbon monoxide [12]. Although III-nitride-based materials are extensively used as light emitting diodes [13,14], ultraviolet photodetectors [15] and high power electronics [16], only few reports on III-nitride-based sensor for volatile organic compounds can be found in the literature [12]. Compared with metal oxide sensors, we should be able to integrate III-nitride-based gas sensors with III-nitride-based photodetectors and electronic devices on the same chip. Other than the binary GaN, ternary AlInN has attracted much attention in recent years. Compared with AlGaN and InGaN, AlInN is much less known due to the difficulty in growing high quality crystal [17]. It has been shown that AlInN can be grown lattice matched to GaN with an indium content of ~17–18%. However, it is still difficult to grow high quality AlInN due to severe phase separation caused by the large disparity in cation sizes as well as by differences in thermal properties of the binary constituents [18]. It has also been reported that epitaxial AlInN layers are defective in general with a significant amount of aluminum vacancy, indium vacancy or nitrogen vacancy. Similar to metal oxide sensors, these defects should be able to enhance the reaction of gas molecular on sample surface and thus enhance the responsivity of AlInN-based gas sensors. In this study, we report the growth of AlInN. Sensing properties of the fabricated AlInN resistive NH_3 gas sensors will also be discussed.

2. Experimental

Samples used in this study were grown on a *c*-plane (0 0 0 1) sapphire (Al_2O_3) substrate by metalorganic chemical vapor deposition. Details of the growth can be found elsewhere [19]. Prior to the growth, we annealed the sapphire substrates at 1060 °C in H_2 ambient to remove surface contamination. We then deposited a 30-nm-thick low-temperature GaN nucleation layer at 530 °C, a 2-μm-thick n-type unintentionally doped GaN ($n = 3 \times 10^{16}\,cm^{-3}$) buffer layer at 1020 °C, and a 500-nm-thick n-type unintention-

* Corresponding author. Tel.: +886 6 2757575/62400x1208; fax: +886 6 2761854.
E-mail address: tj.Hsueh@gmail.com (T.J. Hsueh).

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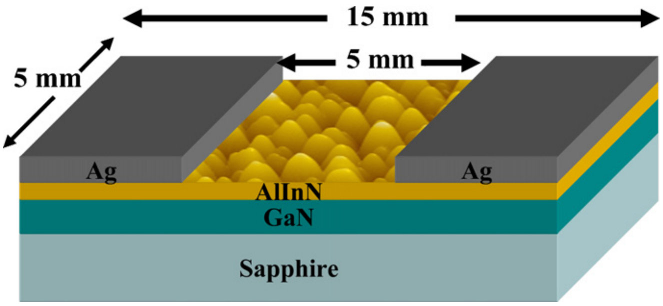

Fig. 1. Schematic diagram of the fabricated AlInN resistive gas sensor.

ally doped AlInN ($n = 5 \times 10^{19}\,\mathrm{cm}^{-3}$) active layer at 650 °C. A JEOL JSM-7000F field emission scanning electron microscope (FESEM) operated at 10 keV was then used to characterize structural properties of the as-grown AlInN epitaxial layer. The cross-sectional image of the AlInN layer was prepared by an FEI Nova-200 NanoLab Dual-Beam Focused Ion Beam (DB-FIB) system. Crystal qualities of the as-grown samples were evaluated by a BEDE D1 double-crystal X-ray diffraction (DCXRD) system. The source of X-ray is 1.54056 Å wavelength (Cu Kα).

For the fabrication of NH_3 gas sensors, we carefully smeared the colloidal silver onto the sample surface to serve as contact electrodes. The sample was then annealed at 350 °C for 15 min in Ar ambient to form good ohmic contacts between sliver and the underlying AlInN. Fig. 1 shows schematic diagram of the fabricated AlInN resistive gas sensor. To evaluate NH_3 gas sensing properties, we placed the fabricated sensor in a sealed chamber and measured current–voltage (I–V) characteristic of the sample in air from the two electrodes. It should be noted that the sealed chamber has an inlet port connected to a gas inlet valve and an outlet port connected to an air pump. We first closed the outlet port and injected NH_3 gas into the chamber through a gas-injecting syringe. At this stage, we measured I–V characteristic of the sample continuously in the presence of NH_3 gas (i.e., air + NH_3). After the chamber was stabilized, we opened the outlet port so that the air pump can pump the NH_3 gas away. At the same time, we also opened the inlet valve to introduce air into the chamber. In other words, the chamber was kept in atmospheric pressure throughout the experiment. At the end of the experiment, we measured I–V characteristic of the sample in air again.

