Supplementary materials

Piezoelectric nanogenerator using p-type ZnO nanowire arrays

Ming-Pei Lu1, Jinhui Song2, Ming-Yen Lu2,3, Min-Teng Chen3, Yifan Gao2,
Lih-Juann Chen3, and Zhong Lin Wang2, *

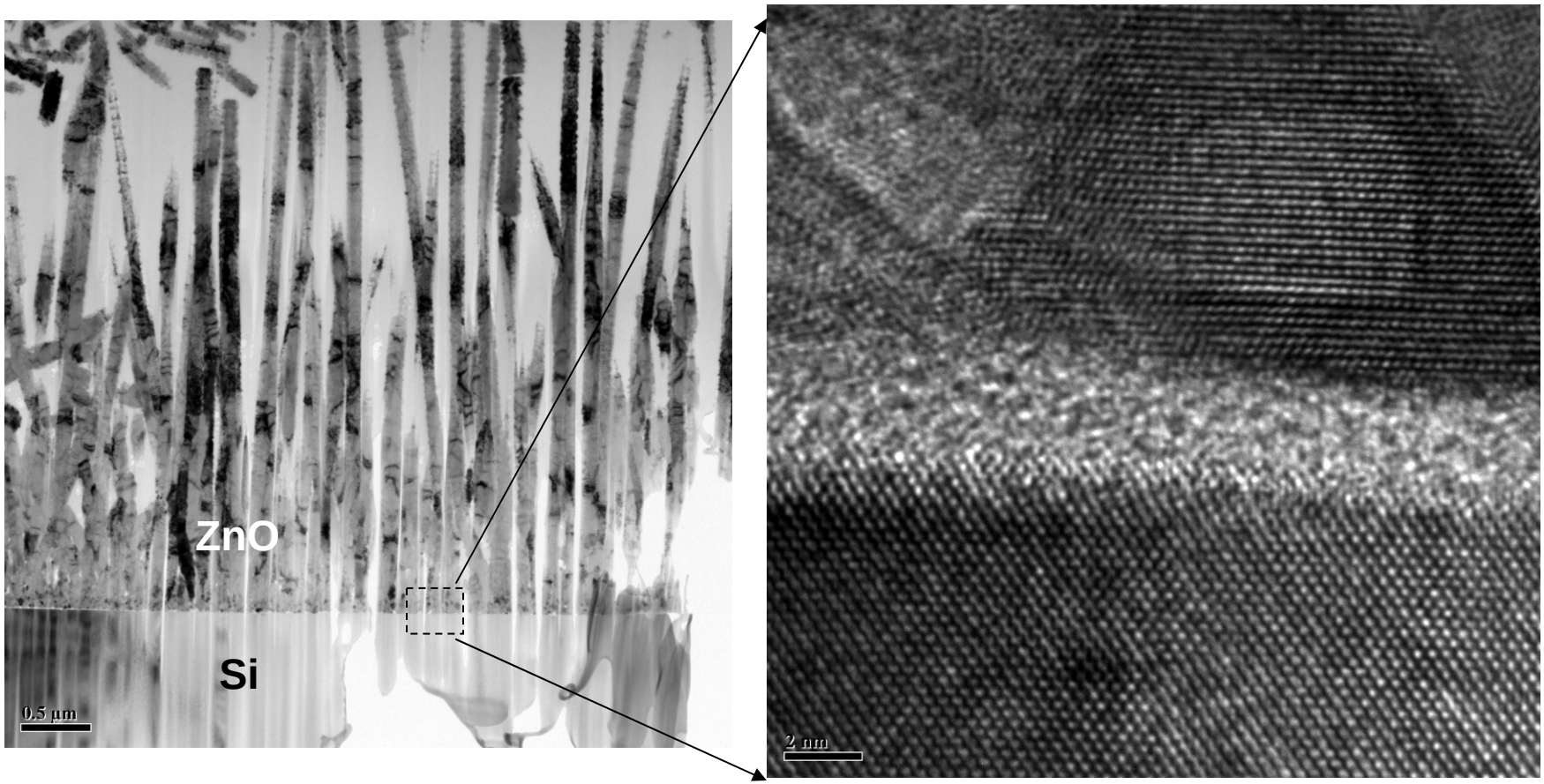

Fig. S1: TEM of the interface between the p-type NWs and the Si(001) substrate. Although a thin oxide layer is present at the interface, the orientation relationship between the two preserves:

