Synthesis of p-type GaN nanowires†

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GaN has been utilized in optoelectronics for two decades. However, p-type doping still remains crucial for realization of high performance GaN optoelectronics. Though Mg has been used as a p-dopant, its efficiency is low due to the formation of Mg–H complexes and/or structural defects in the course of doping. As a potential alternative p-type dopant, Cu has been recognized as an acceptor impurity for GaN. Herein, we report the fabrication of Cu-doped GaN nanowires (Cu:GaN NWs) and their p-type characteristics. The NWs were grown vertically via a vapor–liquid–solid (VLS) mechanism using a Au/Ni catalyst. Electrical characterization using a nanowire-field effect transistor (NW-FET) showed that the NWs exhibited n-type characteristics. However, with further annealing, the NWs showed p-type characteristics. A homo-junction structure (consisting of annealed Cu:GaN NW/n-type GaN thin film) exhibited p–n junction characteristics. A hybrid organic light emitting diode (OLED) employing the annealed Cu:GaN NWs as a hole injection layer (HIL) also demonstrated current injected luminescence. These results suggest that Cu can be used as a p-type dopant for GaN NWs.

1 Introduction

Wide band gap gallium nitride (GaN) has been the subject of interest over the last two decades due to its potential applicability in optoelectronic devices.1–4 Accordingly, intensive development of key technologies for unlocking this potential has been undertaken. One of the issues to be addressed is the p-doping efficiency of GaN. Though Mg has been used as a p-dopant, its efficiency is low due to the formation of Mg–H complexes and/or structural defects in the course of doping. As a potential alternative p-type dopant, Cu has been recognized as an acceptor impurity for GaN. Herein, we report the fabrication of Cu-doped GaN nanowires (Cu:GaN NWs) and their p-type characteristics. The NWs were grown vertically via a vapor–liquid–solid (VLS) mechanism using a Au/Ni catalyst. Electrical characterization using a nanowire-field effect transistor (NW-FET) showed that the NWs exhibited n-type characteristics. However, with further annealing, the NWs showed p-type characteristics. A homo-junction structure (consisting of annealed Cu:GaN NW/n-type GaN thin film) exhibited p–n junction characteristics. A hybrid organic light emitting diode (OLED) employing the annealed Cu:GaN NWs as a hole injection layer (HIL) also demonstrated current injected luminescence. These results suggest that Cu can be used as a p-type dopant for GaN NWs.

2 Experimental details

Single crystalline Cu:GaN NWs were synthesized via a vapor–liquid–solid (VLS) mechanism using Au/Ni catalysts deposited on a sapphire substrate coated with a 30 nm thick layer of GaN films.6,9 The substrates were placed in a quartz tube reactor in a horizontal chemical vapor deposition (CVD) transport system. For the growth of Cu:GaN nanowires, metallic Ga (purity 99.99%) and CuCl2 (purity ≥99%) powder were placed into the reactor before inserting the substrates. H2 was used as a carrier gas and ammonia (NH3) was used as a reactant gas. The furnace was heated to 850 °C under a flow of NH3 and H2 at respective rates of 10 and 500 sccm; this temperature was maintained for 120 min and the furnace was then cooled down to room temperature. The thermal annealing process was subsequently executed at 850 °C for 30 min under a flow of N2.11 The morphology of the NWs was examined via field emission scanning electron microscopy (FE-SEM), and structural analysis was performed using transmission electron microscopy (TEM). The electrical properties were examined by utilizing a nanowire-field effect transistor (NW-FET) employing a single nanowire. The electrical properties of the nanowires were further...
characterized by fabricating homo-junction diode and organic light emitting diode (OLED) structures, in which the nanowires function as the hole injector.

3 Results and discussion

Vertically well aligned Cu:GaN nanowires were grown on the substrate with Au/Ni as two component, multi-catalysts. Fig. 1(a) and (b) show FE-SEM images of Cu:GaN nanowires and annealed Cu:GaN nanowires. The Cu:GaN nanowires with diameters in the range of 80 nm to 150 nm and lengths of 3 \( \mu \text{m} \) to 10 \( \mu \text{m} \) were uniformly vertically grown over the entire substrate. In this study, vertical growth could be achieved via the CVD process by using the multi-catalyst, i.e., Au–Ni.\textsuperscript{19} In the case of GaN nanowires, however, vertical growth via the VLS mechanism has rarely been reported. This is because the vapor–solid (VS) mechanism results in the formation of an interfacial layer on the substrates prior to growth of the GaN nanowires by the VLS mechanism, thereby preventing the establishment of an epitaxial relationship between the nanowires and the substrates.\textsuperscript{20,21} Reliable growth of vertically aligned GaN nanowires using the conventional VLS mechanism, which employs a single catalyst (e.g., Ni), is thus difficult. However, the use of a multi-catalyst can lower the liquid formation temperature and lower the activation energy of the VLS mechanism thus leading to preemptive growth of the nanowires on the substrate relative to deposition of the interfacial layer, thereby enabling vertical nanowire growth. No changes in the morphology of the Cu:GaN nanowires were observed after the thermal annealing process, as shown in Fig. 1(b).

