

# Vertically Grown p-Type ZnO Nanorod on Ag Thin Film

Jihyun Park, Tae Il Lee, Jae-Min Myoung

**Abstract**—A Silver (Ag) thin film is introduced as a template and doping source for vertically aligned p-type ZnO nanorods. ZnO nanorods were grown using an ammonium hydroxide based hydrothermal process. During the hydrothermal process, the Ag thin film was dissolved to generate Ag ions in the solution. The Ag ions can contribute to doping in the wurzite structure of ZnO and the (111) grain of Ag thin film can be the epitaxial template for the (0001) plane of ZnO. Hence, Ag-doped p-type ZnO nanorods were successfully grown on the substrate, which can be an electrode or semiconductor for the device application. To demonstrate the potentials of this idea, p-n diode was fabricated and its electrical characteristics were demonstrated.

**Keywords**—Ag-doped ZnO nanorods, Hydrothermal process, p-n homo-junction diode, p-type ZnO.

## I. INTRODUCTION

ZnO is a semiconductor material having a wide direct band gap of 3.37 eV and 60 meV of a large exciton binding energy due to the high mechanical and thermal stability [1]–[3]. But p-type doping of ZnO is difficult due to the native defects incorporated in during the growth process [4]. Zinc oxide (ZnO) nanorods (NRs) grown on a substrate by using a hydrothermal process have firstly been introduced [5]. They have been used in electronic devices for examples, light emitting diode [6], ultraviolet sensor [7], gas sensor [8], nanogenerator [9], solar cell [10], and so on. The strategy for the growth of the ZnO NR has been developed and suggested to meet the needs for high performance in a given application [11]. There have been two important issues, which are remained in producing the ZnO NRs on a substrate; controlling growth density and obtaining p-type semiconducting property.

For the device application, ZnO NRs should be grown on a defined electrode pattern. Generally, the ZnO NR does not prefer to densely grow on metallic surface in a conventional hydrothermal process using a hexamethylenediamine, so a seed which is deposited using a ZnO sol–gel solution or a sputtering ZnO thin film has been used to guide the growth of the ZnO NRs on an intended position of a substrate [12]. The ZnO NRs can grow on any substrate on which the seed is coated.

However, the defects in the seed layer cause to increase in the electrical junction resistance, which deteriorate the carrier

transportation of a device from the electrode to the NRs. To solve this problem, we introduced a unique–template, a cobalt hydroxide nanoplate, in our previous work forming electrical contact with an electrode substrate [13].

As an extended concept of the sacrificial epitaxial template, we invented a process to simultaneously achieve p-type doping and growth initiation of the ZnO NRs in a step. The main idea in our process is based on the fact that a thin film template can be dissolved into a solution to be ions and the dissolved ions can contribute to the doping of ZnO NRs. We choose Silver (Ag) as a temporal template and dopant source for p-type ZnO NRs in this work because Ag can basically be dissolved in high pH aqueous solution and be a p-type doping element in a crystal ZnO [14].

This approach may be a simple way to design of material processing and a route for efficient fabrication of ZnO NR–based electronic devices.

## II. EXPERIMENTAL PROCEDURES

Silver (Ag) film was used as the temporal epitaxial template and dopant source for vertically aligned p-type ZnO nanorods (NRs). At first, a 50 nm–thick Ag film was coated onto a substrate using a thermal evaporator. Then, ZnO NRs were grown onto the Ag film under hydrothermal growth conditions. In the typical process, the ZnO NRs were grown by hydrothermal treatment of the Ag film in the presence of 30 mL aqueous solution of 0.2 g of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) mixed with 1 mL of ammonium hydroxide solution at 90°C. The synthesized ZnO NRs were washed with deionized water and dried at 60°C for 6 h. Besides, ZnO NRs with gradient Ag doping concentrations were obtained by changing the growth time in hydrothermal process.

The diode test GZO deposited on slide glass for ZnO nanorods grown on the Ag thin film evaporator is above the aforementioned deposition conditions, ZnO nanorods grown in the same way as the saw. To complete this Homo–junction p–n diode, a toluene solution 10 wt % of poly(methyl methacrylate) (PMMA) was covered over the ZnO NRs with spin coating at 3000 rpm for 40 s. The top side of the ZnO NRs was exposed to the pure oxygen plasma at 100 W with direct current pulse power for 20 s and then 100 nm–thick gold (Au) or aluminum (Al) was deposited on it by thermal evaporator.