3. Result and discussion

From Hall measurements, it was found that the sheet resistances of our GaN and AlInN layers were $1.09 \times 10^6\,\Omega$/sq and 394 Ω/sq, respectively. These values suggest that parallel conduction which might occur in the GaN buffer layer should be negligible. Fig. 2 shows top-view FESEM image of the AlInN epitaxial layer. The inset shows cross-sectional image of the AlInN layer that prepared by DB-FIB. It was found that thickness of the AlInN epitaxial layer was around 545 nm, which agreed well with our initial design. It was also found that surface morphology of the AlInN was rough with quantum dot like nano-islands. Similar result has also been reported previously [20]. It also was found that the diameter and height of the nano-islands were around 100 and 160 nm, respectively. It should be noted that these nano-islands could provide us a larger surface area, which in term will result in a large sensor response. It should also be noted that the Pt layer shown in the inset was intentionally deposited to protect the underneath AlInN and GaN from e-beam etching during DB-FIB sample preparation. No such Pt layer was used during the fabrication of NH_3 sensors. Fig. 3(a) shows DCXRD spectrum of the sample with two clear peaks. It was found that full-width-half-maximum (FWHM) of the (0 0 0 2)

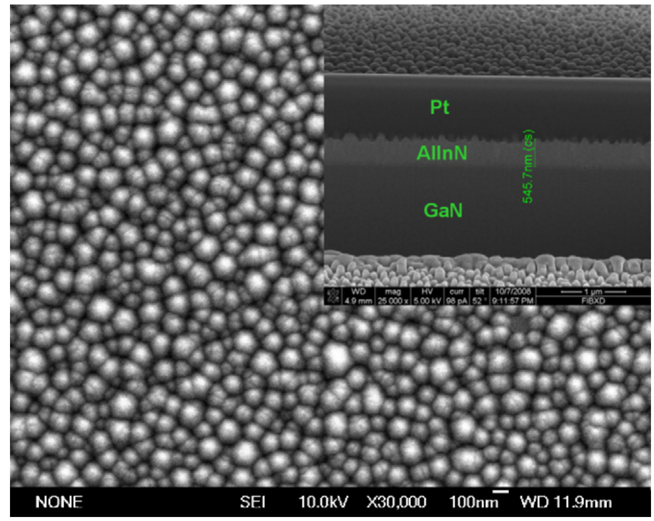

Fig. 2. Top-view FESEM image of the AlInN epitaxial layer. The inset shows cross-sectional image of the AlInN layer.

GaN peak was around 130 arcs, suggesting good crystal quality. In contrast, FWHM of the AlInN peak was significantly larger (i.e., 758 arcs). Based on Vegard's rule, it was found that indium content in the AlInN layer was around 62%. The fact that no other peaks were observed suggests that no phase separation occurred in the sample [21]. Fig. 3(b) shows energy dispersive spectrum (EDS) measured from the fabricated devices. It can be seen that aluminum, indium and nitrogen peaks could all be clearly observed in the spectrum.

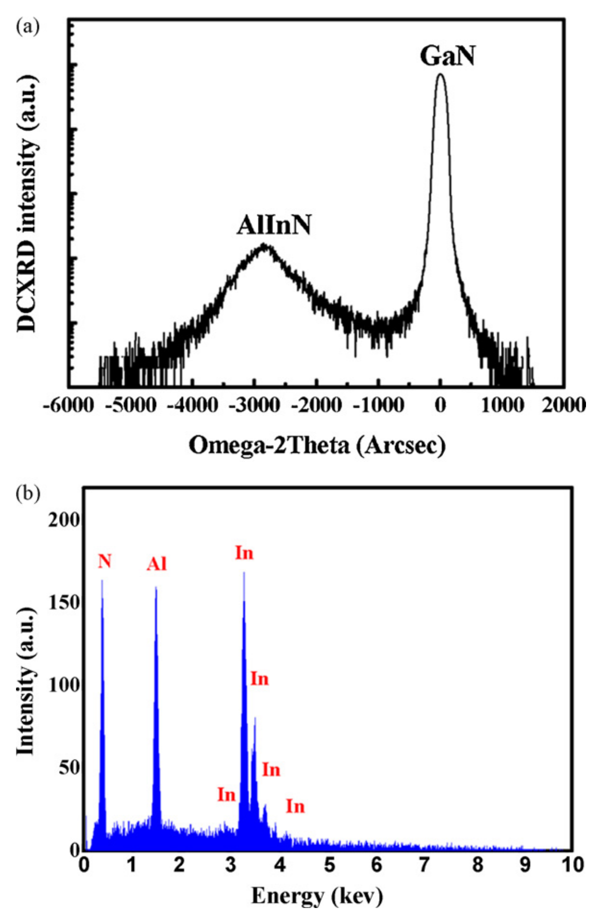

Fig. 3. (a) DCXRD and (b) EDS spectra of the AlInN layer.