

Performance Improvement of Ultraviolet Sensor of ZnO Nanorod Arrays

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In this letter, large-area, high-quality, evenly distributed, and vertically oriented Na-doped ZnO nanorod arrays (NRAs:Na) are prepared by chemical vapor deposition. The properties of the relevant ultraviolet sensors are studied, indicating that by providing an intrinsic ZnO coating via the hydrothermal method and annealing treatment, the performance of the sensors could be improved dramatically. Photoluminescence analyses show that Na doping suppressed the green emission of NRAs:Na, which is commonly ascribed to the singly V_O located at the surface of the nanorods. For the optimized NRAs:Na sensors with a core-shell structure, the V_O - O_i annihilation mechanism is proposed to interpret the reduction of the persistent photocurrent. © 2013 The Japan Society of Applied Physics

Among the many available nanoscale sensors, photo-sensors are critical for applications as binary switches in imaging techniques and light-wave communications, as well as in future memory storage and optoelectronic circuits.¹⁾ With large surface-to-volume ratios and Debye length comparable to their small sizes, one-dimensional (1D) inorganic nanostructures have already displayed superior sensitivity to light in diverse experiments.²⁻⁴⁾ As wide-band-gap semiconductors, ZnO and related materials have relatively high radiation resistance⁵⁾ and high electron saturation velocity.⁶⁾ These properties make ZnO nanostructures a promising candidate for UV photosensors operating in harsh environments. For an ideal UV photodetector, it should be very sensitive in the UV region with a high signal-to-noise ratio and a high response speed. In previous reports, most of the studies have been focused on the enhancement of responsivity and reset time.^{7,8)} Nevertheless, the performance of ZnO-based UV photosensors is still below expectation, which is one of the largest hurdles that hinder the practical applications of ZnO-based UV photodetectors.

In this letter, perfect NRAs:Na were prepared. By controlling the density of NRAs:Na, nanorods were coated by intrinsic ZnO successfully. The properties of the relevant UV sensors were studied. The performance of the sensors was improved and a possible mechanism was proposed. Owing to the large area, core-shell structure, and mono-crystal features, the sensors have the advantage of large signal intensity of traditional planar ZnO polycrystalline film sensors on the one hand and its transient photoresponsivity is faster than that of ZnO polycrystalline film sensors or even single ZnO nanowire sensors on the other hand.

ZnO nanorod arrays (NRAs) were synthesized by chemical vapor deposition, which was carried out in a quartz boat covered with a quartz plate in a low-pressure horizontal tube furnace. Zn powder (1 g) and sodium tripolyphosphate powder (0 and 0.1 g) grinded together served as source materials. Si(100) wafers, with the 200-nm-thick polycrystalline ZnO films deposited by pulsed laser deposition (PLD), were used as the substrates. The furnace was ramped to 550 °C at a rate of 15 °C/min and held for 30 min under a constant flow of nitrogen (99 sccm) and oxygen (1 sccm). Under the above-mentioned conditions, undoped and Na-doped ZnO NRAs were prepared, named as sample P and sample A, respectively. Then, an undoped ZnO monocrystal layer was coated on Na-doped ZnO nanorods (NRs:Na) by

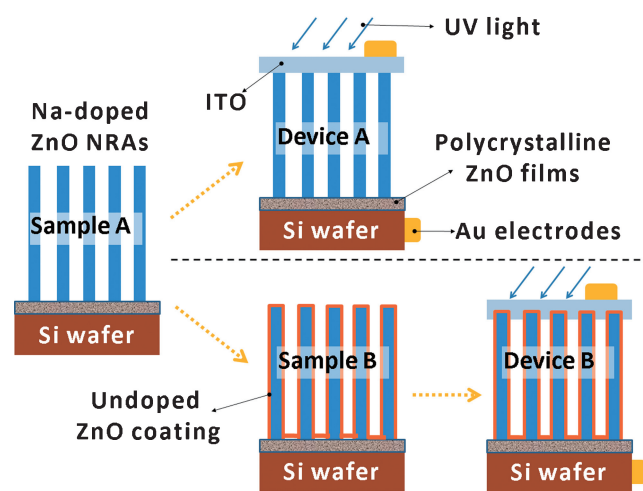


Fig. 1. Schematic diagram of the fabrication of devices A and B.

hydrothermal method under 90 °C for 10 h in an aqueous solution of hexamethylenetetramine ($C_6H_{12}N_4$) and zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$]. Meanwhile, intrinsic ZnO NRAs were also prepared by the hydrothermal method under the same condition. Then, we had sample B and sample H, respectively. Samples A and B were annealed at 500 °C under air condition. Following the procedures shown in Fig. 1, UV sensors were fabricated by depositing indium tin oxide (ITO) and Au electrodes.

