



Performance improvement mechanisms of *i*-ZnO/(NH₄)₂S_x-treated AlGaIn MOS diodes

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ABSTRACT

The intrinsic ZnO (*i*-ZnO) film was deposited by a vapor cooling condensation system and used as the dielectric layer of the AlGaIn metal–oxide–semiconductor (MOS) diodes. Before the deposition of the *i*-ZnO dielectric layer, the AlGaIn surface was treated using (NH₄)₂S_x solution. In view of the lattice match of the *i*-ZnO film and the reduced surface state density of the (NH₄)₂S_x-treated surface, the quality of the *i*-ZnO/AlGaIn interface was improved. According to the experimental results, the *i*-ZnO/(NH₄)₂S_x-treated MOS diodes revealed the lower leakage current, the lower interface state density, and the high electrical performances compared with the *i*-ZnO/untreated ones. Furthermore, the X-ray photoelectron spectroscopy and the charge neutrality level model were used to analyze the conduction band offset and the valence band offset of the *i*-ZnO/AlGaIn interface. The valence band offset of the *i*-ZnO film contacted with the untreated and the (NH₄)₂S_x-treated AlGaIn layer was 1.53 eV and 1.96 eV, respectively. The conduction band offset of the *i*-ZnO film contacted with untreated and (NH₄)₂S_x-treated AlGaIn layers was 0.77 eV and 1.20 eV, respectively. The mechanisms of the enhanced conduction band offset were attributed to the effective reduce of interface states by using the (NH₄)₂S_x surface treatment.

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1. Introduction

Recently, in view of the significant progress of epitaxial growth and fabrication techniques [1–4], nitride-based compound semiconductors have been widely and successfully used in the gas sensors [5,6], electronic devices [7,8] and optoelectronic devices [9,10]. To reduce the leakage current and improve the power-handling capacity, the GaN-based metal–oxide–semiconductor high-electron mobility transistors (MOS–HEMTs), in which the gate dielectric layer was inserted between the metal gate and the GaN-based compound semiconductors, were developed. Various gate dielectric layers have been investigated [11–13]. To avoid the possible defects and the surface states caused by the lattice mismatch interface between the gate dielectric layer and the GaN-based semiconductors, the zinc oxide (ZnO) is a promising material due to the advantage of the same wurtzite crystalline and the nearly identical lattice constant with the GaN-based semiconductors. Recently, the intrinsic ZnO (*i*-ZnO) film with low carrier concentration and high resistivity was grown at low

temperature by our designed vapor cooling condensation system [14,15]. Furthermore, the resulting AlGaIn/GaN MOS–HEMTs with *i*-ZnO gate dielectric layer deposited by the vapor cooling condensation system were reported, previously [16]. However, the native oxide resided on the surface of the GaN-based semiconductors led to the formation of high surface state density and Fermi level pinning. To improve the performances of the resulting devices by using the (NH₄)₂S_x surface treatment, not only could native oxide on the surface of the GaN-based semiconductors be completely removed, but also Ga–S bonds were formed and nitrogen-related vacancies occupied as well [17,18]. By using the (NH₄)₂S_x surface treatment, the improved performances of the ZnO-gated AlGaIn/GaN MOS–HEMTs were previously demonstrated [19,20]. To investigate the physical mechanisms, the study of the interface state density and the band alignment of the *i*-ZnO/AlGaIn interface is an important issue. In this work, the electrical characteristics of the *i*-ZnO/AlGaIn MOS diodes with and without the (NH₄)₂S_x surface treatment were measured and compared. Furthermore, the X-ray photoelectron spectroscopy (XPS) measurement was carried out to determine the valence band offset and the conduction band offset of the *i*-ZnO film contacted with the untreated and the (NH₄)₂S_x-treated AlGaIn layers. A systematic analysis was used to verify the function of the (NH₄)₂S_x surface treatment.