$$\mathrm{Si(001)\ ||\ ZnO\ (0001),\ Si[1\bar{1}2]\ ||\ ZnO[01\bar{1}0],\ Si[110]\ ||\ ZnO[2\bar{1}\bar{1}0]}$$

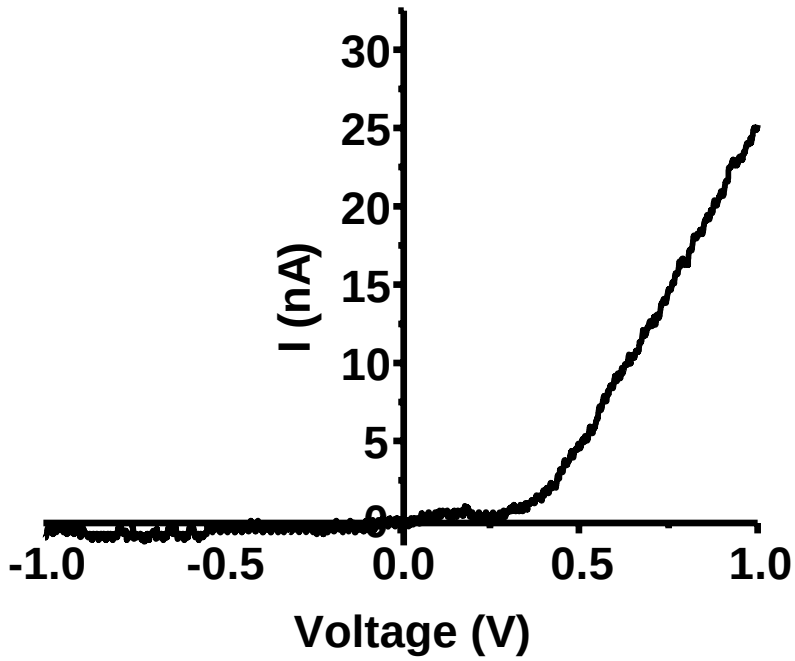

Fig. S1: Transport measuement between the AFM tip Si/Pt and the p-type NWs, showing the presence of a Schottky barrier.

Calculation of the piezoelectric potential distribution in a p-type nanowire with finite doping

In order to calculate the piezoelectric potential in a bent semiconductive nanowire, we only need to consider the direct piezoelectric effect:

$$\begin{cases} \sigma_p = c_{pq}\varepsilon_q \\ D_i = e_{iq}\varepsilon_q + \kappa_{ik}E_k \end{cases} \quad (1)$$

where σ is the stress tensor, ε is the strain, $\vec{E}$ is the electric field, and $\vec{D}$ is the electric displacement. κ_{ik} is the dielectric constant, e_{kp} is the piezoelectric constant, and c_{pq} is the mechanical stiffness tensor. Substituting the second equation into the Gauss's law, we get the equation for the electric field:

$$\nabla \cdot \vec{D} = \frac{\partial}{\partial x_i}(e_{iq}\varepsilon_q + \kappa_{ik}E_k) = \rho_e^{(b)} = ep - en + eN_D^+ - eN_A^- \quad (2)$$

where p is the hole concentration in the valance band, n is the electron concentration in the conduction band, N_D^+ is the ionized donor concentration, and N_A^- is the ionized acceptor concentration. For p-type ZnO NWs, we have $n = N_D^+ = 0$. By introducing

$$\vec{D}^R = e_{kq}\varepsilon_q \hat{i}_k \quad (3.1)$$

as the polarization due to piezoelectricity and

$$\rho^R = -\nabla \cdot \vec{D}^R \quad (3.2)$$

as the corresponding piezoelectric charge, equation 2 can be rewritten for the electric potential φ:

$$\kappa_{ik}\frac{\partial^2}{\partial x_i \partial x_k}\varphi = -(\rho^R + ep - eN_A^-) \quad (4)$$