The shape, morphology and length of Ag-doped ZnO NRs were investigated using a field-emission scanning electron microscope (SEM, JSM-6701F). Besides, the crystal structure of Ag-doped ZnO NRs was determined by an X-ray diffractometer (XRD, Ultima IV, Rigaku). The O 1s and Zn 3d core level binding energy spectra from the ZnO NRs were

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obtained by using X-ray photoelectron spectroscopy (XPS, K $\alpha$ ).  $I$ - $V$  characteristics of the homo-junction p-n diode, gold or aluminum/undoped ZnO NRs/Ag doped ZnO NRs/p<sup>++</sup> Si was investigated by a semiconductor parameter analyzer (HP-4145B).

### III. RESULTS AND DISCUSSION

The growth of ZnO NRs on our Ag thin film template was composed of four steps. At the first step, a small crystal seed of ZnO NRs is grown on a (111) oriented grain of the polycrystalline Ag film and the film is continuously dissolved at grain boundaries that are highly active energy sites. In the second step, basins are generated near the grain boundaries and the ZnO NR is doped by the dissolved Ag ions while being grown. Another crystal seeds are typically grown on several (111) oriented sites disclosed on the slope of the basins.

Dissolving of Ag film lasts until it is entirely disappeared and the Ag-doped ZnO NRs are further grown as shown in the third step. When the bottom side Ag layer supporting the ZnO NRs is gradually dissolved, the NRs are more and more extending in the descending direction and finally reaching at the substrate. In the final step, we obtain p-n homo-junction of ZnO NRs through further growth of n-type ZnO NRs after depleting Ag ions in the hydrothermal solution.

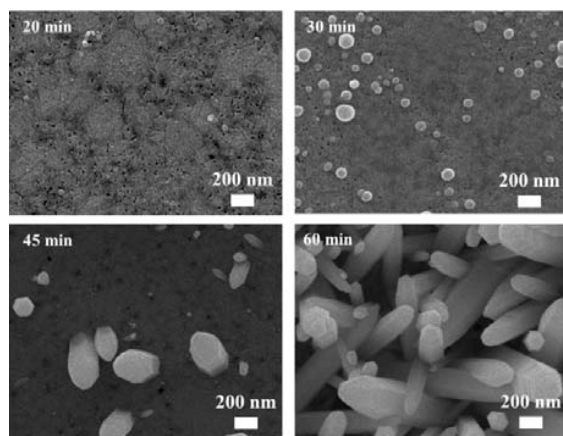


Fig. 1 Top-sectional SEM images of the transitorily epitaxial growth of ZnO NRs on Ag film

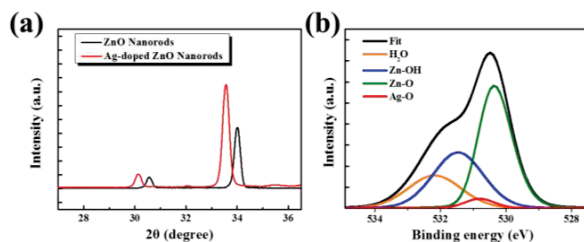


Fig. 2 (a) XRD, (b) XPS characteristics of ZnO NRs grown on Ag film

The growth feature of ZnO NRs by changing reaction time on an Ag film was experimentally determined and the results are shown in Figs. 1 (a)–(d). The descriptions mentioned above paragraph for dissolving Ag and growing ZnO NRs by four

steps were clearly observed and confirmed. At 60 min, the Ag film was perfectly dissolved and ZnO NRs were densely grown on the substrate. A main role of ammonium hydroxide was dissolving in hydrothermal process.

The Ag doping into the ZnO NRs was confirmed by X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS) as shown in Figs. 2 (a) and (b). The (0002) peak of silver-doped ZnO was shifted from the original one; 34.2° for (0002) pure ZnO's the wurzite structure, by silver doping as shown in Fig. 2 (a). Based on the shift, it was confirmed that the inter-planar distance of (0002) increased from 2.587 nm to 2.613 nm by the Ag doping. The increase of c-axis lattice constant is caused by substitution Zn<sup>2+</sup> ions with Ag<sup>3+</sup> ions. By increasing the doping concentration, the partial substitution of Zn with silver caused the overall Ag–O bond length to be shorten which means that the lattice spacing of whole plane is reduced. As a result, the band edge peak of Ag-doped ZnO was shifted to the left.

For the significantly quantitative determinations of the Ag doping, XPS O 1s peak from the Ag-doped ZnO NRs was analysed as shown in Fig. 2 (b). We established O 1s peak by the defective arranging, fitting and coupling of ZnO, Zn–OH bonds, the adsorbed oxygen species and Ag–O, which existence of Ag–O bonding represents that the Ag ions are actually doped into ZnO crystal structure in this work. The quantitative atomic fractions of the bondings were 60.4%, 34.1%, 22.3% and 1.2%, appropriately.

