Supplementary Information

Passivation of Surface States in ZnO Nanowire with Thermally Evaporated Copper Phthalocyanine for Hybrid Photodetectors

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Experimental section

Materials growth

The ZnO nanowires (NWs) array were grown in a dual-temperature-zone horizontal tube furnace with the vapor phase transport and condensation (VPTC) method. The high-purity ZnO and graphite powders were mixed with a molar ratio of 1:1, which serves as the Zn precursor. Commercially available ZnO (000-1) single crystal with polished surface was used as the substrate. Firstly, the system was evacuated to a base vacuum of about 5 Pa. Under a 50 sccm (standard cubic centimeter per minute) Ar flow, the substrate and the Zn precursor was rapidly ramped to the growth temperature (650°C) and reaction temperature (1000°C), respectively. Once reaches the reaction temperature, a 40 sccm O_2 flow was introduced into the system, then the growth begins and continues for 20 min. During the growth, the vacuum was maintained typically at about 65 Pa. Once the growth time reaches the target value, the O_2 flow was immediately cut off and the Zn precursor was stopped heating. When the temperature < 800 °C, the substrate was also stopped heating, both

were cooled down naturally to room temperature.

Devices fabrication

The diameters of ZnO NWs range from 100nm to 130 nm, and their lengths are about 15 μm. A piece of flat and pattern-free PDMS stamp was used to transfer NWs onto ~0.7 Ω·cm Si(100) wafer (act as a back gate) coated with 300nm or 600nm of thermal oxide. Electron-beam lithography or photolithography were used to define electrodes pattern with 10 μm finger spacing, and Ti/Au (20 nm/200 nm) contacts were deposited via electron beam evaporation. After lift-off, rapid thermal annealing was carried out at 300-400℃ in N_2 to improve the contacts. Then, shadow mask with 3μm slit opening was used to deposite CuPc (>99.9%) on ZnO NW device channel via thermal evaporation, and the thickness of CuPc film is 20 nm.

Devices characterization and measurement

The morphology of ZnO nanowire devices were characterized by Hitachi S-4800 cold tip field emission scanning electron microscopy (Hitachi Hi-Tech Corp., Tokyo, JP) and Leica DM4000 M (Leica Microsystems Inc., Wetzlar, GER). Absorption spectrum of CuPc film were measured with Lambda 750 UV/Vis/NIR spectrometer (PerkinElmer, Inc., Shelton, CT, U.S.)

The current–voltage (I–V) characteristics of the devices were measured using Keithley 4200-SCS (Keithley Instruments Inc., Cleveland, OH, U.S.A.) and Agilent B1500A-SDA (Agilent Technologies Inc., Santa Clara, CA, U.S.A.). A spectral response for different wavelengths was recorded using a 300W xenon lamp, and a 74125 Oriel Cornerstone 260 1/4 m monochromator with order sorting filters (Newport, Irvine, CA, U.S.) was used. The light intensity of different wavelength was modulated through an aperture and calibrated by using a 70356 UV-enhanced Si photodiode (Newport, Irvine, CA, U.S.). A photocurrent was measured by fixing certain light wavelengths and intensity. All the measurements were carried out at room temperature in ambient condition.

Supplementary results and discussion

Electrical properties of the ZnO NW/CuPc device

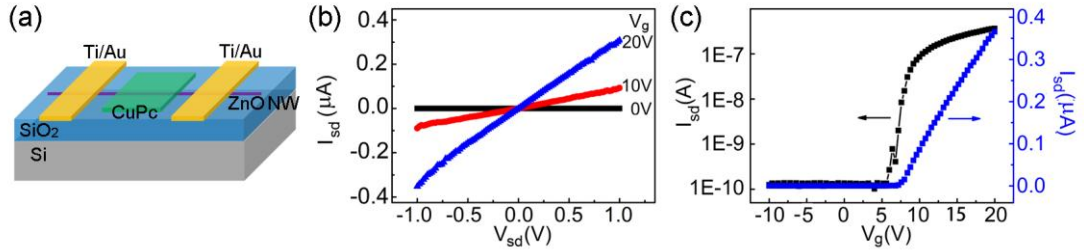

Figure S1. Electrical properties of the ZnO NW/CuPc device characterized via field-effect transistor (FET) transport measurements. (a) Schematic illustration of the ZnO NW/CuPc device. (b) Current (I_{sd}) versus voltage (V_{sd}) characteristics of the ZnO NW/CuPc FET under different gate voltage (V_g) changes. (c) Transconductance of the same device measured at a bias voltage (V_{sd}) of 1V on a logarithmic scale (black) and a linear scale (blue).

To investigate effects of CuPc film, a shadow mask with 3 μm slit was used to deposite CuPc on channel of ZnO NW device, linear characteristics indicates good ohmic contact as before. The electron mobility and concentration in the ZnO NW/CuPc are extracted to be 64.7 $cm^2/V{\cdot}s$ and 1.4×10^{14} cm^{-3}. In addition, dark current decrease significantly, and threshold voltage shifting from -5V to 5V.

