Silver Nanoplate Array for Vertically Aligned P-type ZnO Nanorods

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ABSTRACT

A monolayer of silver nanoplate was introduced as an epitaxial template and doping source for vertically aligned p-type ZnO nanorods. During the hydrothermal process for the growth of ZnO nanorods, the silver nanoplate was dissolved to generate silver ions in the reaction solution. These silver ions can be doped in the wurzite structure of ZnO. And also the (111) plane of silver nanoplate can be the epitaxial template for the (0001) plane of ZnO. Therefore, using this idea, Ag-doped p-type ZnO nanorods were successfully grown on the substrate, which can be an electrode or n-type semiconductor for the device application. The process to synthesize silver nanoplate was optimized to get high yield for changing the number of the monolayer on a substrate modulated nanoplate and doping concentration. To show the capability of this idea, Schottky and p-n diodes were fabricated and flexible organic-inorganic hybrid lighting emitting diode was also fabricated.

***Keywords**: Silver nanoplate, epitaxial template, p-type ZnO nanorods, p-n diodes, hydrothermal method*

BACKGROUND

Vertically aligned zinc oxide (ZnO) nanorods (NRs) grown on a substrate by using a low temperature hydrothermal process have firstly been introduced [1]. They have been applied to electronic devices for examples, light emitting diode [2], ultraviolet sensor [3], gas sensor [4], nanogenerator [5], solar cell [6] and so on. The process for the growth of the ZnO NR has been developed and designed to meet the requirements for good performance in the applications [7]. There are two critical problems, which are remained in growing the ZnO NRs on a substrate; controlling growth density and obtaining p-type semiconducting property.

For the device using vertically aligned ZnO NRs, they should be grown on a defined electrode. The ZnO NR does not prefer to densely grow on typical electrodes in a conventional low-temperature hydrothermal process using a hexamethylenediamine, a seed layer which is deposited using a spin-coating ZnO sol-gel solution or a sputtering ZnO thin film has been used to initiate the growth of the ZnO NRs on an electrode defined on a substrate in applications [8]. The ZnO NRs can grow on any substrate on which the seed is coated. However, the crystallographic defects in the seed layer cause to increase in the electrical junction resistance, which degrades the carrier transportation of a device from the electrode to the NRs. To solve this problem, we introduced a unique epitaxial-template, a cobalt hydroxide nanoplate, in our previous work for the growth of ZnO NRs forming electrical contact with an electrode on a substrate [9].

In aspect of an extended concept of the sacrificial epitaxial-template, we designed a process to simultaneously achieve p-type doping and growth initiation of the ZnO NRs in a single step. The fundamental principle in our process is based on that an epitaxial-template is dissolved and the dissolved ions are then contributed to doping for p-type ZnO NRs. We selected silver as a short-term epitaxial-template and dopant source for vertically aligned p-type ZnO NRs in this work because silver can basically be dissolved in high pH aqueous solution and be a p-type doping element in a crystal ZnO [10].

CURRENT RESULTS

Ag nanoplate was synthesized with $AgNO_3$ in water and aniline (100 μl) mixed polyvinylpyrrolidone(PVP) (MW = 29000) solution in Ethanol. Then the product was prepared in Butanol solution for assembling the monolayer of Ag nanoplate. The monolayer was scooped on a p-type Si (100) substrates (having the resistivity of 0.005 Ωcm). Ag-doped ZnO NRs were synthesized through a hydrothermal process with zinc acetate [$Zn(AC)_2 \cdot 2H_2O$, 0.02 M], NH_3 aqueous solution [NH_4OH, 1 vol%, pH 13.9] at 90 ℃. At this time, the source for the production of ZnO nanorods is the same as the previous concentration. Ga-doped ZnO thin film was formed using a rotatable cylindrical ZnO target including diameter of 45 nm, length of 250 nm, containg Ga of 3 wt %. And they were deposited at 3×10^{-3} mtorr and temperature of 230 ℃ with the Ar flow rate of 30 sccm.