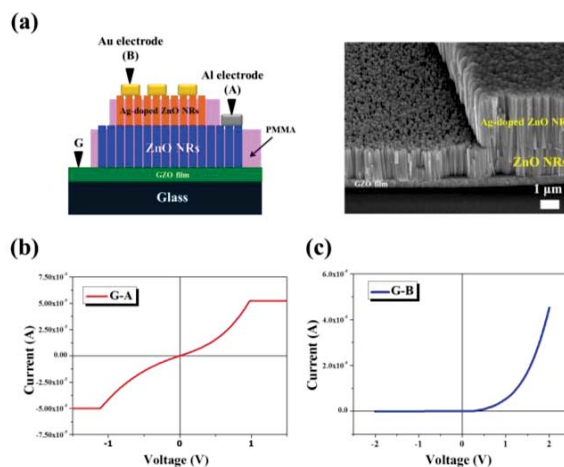


Fig. 3 (a) Schematic diagram with SEM of the p-n homo-junction diode,  $I$ - $V$  characteristics (b) between the ground and the electrode A (c) between the ground and the electrode B

To investigate the electronic property of the Ag-doped ZnO NRs, a device composed of Au/Ag-doped ZnO NR/undoped ZnO NR/gallium doped ZnO (GZO) film was fabricated as shown in Fig. 3 (a). At first, n-type ZnO NRs were grown on the GZO substrate which is a bottom electrode. Then, a 50 nm-thick Ag film was deposited on the n-type ZnO NRs and Ag-doped ZnO NRs were grown for 120 min. Moreover, to check the junction's property between undoped ZnO NR and GZO, Al was deposited on the undoped ZnO NRs grown on GZO thin

film. The cross-section of the device was shown in Fig. 3 (a). The Ag-doped ZnO NRs were triumphantly stacked on the undoped ZnO NRs grown on a GZO film. Ground (G) probe was connected to the GZO film and active probe A and B were connected to the Al and Au electrodes, respectively. In the probe combination of G and A, a typical Ohmic contact  $I$ - $V$  characteristic was observed as shown in Fig. 3 (b). On the other hand, a p-n junction's  $I$ - $V$  characteristic was detected in the G-B probe combination stacked as shown in Fig. 3 (c). In consequence, it was confirmed that the Ag-doped ZnO NRs show p-type semiconducting p-n junction's  $I$ - $V$  properties.

The combination about concentration of Ag ions in the hydrothermal solution decreases with time due to the Ag film which is a temporally dopant source. This result leads the gradient of Ag doping concentration along the growth direction of the ZnO NRs.

The ZnO NR's direction with the Ag doping concentration by the growth time and the atomic % of Ag-O bonding of ZnO NRs was measured at every 30 min from 45 min to 120 min, respectively. Several XPS data were analysed shown in Fig. 4 (a). Then, between 45 min and 60 min, the doping concentration greatly decreased, and this result represents that the 50 nm-thick Ag film was nearly dissolved within 60 min which is consuming Ag source, the 1 at% of Ag was doped into the ZnO NRs.

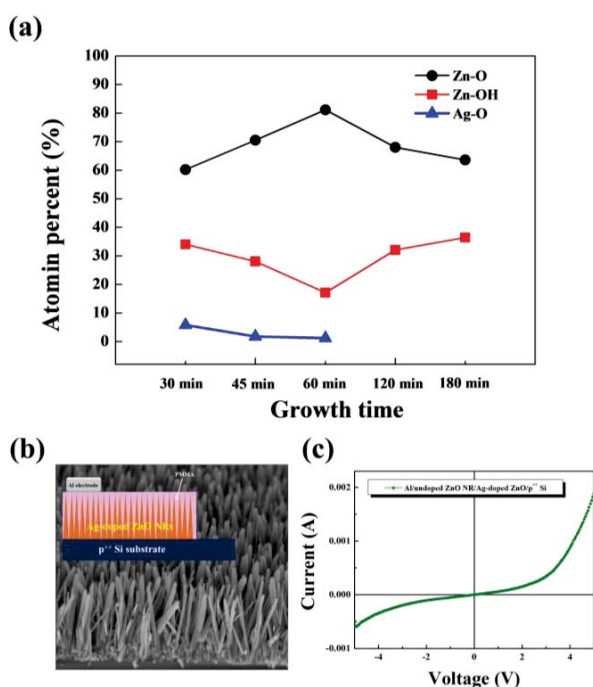


Fig. 4 (a) Atomic percents of Zn-O, O-deficient, Ag-O in wurzite structure of ZnO nanorods with different growth times (b) Schematic diagram with SEM and (c)  $I$ - $V$  characteristics of the p-n homo-junction diode on  $p^{++}$  Si substrate