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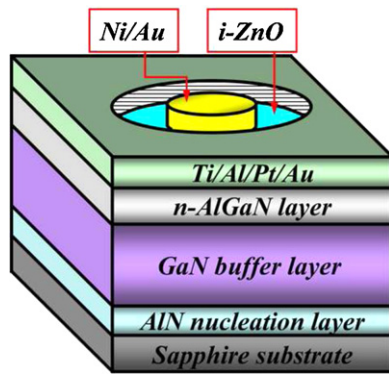


Fig. 1. Schematic configuration of the *i*-ZnO/AlGaIn MOS diodes.

2. Device structure and fabrication

Fig. 1 shows the schematic configuration of the *i*-ZnO/AlGaIn MOS diodes. The epitaxial layers used in this work were grown on *c*-plane sapphire substrates by a metalorganic chemical vapor deposition system. The epitaxial structure consisted of a 20-nm-thick AlN nucleation layer, a 2- μ m-thick GaN buffer layer, and a 0.1- μ m-thick Al_{0.22}Ga_{0.78}N layer (referred as AlGaIn layer, hereafter) with electron concentration of $6.8 \times 10^{17} \text{ cm}^{-3}$. The ohmic metals of Ti/Al/Pt/Au (25/100/50/150 nm) were deposited by an electron-beam evaporator and the ohmic contact was formed by rapid thermal annealing at 850 °C in N₂ ambient for 2 min [21]. The inner radius and the outer radius of the concentric ohmic contact ring were 150 μ m and 400 μ m, respectively. Before the deposition of *i*-ZnO film, the (NH₄)₂S_x surface treatment was performed to passivate and completely remove the surface states resided on the AlGaIn surface. During the (NH₄)₂S_x surface treatment, the samples were first dipped into the yellow (NH₄)₂S_x solution at 60 °C for 30 min, and the samples were then rinsed with deionized water and blown dry with nitrogen gas. A 50-nm-thick *i*-ZnO film was deposited on the AlGaIn layer using the vapor cooling condensation system. During the deposition of the *i*-ZnO film, the samples were attached on the liquid nitrogen-cooled stainless steel plate in the chamber of the vapor cooling condensation system. The sublimated ZnO vapor materials originated from the heated ZnO powder (purity of 99.99%) were deposited and condensed on the cooled AlGaIn layer. The electron concentration and mobility of the deposited ZnO films were $7.6 \times 10^{15} \text{ cm}^{-3}$ and $3.2 \text{ cm}^2/\text{V s}$, respectively. Finally, the circular pattern Ni/Au (20/100 nm) metals with a radius of 100 μ m were deposited by an electron-beam evaporator. For the comparison purpose, the *i*-ZnO/untreated AlGaIn MOS diodes were fabricated on the same samples by the same fabrication process except the (NH₄)₂S_x surface treatment.

To investigate the function of the (NH₄)₂S_x surface treatment on the *i*-ZnO/AlGaIn interfacial property, the band alignment, the conduction band offset, and the valence band offset of the *i*-ZnO/AlGaIn interface were analyzed. The epitaxial samples were divided into five groups and cleaned in the chemical solutions of trichloroethylene, acetone, and methanol. Among them, three group samples (referred to as group A, group B, and group C) were maintained in the as-cleaned condition. The other two group samples (referred to as group D and group E) were dipped into the yellow (NH₄)₂S_x solution at 60 °C for 30 min, and then were rinsed with deionized water and immediately blow dried by N₂ gas. The group E samples were maintained in the (NH₄)₂S_x-treated condition. An 1- μ m-thick *i*-ZnO film was deposited on the group B samples using the vapor cooling condensation system. Moreover, a 5-nm-thick *i*-ZnO film was deposited on the as-cleaned group C samples and the