The shape and length of Ag-doped ZnO NRs was determined by using the field-emission scanning electron microscope (FESEM, JSM-6701F). Also, the crystalline characteristics of the Ag-doped ZnO NRs was determined using a x-ray diffractometer (XRD). The optical properties were analyzed at room temperature micro-photoluminescence (μ-PL) spectroscopy using a He-Cd laser (λ = 325 nm). The O 1s and Ag 3d core level binding energy spectra were evaluated using x-ray photoelectron spectroscopy (XPS) to analyze a composition change of the surface. After 100 nm-thick Au and

Al were deposited on top surface using an electron beam evaporation, respectively, the current-voltage (I-V) characteristics of ZnO homo-junction diode were measured using a semiconductor parameter analyzer. Fig.1 shows a camera image of a Ag monolayer on a water surface. The monolayer was formed by dropping method of alcohol solution in our previous work.[9] After scooping the monolayer on a silicon wafer, its microstructure was observed by SEM as shown the Fig. 1(b). There were nanoparticles and nanoplates simultaneously because of various shaped nucleation in the polyol process. Therefore, to control the yield of the nanoplate, we varied the concentration of Ag ion sources.

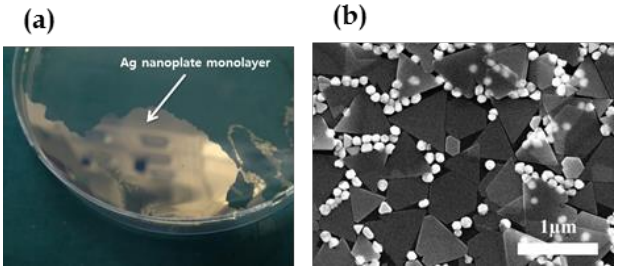

Figure 1. (a) A monolayer of Ag nanoplate on a water surface and (b) a SEM image of a monolayer of Ag nanoplates

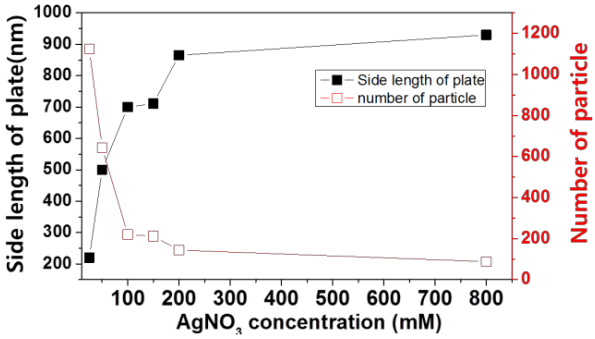

Figure 2. Optimization of the yield of Ag nanoplate

As shown in Fig. 2, the number of nanoparticle and the side length of the nanoplate were determined with the concentration of $AgNO_3$. As the concentration increased, the number of nanoparticle decreased and the size of the nanoplate's side increased. So we chose the 800 mM to synthesize Ag nanoplate for the future use of it as a growth template.

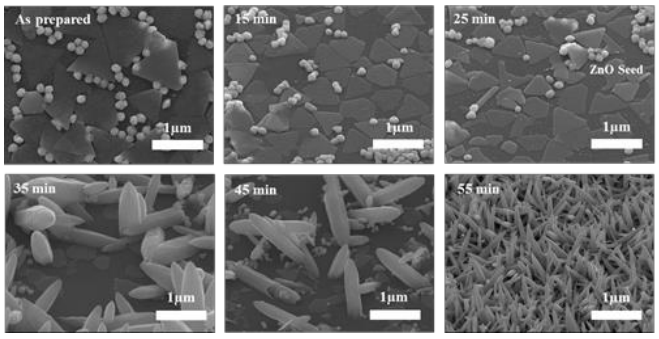

Figure 3. Temporal growth of ZnO NRs on Ag nanoplates

The Ag nanoplate was designed as a doping source and epitaxial template for the growth of ZnO NRs, respectively. Actually this idea is based on that Ag is easily dissolved in ammonia solution and Zn $(OH)_4^{2-}$ can form a crystal structure of wurzite having (0001) direction on the Ag (111) surface as an epitaxial growth.

To observe these procedures, we pictured SEM image during the growth process of ZnO NRs on a Ag nanoplate under the ammonia solution and the results were shown in Fig. 3. Cleary, the Ag nanoplate was dissolved and the ZnO NRs was epitaxially grown on a remained nanoplate. As shown in Fig.3, SEM images of the growing Ag-doped ZnO NRs reflect the temporal growth of the NRs, respectively. At 25 minutes, a small ZnO seed was formed on a dissolving Ag film. After 35 minutes more, the density of the Ag-doped ZnO nanorods are increased up to 55 minutes. After 55 min, Ag nanoplates were fully dissolved and ZnO NRs were densely grown on them. And, to determine how much the Ag ion can dope into the ZnO NRs in our work, we investigated the surface electronic and chemical structure of Ag-doped ZnO NRs using PL and XPS analyses. Fig. 4 shows SEM, XRD, PL and XPS characteristics of Ag-doped ZnO NRs.