Based on the data in Fig. 4 (a), we could observe that the Ag film was completely disappeared after 120 min, whereas the ZnO NRs were continuously grown without Ag doping to be n-

type semiconductor. With increasing the growth time, the length of the NRs also increases and is saturated owing to the running low of zinc ions in the solution. As a consequence, p-n homo-junction ZnO NRs was easily formed during this simple process. To considerate the p-n junction, electronic device configurations shown in Figs. 4 (b) were fabricated and their  $I$ - $V$  characteristics were measured. The Ag-doped ZnO NRs were grown on a heavily doped p-type silicon wafer. For the ZnO NRs grown for 180 min, a typical p-n junction's  $I$ - $V$  characteristic was measured in the structure, Al/undoped ZnO NR/Ag-doped ZnO NR/ $p^{++}$  Si substrate. As shown in Fig. 4 (c), a clear p-n junction  $I$ - $V$  characteristic was obtained. Consequently, we can conclude that the diode curves are from the p-n homo-junction of ZnO NRs.

#### IV. CONCLUSIONS

In summary, an Ag thin film is used as an epitaxial template and a dopant source for vertically aligned p-type ZnO nanorods. During the hydrothermal process, the Ag film was dissolved to generate Ag ions in the reaction solution. The Ag ions can be doped in the wurzite structure of ZnO and also the (111) plane of Ag can be the epitaxial template for the (0001) plane of ZnO.

Hence, Ag-doped p-type ZnO NRs were successfully grown on the substrate with n-type semiconductor for electronic device applications. Ag-doping was successfully demonstrated through XRD, XPS. The electronic p-type characteristics of Ag-doped ZnO NRs were demonstrated through the fabrication of p-n diodes with depletion of the Ag and Zn sources.

#### ACKNOWLEDGMENT

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#### REFERENCES

- [1] C. Bekeny, "Origin of the near-band-edge photoluminescence emission in aqueous chemically grown ZnO nanorods" J. Appl. Phys. 100, 104317-104320, 2006.
- [2] H. Zhu, "Ultralow-threshold laser realized in Zinc Oxide," Adv. Mater. 16, 1613-1617, 2009.
- [3] T. Yamada, "Low resistivity Ga-doped ZnO thin films of less than 100 nm thickness prepared by ion plating with direct current arc discharge" Appl. Phys. Lett. 91, 051915, 2007.
- [4] C. Wang, "Fabrication and characteristics of the low-resistive p-type ZnO thin films by DC reactive magnetron sputtering" Mater. Lett. 60, 912-914, 2006.
- [5] S. Baruah, "Hydrothermal growth of ZnO nanostructures," Sci. Technol. Adv. Mater., 10, 013001, 2009.
- [6] X. Fang, "Phosphorus-Doped p-Type ZnO Nanorods and ZnO Nanorod p-n Homo Junction LED Fabricated by Hydrothermal Method", J. Phys. Chem. C., 113, 21208-21212, 2009.
- [7] H. Chang, "A highly sensitive ultraviolet sensor based on a facile in situ solution-grown ZnO nanorod/graphene heterostructure", Nanoscale, 3, 258-264, 2011.
- [8] J.X. Wang, "Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications", Nanotechnology, 17, 4995-4998, 2006.
- [9] Z.L. Wang, "Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays", Science, 312, 242-246, 2006.
- [10] B.-K. Shin, "Bottom-up grown ZnO nanorods for an antireflective moth-eye structure on CuInGaSe2 solar cells", Sol. Energy Mater. Sol. Cells, 95, 2650-2654, 2011.

- [11] Y. Wei, "Enhanced photoelectrochemical water-splitting effect with a bent ZnO nanorod photoanode decorated with Ag nanoparticles", *Nanotechnology*, 23, 235401, 2012.
- [12] S. Xu, "Optimizing and Improving the Growth Quality of ZnO Nanowire Arrays Guided by Statistical Design of Experiments", *ACS Nano*, 3, 1803–1812, 2009.
- [13] T.I. Lee, "Playing with Dimensions: Rational Design for Heteroepitaxial p–n Junctions", *Nano Lett.*, 12, 68–76, 2012.
- [14] J. Fabrega, "Silver Nanoparticle Impact on Bacterial Growth: Effect of pH, Concentration, and Organic Matter", *Environ. Sci. Technol.*, 43, 7285–7290, 2009.