Fig. 1(c) and (d) show the TEM images of the Cu:GaN nanowire and annealed Cu:GaN nanowire. Fig. 1(c) indicates the single crystalline nature of the Cu:GaN nanowires. The preferential growth of the nanowires along the [001] direction is evidenced by the selected area electron diffraction (SAED) pattern. The composition of the Cu:GaN nanowires determined on the basis of transmission electron microscopy energy-dispersive X-ray spectroscopy (TEM-EDS) analysis shows an average concentration of Cu of about 2.1 at.%. The structural and chemical nature of the Cu:GaN nanowires were maintained in the course of annealing. The selected area electron diffraction (SAED) pattern presented in Fig. 1(d) shows that the nanowires had the same crystallographic [001] orientation of the growth direction; high resolution TEM images show that the morphology of the nanowires also remained unchanged after annealing. Furthermore, EDS analysis also indicates that the annealing process did not induce any compositional changes.

The electrical properties of the nanowires were evaluated by fabricating a nanowire-based field effect transistor (NW-FET) using the Cu:GaN nanowire and acquiring current–voltage (\( I–V \)) curves at 300 K. Fig. 2(a) and (b) show a schematic and SEM image of the top-gate four-probe NW-FET device. The nanowires were prepared and drop-cast onto a pre-patterned Si substrate. After drying, the location of the nanowire was identified, and the source and drain electrodes (Ti/Au, 10 nm/100 nm) were deposited using lithography to generate the NW-FET structures. The \( I–V \) curve of the Cu:GaN NW-FET device displayed linear characteristics, suggesting that the metal-electrical contacts for the device were ohmic. The conductance increased for gate voltages (\( V_g \)) greater than zero and decreased for \( V_g \) less than zero, indicative of the n-type semiconductor characteristics of the Cu:GaN nanowire (Fig. 2(c)). These n-type characteristics may be due to the formation of a stable complex between

![Fig. 1](image1.png)  
**Fig. 1** SEM and TEM images demonstrating vertical growth of Cu:GaN nanowires with and without the annealing process. (a) Cu:GaN nanowires without annealing, (b) with annealing, (c) HR TEM image of a Cu:GaN nanowire indicating a single crystal structure, and (d) single crystalline state of Cu:GaN nanowires maintained after annealing.

![Fig. 2](image2.png)  
**Fig. 2** (a) Schematic illustration of the top-gate four-probe Cu:GaN nanowire-FET device. (b) \( I–V \) characteristics of a Cu:GaN nanowire device in contact with a Ti/Au electrode for various top gate voltages (\( V_g \)) and \( I = 10 \text{nA} \) at 300 K. The inset is an enlarged plot of (c).
hydrogen and shallow acceptors at the GaN nanowire surface, given that the Cu:GaN nanowires were synthesized under a hydrogen atmosphere. Moreover, Cu may be interstitially doped into GaN given that this doping is energetically more favored than substitutional doping, thereby creating dangling bonds. Incorporation of hydrogen and GaN dangling bonds by Cu-doping may account for the observed n-type conductivity.

In order to further resolve this issue, thermal annealing was performed under a flow of N₂ gas. It is known that annealing dissociates the neutral hydrogen complex as well as Cu by occupying the interstitial sites or substituted Ga vacancies in the GaN lattice, leading to an increase in the hole concentration. The electrical properties were characterized by using nanowire FET devices. I–V measurements of the annealed Cu:GaN nanowires indicated a low resistivity of several mΩ cm for \( V_{g} = 0 \) V at room temperature. A weak gating effect, evidenced as a decrease in conductivity with positively increasing \( V_{g} \), is suggestive of a p-type carrier character for the annealed Cu:GaN nanowires. This low resistivity, along with the weak gating effect, indicates that a high carrier concentration was achieved within these nanowires. It is difficult to calculate the carrier density of heavily doped and carrier-confined nanowires due to challenges in achieving full depletion of carriers. In fact, incomplete depletion was observed in the \( V_{g} \) range of −5 to 5 V, which indicates that the FET approach is inadequate for accurate elucidation of the electrical type of heavily doped nanowires.