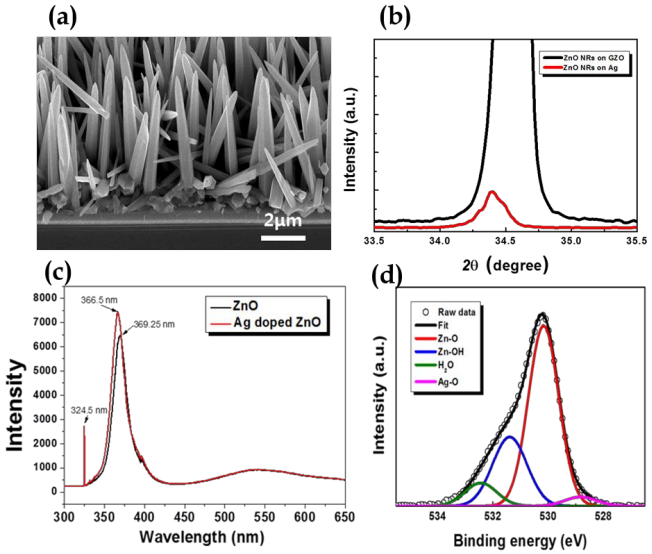

Figure 4. (a) SEM (b) XRD, (c) PL, and (d) XPS characteristics of Ag-doped ZnO NRs

The (0002) peak of Ag-doped ZnO was shifted from the original one, 34.2° for (0002) pure ZnO's the wurzite structure, by Ag doping as shown in Fig 4(b). By the calculation of the lattice parameter based on the shift, the inter-planar distance of (0002) changed from 2.5937 nm to 2.6085 nm. The increase of c-axis lattice constant is caused by substitution Zn^{2+} ions with Ag^{3+} ions. Fig. 4(c) shows PL spectra of ZnO NRs and Ag-doped ZnO NRs. The intensity of peak depends strongly on Ag concentration with the increase of Ag doping concentration into ZnO lattice. By increasing the doping concentration, the average distance between the donor and acceptor was decreased and the PL peak position showed blue shift. Thus, the partial substitution of Zn with Ag 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. Fig. 4 (d) represents XPS analysis results of O 1s peak from the Ag-doped ZnO NRs. We identified XPS O 1s peak by the defective fitting and coupling of ZnO, Zn-OH bonds, the adsorbed oxygen species and Ag-O. The quantitative atomic fractions of the bondings were 50.3%, 22.3%, 26.3% and 1.2%, respectively. Therefore, from this result, the formation of Ag-O in ZnO crystal structure was confirmed.

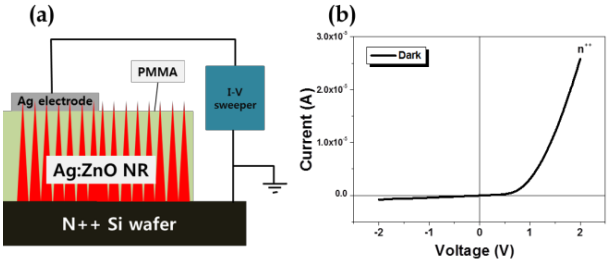

Figure 5. (a) Schottky diode consisting of Ag-doped ZnO NRs, n^{++} Si and (b) I-V characteristics of the Schottky diode

To prove electrically p-type characteristics of Ag-doped ZnO NRs, a Schottky diode was fabricated as shown in Fig. 5(a). Ag nanoplate was scooped on a n^{++} Si wafer and then Ag-doped ZnO NRs were grown. For the Ag deposition, the void between the NRs was filled with a PMMA. Finally, Ag was deposited as a top electrode. Rectifying characteristics in this device configuration were clearly shown in Fig. 5(b).