The surface charge due to piezoelectricity is calculated by $\Sigma^R = -\vec{n} \cdot \Delta\vec{D}^R$, where $\Delta\vec{D}^R$ is the change of $\vec{D}^R$ astride the material surface and $\vec{n}$ is the normal to the surface. For simplicity, we have ignored the surface charges introduced by polar surfaces of ZnO.

The redistribution of holes under thermal equilibrium is given by the Fermi-Dirac statistics:

$$p = N_v F_{1/2}(\eta), \quad \eta = \frac{E_v(\vec{x}) - E_F}{kT} \quad (5.1)$$

$$N_v = 2\left(\frac{2\pi m_h kT}{h^2}\right)^{\frac{3}{2}} \quad (5.2)$$

where the valance band edge $E_v(\vec{x})$ is a function of space coordinates. N_v, the effective state density of valance band, is determined by the effective mass of holes $m_h = (m_{h,A}^{3/2} + m_{h,B}^{3/2})^{2/3}$ and the temperature T. Here $m_{h,A} = m_{h,B} = 0.59m_e$ [1], $c\Gamma_7$ band is deep beneath and not considered. Although the fine structure of the valence band at the Γ point is not completely unified in the literature [1], the ignorance of the $c\Gamma_7$ band will not affect our qualitative discussion.

Due to the large strain, the deformation potential might be important. To be specific, the band edge shift ΔE_v is the sum of the electro-static energy part and the deformation potential part:

$$E_v - E_{v_0} = \Delta E_v = -e\varphi + \Delta E_v^{deform} = -e\varphi + a_v \frac{\Delta V}{V} \qquad (6)$$

where E_{v_0} is the valance band edge of a free-standing un-deformed semiconductor material; $\Delta E_v^{deform} = a_v \Delta V / V$ is the band edge shift due to the deformation potential, which is proportional to the relative volume change $\Delta V / V$, and a_v is the deformation potential constant. Finally, the activation process of the acceptors is given by:

$$N_A^+ = N_A \frac{1}{1 + g\exp(\frac{E_A - E_F}{kT})} = N_A \frac{1}{1 + g\exp(\eta + \frac{\Delta E_A}{kT})} \qquad (7)$$

where $E_A(\vec{x}) = E_v(\vec{x}) + \Delta E_A$ is the position-dependent acceptor energy level. The constant ΔE_A is the activation energy of the acceptors. N_A is the concentration of the acceptors. *g=4* is assumed degeneracy factor for acceptor levels, which is good enough for qualitatively understanding the phenomenon.

The parameters used are: Young's modulus $E = 129.0$ GPa and Poisson ratio $\nu = 0.349$ [2]; relative dielectric constants $\kappa_{\perp}^r = 7.77$, $\kappa_{\parallel}^r = 8.91$ [2], and the piezoelectric constants $e_{31} = -0.51 C/m^2$, $e_{33} = 1.22 C/m^2$, $e_{15} = -0.45 C/m^2$ [2]. Effective mass is $m_{h,A} = m_{h,B} = 0.59m_e$ [1], and deformation potential constant is $a_v = -2.13eV$ [3]. The activation energy of acceptors is: $\Delta E_A = 130meV$ [1]. The nanowire is geometrically approximated as a cylinder, with radius *a* = 25 nm, and length *l* = 600 nm. The external force is $\vec{f} = f_y \vec{e}_y$, f_y = 80nN, uniformly applied at the top surface of the nanowire in a direction $\vec{e}_y$ perpendicular to the nanowire axis.

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3. Shan, W.; Walukiewicz, W.; Ager, J. W.; Yu, K. M.; Zhang, Y.; Mao, S. S.; Kling, R.; Kirchner, C.; Waag, A. *Appl Phys Lett* **2005,** 86, (15), 153117.