For more adequate elucidation of the electrical characteristics, a Cu:GaN nanowire/n-GaN film homo p–n junction device was fabricated as shown in the schematic in Fig. 3(a). For these devices, an n-type GaN thin film was grown using a metal organic chemical vapor deposition (MOCVD) system. The vertically aligned Cu:GaN nanowires were then grown on the n-GaN films followed by thermal annealing. Subsequently, spin-on poly(methylmethacrylate) (PMMA) was used to fill the space between the nanowires, acting as an electrical isolation between the p- and n-side contacts of the structures. Ohmic contacts were formed on the top of the GaN films by depositing a 2 nm Ni/50 nm Au layer. Subsequently, p-type ohmic metal indium tin oxide (ITO)/Au (20 nm/50 nm) was sputter deposited. The measurements indicated ohmic n- and p-type contacts, respectively. Fig. 3(b) shows the electrical characteristics of the junction structures with and without annealing. Without annealing, the curve was simply ohmic; however, nonlinear rectifying behavior was observed with annealing. The device exhibited a forward turn-on voltage of about 2.4 V and good rectification behavior over repeated measurements, indicative of the formation of a p–n homojunction at the interface. The reverse leakage current is about 70 μA at −4 V. This reverse leakage current was estimated relative to the wide interface between the n-GaN film and the p-Cu:GaN nanowire region. The I–V data recorded from the nanowires and substrate were symmetric, and thus, can be attributed to the rectification to the p–n junction between the nanowires and the substrate, and not to the junction between the nanowires and the metal contacts. The rectifying curve of the homojunction device was further considered by plotting the current in the log scale as given in the ESIF, which shows that the leakage currents are as small as \( \sim 10^{-4} \) A.

A hybrid organic LED (OLED) device was constructed to further confirm the p-type characteristics of the annealed Cu:GaN nanowires. Hybrid OLED structures were assembled based on the LED device utilizing the ZnO-graphene quasi quantum dots, by first fabricating OLED structures comprising a p–i–n structure and 6 layers: the p-type PEDOT:PSS polymer as a hole injection layer (HIL), the active layer ZnO-graphene quantum dots as an emissive layer, and n-type Cs₂CO₃ as an electron injection layer (EIL) were sandwiched between the patterned ITO glass and an aluminum metal contact. A poly-TPD polymer was used as the hole transport layer (HTL). This device emitted white light. Cu:GaN nanowires were then used as a HIL instead of the PEDOT:PSS polymer, as schematically illustrated in Fig. 4(a). The conduction band edge of the Cu:GaN nanowire is estimated to be within the range of 3–4 eV, and the valence band edge is estimated to be in the range of 6–7 eV when the vacuum level is set at \( E = 0 \). This band edge is similar to that of the PEDOT:PSS polymer. Therefore, there is no impact depending on the band edge level of the Cu:GaN nanowires. The device utilizing the
Cu:GaN nanowires that were not annealed did not emit. However, the device using the annealed Cu:GaN nanowires emitted white light (Fig. 4(b)).\textsuperscript{18} This result further indicates that the annealed Cu:GaN nanowires function as hole injection materials, and thus have p-type characteristics induced by annealing, as a result of the dissociation of the neutral CuGa hydrogen complex and Cu in the interstitial sites occupying the Ga vacancies.

4 Conclusion

The present study reports the properties of a vertically aligned Cu:GaN nanowire before and after being subjected to the annealing process. Characterization of the Cu:GaN nanowires using fabricated field-effect transistors indicated n-type characteristics. However, the annealed Cu:GaN NWs were found to exhibit p-type characteristics, p–n junction, and current injected luminescence using the FET and two types of LED structures. These results indicate that the annealing process led to an increase in the hole concentration in the Cu:GaN NWs, and thus the Cu atoms could contribute as hole carriers. These results indicate that Cu can be used as a p-type dopant for GaN, and the annealed Cu:GaN nanowire-based homogeneous LED and hybrid OLED devices are promising as advanced optoelectronic materials. Given that the III–V semiconductor system has similar semiconducting properties, Cu may also be investigated as a p-dopant for these III–V semiconductor groups.

Acknowledgements

This work was supported by a grant (No. 2012R1A2A1A03010558), the Pioneer Research Program for Converging Technology (2009-008-1529) and NRF-2011-Global Ph.D. Fellowship Program from the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science, and Technology (MEST), Korea.

Notes and references