Supporting Information

Enhanced UV detection performance by using Cu-doped ZnO nanorod array

film

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Characterization

The crystalline structure of the products were analyzed by X-Ray diffraction (XRD) with a Cu K α radiation source (λ =1.54056 Å). The morphology of Cu-doped ZnO NR array film and ZnO NR was characterized by field-emission scanning electron microscopy (FE-SEM Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) was employed to study the elemental composition of the samples. An Edinburgh Instruments FLS-920 fluorescence spectrophotometer with a closed cycle helium cryostat was employed to perform steady state photoluminescence (PL), PL excitation (PLE) and temperature-dependent PL measurements. The electrical properties of the samples were studied by current-voltage (I-V) measurements, which were carried out using Agilent E5270B parameter analyser under ambient conditions. The temporal response of the UV detector was measured by illuminating the devices with a UVA-LED (60 mW cm⁻²).

Seed layer deposition details

Zinc acetate dehydrate $[Zn(CH_3COO)_2 \cdot 2H_2O]$ was dissolved in the mixed solution of ethanolamine and 2-methoxyethanol. The concentrations of both $Zn(CH_3COO)_2 \cdot 2H_2O$ and ethanolamine in the resulting solution are 0.75 M. The coating solution was spin-coated onto glass substrates at 3000 rpm for 30 s. Two layers were spin-coated, and a hot plate heated to 200 °C was used to evaporate the solvent. Finally, the coated glass substrates were annealed at 400 °C for 1 h in order to convert Zinc acetate to ZnO.



Fig. S1 Typical SEM images of as-prepared ZnO seed layer on glass substrate.

The morphological evolution



Fig. S2 SEM images of representative samples. (a) 1.0% Cu doped, (b) 3.5% Cu doped, (c) 5% Cu doped, and (d) cross-secction image of 5% Cu doped samples. The lengths of the scale bars are 200 nm for all images.

Morphological evolution



Scheme S1 Schematic diagram of morphological evolution in the hydrothermal reaction and annealing process.

<u>PL spectrum</u>



Fig. S3 Room temperature PL spectrum of undoped ZnO NR, obtained by excitation by a 325 nm Xe lamp.

<u>UV-vis absorbance spectrum</u>

The UV-vis absorbance spectra of the ZnO NR and Cu-doped ZnO NR array film are shown in Fig. S4. It is shown that the Cu-doped ZnO NR array film displays a red-shifted absorption peak compared with that of un-doped ZnO NR. Cu acting as a deep acceptor may affect energy band structure of ZnO. The inset shows the band gap values ($E_{\rm g}$) of the ZnO NR and Cu-doped ZnO NR array film estimated from $(\alpha hv)^2$ vs. hv, which are derived from its corresponding UV-vis absorbance spectra. The absorption characteristics of the sample obey the model equation: $(\alpha hv)^2 = B(hv - E_g)$, where α is the optical absorption coefficient, h is Planck constant, v is the photon frequency, and B is a constant. The extrapolated value (the straight line to the x-axis) of hv at 0 gives an absorption E_{g} , corresponding to 3.25 eV and 3.22 eV for ZnO NR and Cu-doped ZnO NR array film, respectively. It can be seen that the $E_{\rm g}$ of Cu-doped ZnO NR array film is smaller than that of ZnO NR and this shrinkage trend will be larger with more Cu doping. Furthermore, theoretical study based on density functional theory (DFT) has revealed $E_{\rm g}$ reduction with Cu doping in ZnO due to strong p-d mixing of Cu and O in ZnO:Cu (Appl. Phys. Lett. 2009, 94, 142502), which is consistent with our deduction.



Fig. S4 UV-vis spectra of the ZnO NR and Cu-doped ZnO NR array film. The inset is the corresponding band gap values derived from extrapolating the graph of $(\alpha hv)^2$ vs. $hv - E_g$.