The morphology of the as-grown NRAs:Na was characterized by field-emission scanning electron microscopy (FESEM; Hitachi S-4800). The contents of Na were measured by X-ray photoelectron spectroscopy (XPS; Thermo ESCALAB 250) with an Al $K\alpha$ (= 1486.6 eV) source. The microstructures of ZnO NRAs were characterized by transmission electron microscopy (TEM; FEI F20). PL measurements were carried out on an FLS920 fluorescence spectrometer (Edinburgh Instruments). The photoresponse was measured at room temperature using an Agilent E5270B parameter analyzer.

Figures 2(a) and 2(b) show the SEM images of samples A and B, respectively. The sword-shaped NRs:Na were grown vertically from the substrate and most of the rods taper off to a point, as shown in Fig. 2(a) and its inset, which is dramatically different from nominally undoped ZnO nanorods. The morphological changes may be counted as the results of the presence of Na atoms in the ZnO matrix. In

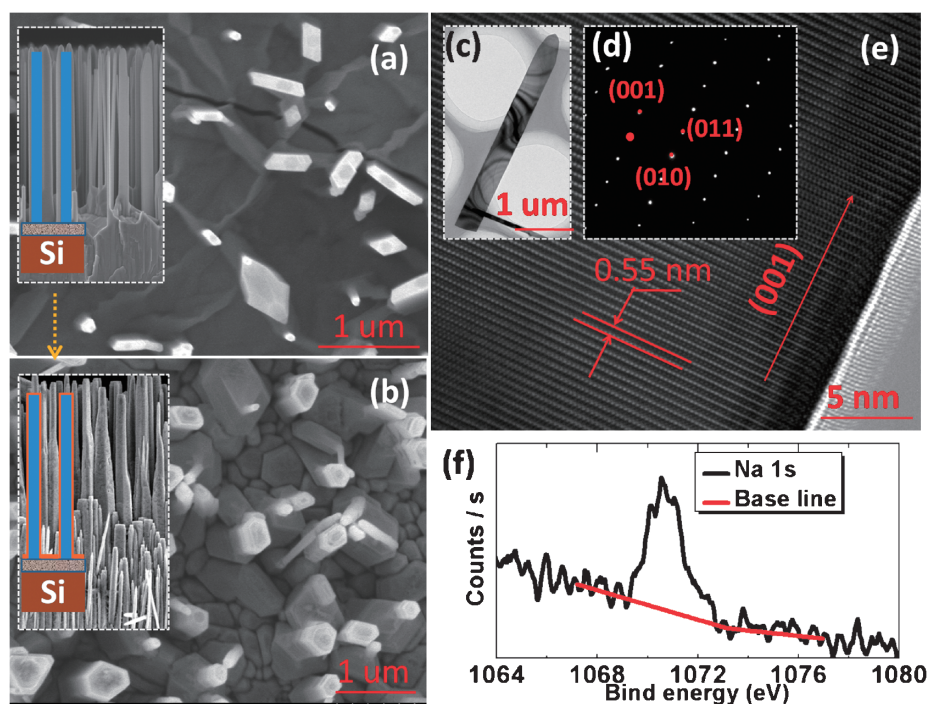


Fig. 2. (a, b) SEM images of (a) samples A and (b) B. (c–e) Low-magnification (c) TEM image, (d) SAED image, and (e) HRTEM of sample A. (f) XPS spectra of Na 1s of sample A.

