Supporting Information

Effect of SiO_2 Spacer-Layer Thickness on Localized Surface Plasmon-Enhanced ZnO Nanorod Array LEDs

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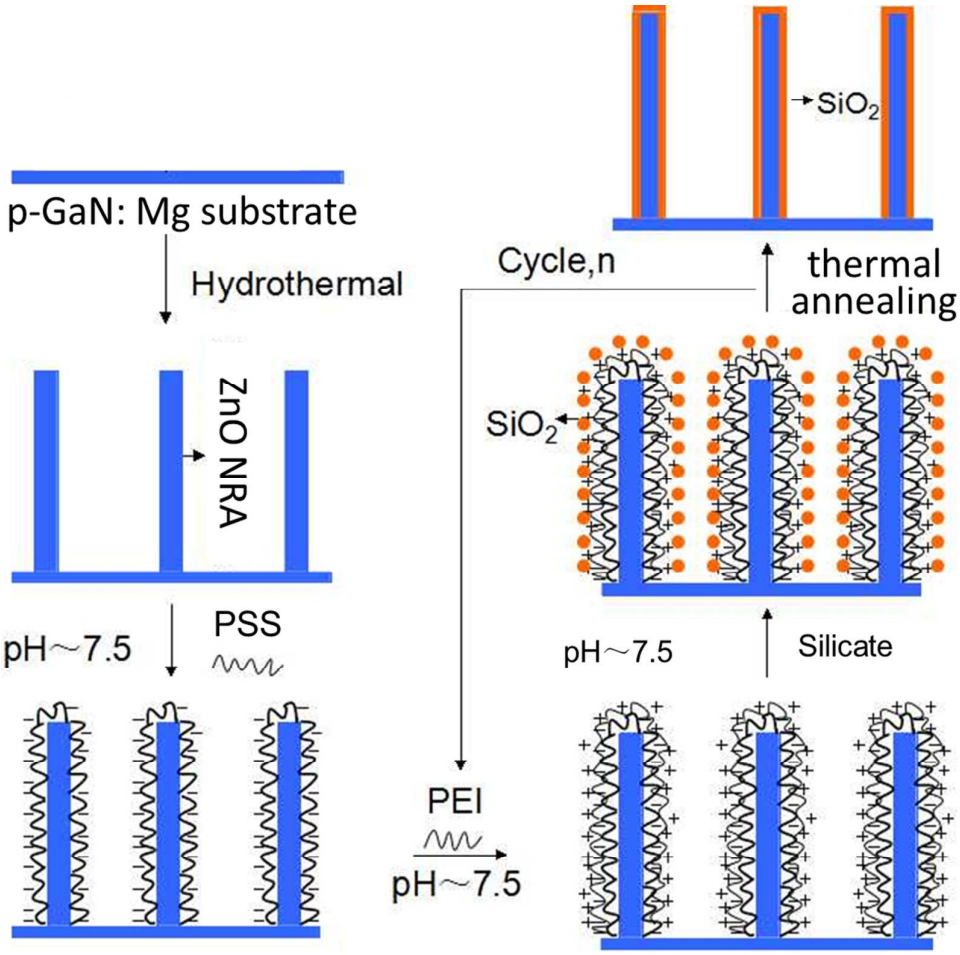

Figure S1. Schematic flow charts for the preparation of ZnO/SiO_2 core/shell NRAs.

The preparation of ZnO/SiO_2 core/shell NRAs on p-GaN: Mg substrates, as shown in Figure S1, included three stages: (1) hydrothermal growth of ZnO NRAs, (2) layer-by-layer (LbL) deposition of silica/polyelectrolyte shell, and (3) air thermal annealing to remove residual high-molecular materials.

For the growth of ZnO NRAs, p-GaN: Mg substrates were submerged in a solution containing zinc acetate dehydrate and hexamethylenetetramine at an equimolar concentration of 20 mM; then the mixed solution was placed in a preheated oven at 95 ℃ for 2.5 h. To remove the residual organics and surface contaminations, the products were annealed in air at 500 ℃ for 30 min.