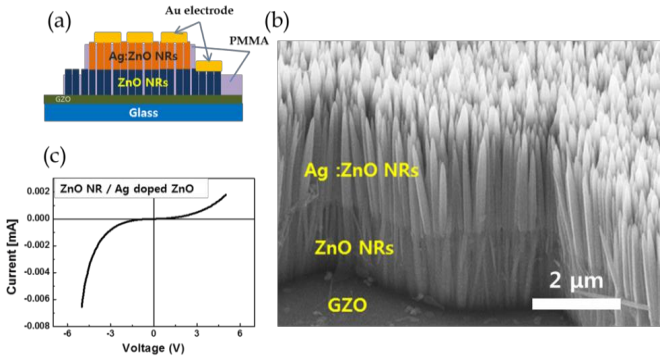

Figure 6. (a) Schematic diagram of p-n homo-junction diode (p-type : Ag-doped ZnO NRs, n-type : ZnO NRs), (b) cross sectional SEM image of the device and (c) I-V characteristics of the p-n diode

Furthermore, p-n diode based on the homo-junction between ZnO NR and Ag-doped ZnO NR was fabricated on a GZO-coated glass substrate as shown in Fig. 6(a). N-type ZnO NR was grown on the GZO which acts as a bottom electrode. GZO can be epitaxial template for the growth of ZnO NRs. The Ag nanoplate was scooped on the n-type ZnO NRs and then Ag-doped ZnO NRs were grown. For the formation of a continuous Au film, the void between the NRs was filled with a PMMA. Finally, Au was deposited as a top electrode. The cross-sectional SEM image of this device configuration was shown in Fig. 6(b). The ZnO NRs and Ag-doped ZnO NRs were successfully stacked on a GZO substrate, and they showed a typical p-n diode's *I-V* characteristics as shown in Fig. 6(c).

Finally, we demonstrated the capability of our Ag-doped ZnO NRs as a p-type material for the organic–inorganic hybrid light emitting diode. We adopted poly (9,9-dioctyl-2,7-fluorene) (PFO) as a n-type light emitting material. On an ITO-coated glass substrate, Ag nanoplate was scooped and then Ag-doped ZnO NRs were grown. PFO was coated using a drop casting on this structure. Finally, LiF and Al electrode were deposited by a thermal evaporator. The full configuration of the device was illustrated in inset of Fig. 7(a). The *I-V* characteristic of the device when it emitted reddish light was demonstrated in Fig. 7(a). The color of light emitting from this device was reddish green. It is thought that the red color comes from Ag-doped ZnO and green color from PFO.

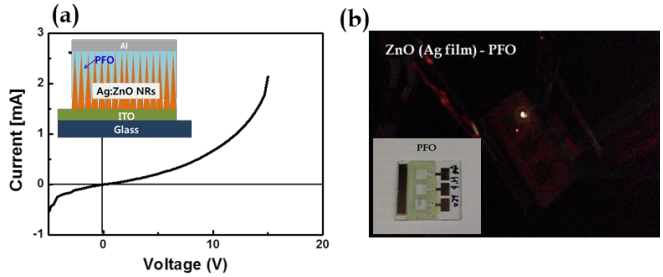

Figure 7. (a) Schematic diagram and I-V characteristics of the organic lighting emitting diode (p-type : Ag-doped ZnO NRs, n-type : PFO) and (b) Lighting image of the diode

In this work, a monolayer of Ag nanoplate is introduced as an epitaxial template and doping source for vertically aligned p-type ZnO nanorods. Ag nanoplates were synthesized through room temperature polyol process and the monolayer consisting of the nanoplates was assembled on the water surface to be scooped on a substrate. For the growth of ZnO nanorods, ammonium hydroxide was used as a mineralizer under the hydrothermal process. During the hydrothermal process, the Ag nanoplate 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 nanoplate can be the epitaxial template for the (0001) plane of ZnO. Therefore, using this idea, Ag-doped p-type ZnO nanorods were successfully grown on the substrate, which can be an electrode or n-type semiconductor for the device application. Experimentally, the process to synthesize Ag nanoplate was optimized to get high yield of Ag nanoplate. The fact of Ag-doping was successfully proved through XRD, XPS, PL analyses and the electrically p-type characteristics of Ag-doped ZnO NRs were demonstrated through the fabrication of a Schottky and p-n diodes. Furthermore, to show the capability of this idea, organic-inorganic hybrid lighting emitting diode was also fabricated and the light emitting property was demonstrated.

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