contrast, when an undoped ZnO layer was coated on the surface of sample A, the tips of the rods were flattened, and the diameters became thicker, as seen in Fig. 2(b) and its inset. Moreover, the substrate was also covered by a newly grown ZnO layer. The low-magnification TEM image [Fig. 2(c)] of sample A also shows clearly sword-shaped nanorods. Figure 2(e) shows the high-resolution TEM images of it, revealing the atomically resolved wurtzite ZnO single crystals with the atomic layer distance of 0.55 nm, which is slightly larger than that in intrinsic ZnO (0.52 nm).⁹ This indicated the lattice expansion due to the expansion of Na, as reported recently.¹⁰ Figure 2(d) shows the corresponding selected area electron diffraction (SAED) pattern of Fig. 2(e), suggesting that the NRs:Na is single crystalline grown along the [002] orientation. Figure 2(f) displays the Na 1s XPS spectra of sample A. The Na 1s peaks are centered at about 1070.7 eV, which were attributed to Na–O bonding within the ZnO phase.¹¹ The Na contents were computed to be 3.36 at. %.

Figure 3 shows room-temperature PL spectra of samples A, B, H, and P. The green emission of sample A is commonly ascribed to the singly V_O located at the surface of the nanorods.^{12,13} We notice that Na doping inhibited the green emission, by comparing the intensity ratio of the UV and green emissions of the black and red line, which would be helpful in suppressing the persistent photocurrent (PPC). However, we know that Na doping would alter the n-type conductivity for the worse, which is a factor against internal optical gain. The yellow emission represents a common feature in samples prepared from aqueous solutions of zinc nitrate hydrate and hexamethylenetetramine.^{14,15} This emission is typically attributed to O_i defects inside the nanorods.^{15,16} We noticed that the coating of sample B enhanced the UV emission and reduced the visible emission further.

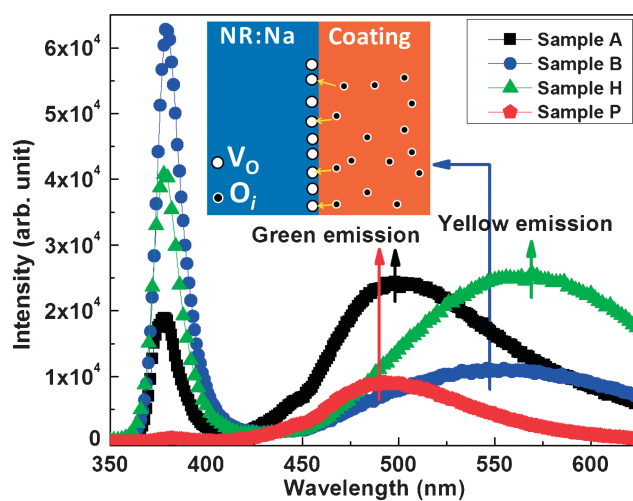


Fig. 3. Room-temperature PL spectra of samples A, B, H, and P. Inset is the schematic of the V_O – O_i annihilation mechanism.

We hold that it might be caused by the annihilation effect of V_O located at the surface of Na-doped nanorods in combination with O_i inside the coating via the annealing treatment, according to the PL analyses, as shown in the inset. Thus, the action of V_O – O_i annihilation and the existence of Na impurity sharply reduced the amount of V_O defects. Thereby, the PPC was suppressed.¹⁷

Figure 4 shows the time-resolved photocurrent of devices A and B in response to the turn-on and turn-off of 0.1 mW/cm² UV illumination ($\lambda = 365$ nm). We noticed that both devices A and B had large photocurrent intensities than the single nanowire devices. The response and decay processes were excellently fitted with a biexponential relaxation equation of the following type,