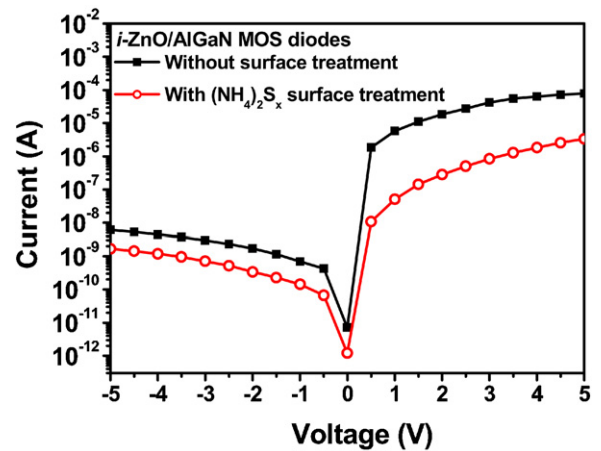


Fig. 2. Current–voltage characteristics of the *i*-ZnO/untreated and the *i*-ZnO/(NH₄)₂S_x-treated AlGaIn MOS diodes.

(NH₄)₂S_x-treated group D samples using the vapor cooling condensation system, respectively. By using the measured XPS spectra, the thick *i*-ZnO film (1 μ m) and the thin *i*-ZnO film (5 nm) deposited on AlGaIn layers were used to determine the energy of the *i*-ZnO film and the energy of the *i*-ZnO/AlGaIn interface, respectively. To avoid possible contamination in the XPS measurement, the five group samples were immediately loaded into the vacuum chamber of the XPS system (ULVAC-PHI, PHI 5000 Versa Probe). The XPS measurements were carried out using a monochromatic Al K α radiation (1486.6 eV) as the excitation source. The C 1s peak at 284.6 eV was taken as the reference energy. To enhance surface sensitivity, the XPS data were taken at a take-off angle of 45° from the surface.

3. Experimental results and discussion

Fig. 2 shows the current–voltage (*I*–*V*) characteristics of the *i*-ZnO/untreated and the *i*-ZnO/(NH₄)₂S_x-treated AlGaIn MOS diodes with the 50-nm-thick *i*-ZnO dielectric layer measured by an Agilent 4156C semiconductor parameter analyzer. Compared with the *i*-ZnO/untreated AlGaIn MOS diodes, the leakage current of the *i*-ZnO/(NH₄)₂S_x-treated AlGaIn MOS diodes operated at +5 V was decreased from $7.79 \times 10^{-5} \text{ A}$ to $3.39 \times 10^{-6} \text{ A}$. On the other hand, the leakage current of the *i*-ZnO/(NH₄)₂S_x-treated AlGaIn MOS diodes operated at –5 V was decreased from $6.16 \times 10^{-9} \text{ A}$ to $1.68 \times 10^{-9} \text{ A}$. It could be seen that the leakage current of the *i*-ZnO/(NH₄)₂S_x-treated MOS diodes was significantly lower than that of the *i*-ZnO/untreated MOS diodes. Fig. 3(a) and (b) shows the high frequency (1 MHz) capacitance–voltage (*C*–*V*) characteristics of the *i*-ZnO/untreated and the *i*-ZnO/(NH₄)₂S_x-treated MOS diodes measured by an HP 4284A, respectively. To estimate the interface state density (*D*_{it}) of the *i*-ZnO/AlGaIn MOS diodes, the photo-assisted *C*–*V* measurement was utilized in this work [22]. In general, the inversion layer of the *i*-ZnO/AlGaIn MOS diodes was difficult to be achieved because of the extremely low minority carrier generation rate of the GaN-based semiconductors. In the photo-assisted *C*–*V* measurement, the light with energy larger than the bandgap of the GaN-based semiconductors was utilized to generate the electron-hole pairs and to form the inversion layer. In the first measurement procedure, the *i*-ZnO/AlGaIn MOS diodes were applied the voltage swept from the accumulation layer (6 V) to the depletion layer (–12 V) in dark. The *i*-ZnO/AlGaIn MOS diodes were illuminated by an Xe lamp (selected wavelength of 325 nm) for 60 s and then were applied by a constant bias voltage of –12 V. The generated holes were attracted toward to the *i*-ZnO/AlGaIn interface to form the inversion layer by applying a bias voltage

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