Calculation of the ZnO NW depletion layer thickness

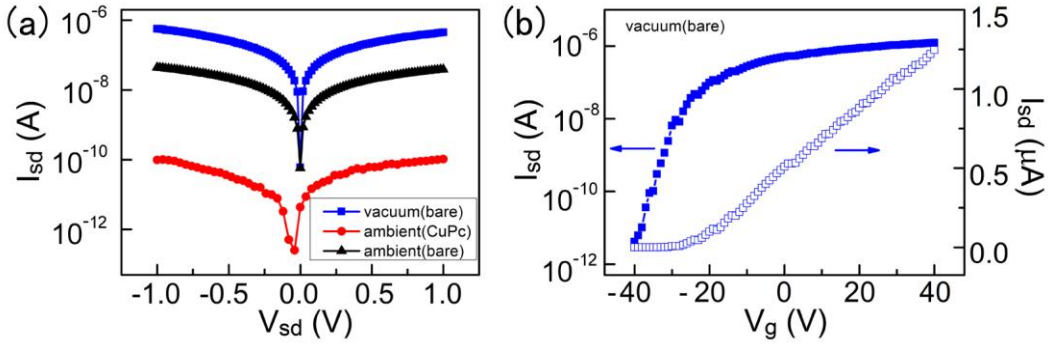

Figure S2. Electrical properties of the NW device characterized via field-effect transistor (FET) transport measurements. (a) Current (I_{sd}) versus voltage (V_{sd})

characteristics of the ZnO NW in vacuum (blue) and in ambient (black), ZnO NW/CuPc device in ambient (red) on a logarithmic. (c) Transconductance of the ZnO NW device measured at a bias voltage (V_{sd}) of 1V on a logarithmic scale and a linear scale in vacuum.

To estimate depletion layer thickness of ZnO NW quantitatively, we further investigate the device transport in vacuum and compare with the data in ambient. From $V_{sd}/I_{sd}=\rho l/\pi(d_c/2)^2$, where ρ is the resistivity of nanowire, l is the device channel length and d_c is conducting channel thickness, diameter of NW conducting channel can be extracted from I-V curves if we assume uniform resistivity across the nanowire conducting channel. Then, depletion layer thickness is extracted to be $(d_{NW}-d_c)/2$, where d_{NW} is the physical diameter of the nanowire. Suppose O_2/H_2O molecules completely desorb from the ZnO nanowire after UV illumination for a long time in vacuum, the entire nanowire is the conduction channel in this case (i.e. $d_{NW} = d_c$). According to I-V curves of ZnO nanowire FET device in vacuum (Fig. S2) and in ambient (Fig. 1 and Fig. S1), the surface depletion layer width of ZnO nanowire device and ZnO nanowire/CuPc device in ambient are estimated to be 40.1 nm and 63.7 nm, respectively.

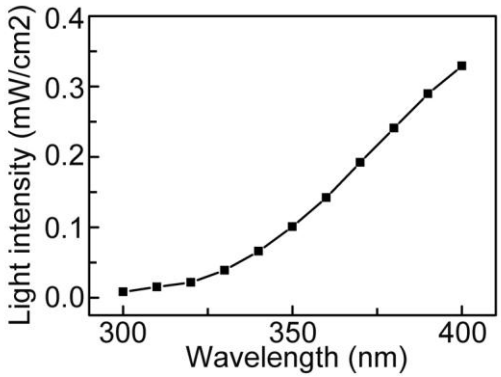

Figure S3. Incident light intensity of the light source from 300nm to 400nm, the circular spot size is 0.25 cm in diamater.

Fitting functions and parameters for the device photoresponse

The rise curves are fitted by a double-exponential function as seen in equation (1):

$$I = I_d + I_{s_1}[1 - e^{-(t/\tau_1)}] + I_{s_2}[1 - e^{-(t/\tau_2)}] \quad \ldots\ldots(1)$$

where I_d is dark current, I_{S1} and I_{S2} reflect photocurrent weight factor of two rise time constants τ_1 andτ_2. The average decay time is defined as:

$$\tau_{avg} = \tau_1 \times \frac{I_{s_1}}{I_{s_1} + I_{s_2}} + \tau_2 \times \frac{I_{s_2}}{I_{s_1} + I_{s_2}} \quad \ldots\ldots(2)$$

The decay dynamics can also be described by a double-exponential function as seen in equation (3):

$$I = I_d + I_{s_1} e^{-(t/\tau_1)} + I_{s_2} e^{-(t/\tau_2)} \quad \ldots\ldots(3)$$

where I_d is dark current, I_{S1} and I_{S2} reflect photocurrent weight factor of two decay time constants τ_1 andτ_2.

Table S1 Time constants of rise process

device	rise				
	τ_1(s)	$I_{S1}/I_{S1}+I_{S2}$	τ_2(s)	$I_{S2}/I_{S1}+I_{S2}$	τ_{avg} (s)
NC	1.6	60.7%	32.9	39.3%	13.9
PC	1.6	70.4%	16.0	29.6%	5.9
FC	0.58	80.9%	10.0	19.1%	2.4

Table S2 Time constants of decay process

device	decay				
	τ_1(s)	$I_{S1}/I_{S1}+I_{S2}$	τ_2(s)	$I_{S2}/I_{S1}+I_{S2}$	τ_{avg} (s)
NC	59.1	47.3%	703	52.7%	398
PC	18.7	87.0%	103	13.0%	32.0
FC	2.5	97.8%	26.6	2.2%	3.0