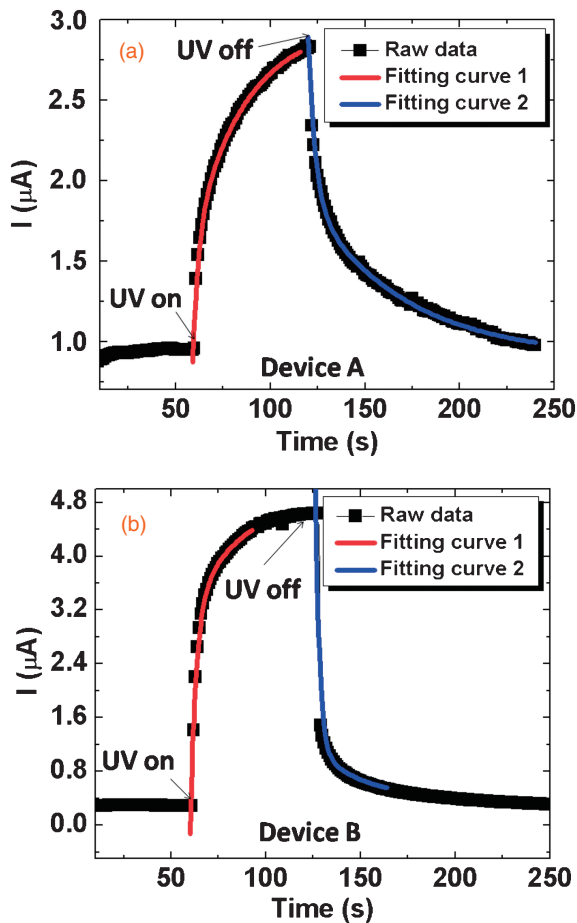


Fig. 4. Time-resolved photocurrent of devices A and B.

$$I = I_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2}, \quad (1)$$

where τ_1 and τ_2 are two relaxation time constants. For device A, $\tau_{1\text{res}} = 3.1$ s, $\tau_{2\text{res}} = 28.3$ s, $\tau_{1\text{dec}} = 3.7$ s, and $\tau_{2\text{dec}} = 50.6$ s, and for device B, $\tau_{1\text{res}} = 2.1$ s, $\tau_{2\text{res}} = 16.4$ s, $\tau_{1\text{dec}} = 1.9$ s, and $\tau_{2\text{dec}} = 26.6$ s (“res” and “dec” denote response and decay, respectively), which demonstrate that the undoped ZnO coating increased the internal optical gain and improved the response speed of the NRs:Na UV sensors, markedly. Considering the coating layer’s passivation effect on the dangling bonds at the interface and the hole-trapping mechanism,¹⁸⁾ the unpaired electrons could mainly be generated by the n-type ZnO coating and then transported into NRs:Na, and finally collected at the anode, as shown schematically in Fig. 5. The much more unpaired electrons produced by the n-type ZnO coating may be the main reason for the improvement of the response speed. The decay time of device B was also reduced. The decay photocurrent dropped by 80% within just 5.1 s. In comparison with this, the decay time of device A, 36.4 s, is much larger. The improvement of decay time could be interpreted by the effect of the V_O – O_i annihilation proposed in the PL analysis section. The fast time constants of our detector are much lower than those of the devices in previous works (about 50 s in Ref. 19 and 7.0 s in Ref. 20). The slow time constants are higher than the fast constants, but they are also lower than in previous works (about 594 s in Ref. 19 and 29.7 s in Ref. 20).

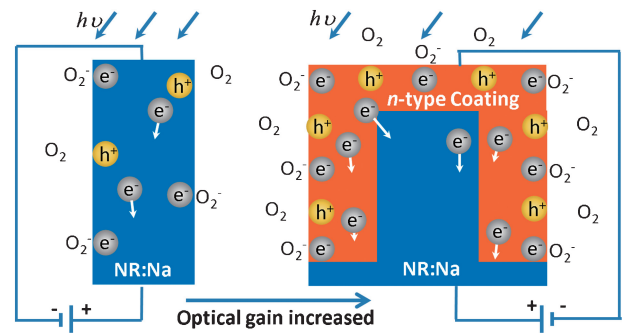


Fig. 5. Schematic of the increase of internal optical gain based on hole-trapping mechanism.

In summary, we prepared large-area, high-quality, densely packed, and vertically oriented NRs:Na by chemical vapor deposition and the performance of the NRs:Na (with V_O defects) UV sensors was improved, by providing an intrinsic ZnO coating (with O_i defects) via the hydrothermal method and annealing treatment. The internal gain was increased by introducing the n-type intrinsic ZnO coating layer. Meanwhile, the PPC was also suppressed by the V_O – O_i annihilation effects, which was proposed here to understand the reduction of PPC for the first time. Generally, our optimized NRs:Na sensors with core-shell structure have advantages of both large signal intensity of ZnO polycrystalline film sensors and faster transient photo-responsivity than that of single ZnO nanowire UV sensors.

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