Next, the SiO_2 shell was prepared on ZnO NRA by an LbL deposition method. Aqueous solutions of poly(sodium p-styrenesulfonate) (PSS, 1 mg/mL),

polyethylenimine (PEI, 1 mg/mL), and sodium silicate (40 mM) were prepared in 0.05 mol/L Tris solution. These solutions were adjusted to pH value of ~7.5 with diluted hydrochloric solution or ammonium solution. The mild pH value prevented the dissolution of ZnO and promoted the polycondensation of silica catalyzed by polyamine, which were critical for the successful LbL deposition of the silica/polyelectrolyte shell. The ZnO NRAs were first dipped into PSS solution for 5 min with intermediate water washing in order to render the surface of nanorods negatively charged. And then they were alternatingly dipped into PEI and sodium silicate solutions for 10 min also with intermediate water washing. Through these procedures, PEI/silica bilayer was conformally prepared on ZnO NRA. The deposition of the PEI/silica bilayer was repeated for several cycles so as to prepare multilayered structure of PEI/silica with different thicknesses. By TEM measurements in our previous work, the average coating rate of SiO_2 shell for LbL deposition is determined to be ~4 nm/cycle.[1,2]

Finally, the multilayer-coated ZnO NRA was annealed at 450 ^{o}C in air for 1 h to remove the polymeric material and form a dense SiO_2 shell on ZnO NRA surface. The LbL deposition method employed here offers some advantages such as uniform coating of entire nanorod and easy controlling of shell thickness, and avoids the shadow effect induced non-uniform sheathing which is commonly seen in some physical deposition methods (e.g. pulsed laser deposition and magnetron sputtering).

REFERENCES

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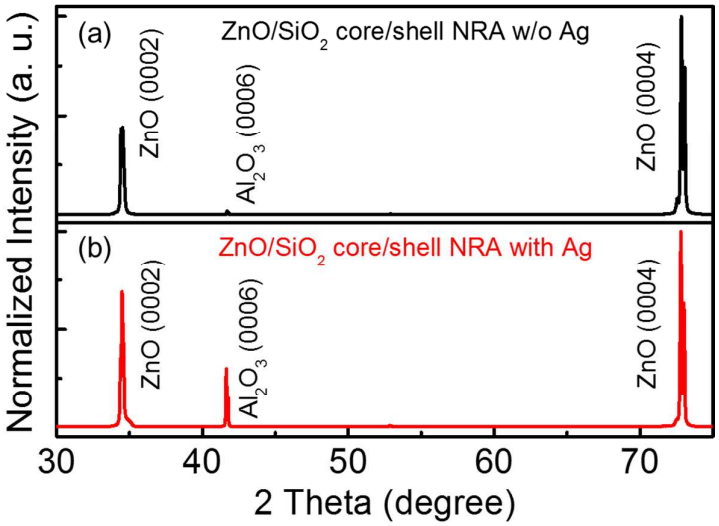

Figure S2. XRD patterns of the ZnO/SiO_2 core/shell NRAs without (a) and with (b) Ag NPs decoration, respectively; the thickness of SiO_2 shell is 12 nm.

Figure S2 shows the XRD patterns of the ZnO/SiO_2 core/shell NRAs with and without Ag NPs decoration. As can be seen, the two patterns exhibit almost the same diffraction features from ZnO NRAs and *c*-sapphire substrates. Due to the amorphous nature of SiO_2 shell and relatively small quantity of Ag NPs, no diffraction peaks of SiO_2 and Ag were observed. The strong and sharp (0002) diffraction peaks confirm that the synthesized ZnO nanorods have good crystallinity and grow along the [0001] direction of hexagonal wurtzite structure. Ag NPs coating dose not degrade the crystallinity of ZnO/SiO_2 core/shell NRAs.