Non-linear nanoscale piezoresponse of single ZnO nanowires affected by piezotronic effect

Helena Lozano\textsuperscript{1,4,5}, Gustau Catalán\textsuperscript{2,3}, Jaume Esteve\textsuperscript{1}, Neus Domingo\textsuperscript{2,4,5} and Gonzalo Murillo\textsuperscript{1,4}

\textsuperscript{1} Instituto de Microelec\textsuperscript{t}tronica de Barcelona, Bellaterra 08193, Spain
\textsuperscript{2} Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Spain
\textsuperscript{3} ICREA – Instituci\textsuperscript{on} Catalana de Recerca i Estudis Avan\textsuperscript{c}ats, 08010 Barcelona, Spain

E-mail: neus.domingo@icn2.cat and gonzalo.murillo@csic.es

Received 16 July 2020, revised 31 August 2020
Accepted for publication 17 September 2020
Published 14 October 2020

Abstract

Zinc oxide (ZnO) nanowires (NWs) as semiconductor piezoelectric nanostructures have emerged as material of interest for applications in energy harvesting, photonics, sensing, biomedical science, actuators or spintronics. The expression for the piezoelectric properties in semiconductor materials is concealed by the screening effect of the available carriers and the piezotronic effect, leading to complex nanoscale piezoresponse signals. Here, we have developed a metal–semiconductor–metal model to simulate the piezoresponse of single ZnO NWs, demonstrating that the apparent non-linearity in the piezoelectric coefficient arises from the asymmetry created by the forward and reversed biased Schottky barriers at the semiconductor–metal junctions. By directly measuring the experimental $I$–$V$ characteristics of ZnO NWs with conductive atomic force microscope together with the piezoelectric vertical coefficient by piezoresponse force microscopy, and comparing them with the numerical calculations for our model, effective piezoelectric coefficients in the range $d_{33}^{\text{eff}} \sim 8.6 \text{ pm V}^{-1}$–$12.3 \text{ pm V}^{-1}$ have been extracted for ZnO NWs. We have further demonstrated via simulations the dependence between the effective piezoelectric coefficient $d_{33}^{\text{eff}}$ and the geometry and physical dimensions of the NW (radius to length ratio), revealing that the higher $d_{33}^{\text{eff}}$ is obtained for thin and long NWs due to the tensor nature proportionality between electric fields and deformation in NW geometries. Moreover, the non-linearity of the piezoresponse also leads to multiharmonic electromechanical response observed at the second and higher harmonics that indeed is not restricted to piezoelectric semiconductor materials but can be generalized to any type of asymmetric voltage drops on a piezoelectric structure as well as leaky wide-bandgap semiconductor ferroelectrics.

Supplementary material for this article is available online

Keywords: PFM, ZnO, nanowire, piezotronics, C-AFM, nanogenerator, piezoresponse

(Some figures may appear in colour only in the online journal)
1. Introduction

Scavenging of ambient mechanical energy for autonomous applications is becoming a hot research topic (Harb 2011, Duque et al 2019, Torah et al 2018, Kim et al 2018a). Energy harvesting relies on a transduction force that converts the ambient mechanical energy into electricity. This mechanical energy can have different forms such as vibrations, random motions, noise, etc. The most common transduction methods are: electrostatic, electromagnetic, triboelectric and piezoelectric. A piezoelectric material has the peculiarity of creating an inherent electric field when strained (direct piezoelectric effect). Some examples of well-known piezoelectric materials are AlN, PVF, PZT, ZnO or quartz (Lee et al 2012, Choi et al 2017, Kim et al 2018b). Among those, zinc oxide (ZnO) has a non-central symmetric wurtzite crystal structure and a hexagonal unit cell. This structure has polar surfaces that can be described as a number of alternating planes composed of tetrahedrally coordinated $O^{2-}$ and $Zn^{2+}$ ions, stacked alternatively along the c-axis as is shown in figure S1 (available online at stacks.iop.org/NANO/32/025202/mmedia). The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (0001)-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis as well as a divergence in surface energy. ZnO has become very popular in material science over the last few years because of its wide variety of nanostructures and its dual property of being both a semiconductor and piezoelectric material (Özgür et al 2005, Janotti and Van De Walle 2009): it has a wide band gap ($\sim$3.37 eV), large exciton binding energy ($\sim$60 mV), it is relatively biosafe and biocompatible (Stitz et al 2016) and it exhibits an abundant configuration of nanostructures as nanowires (NWs) (Espinosa et al 2012), nanobelts, nanosheets or nanorings (Wang 2009). Thanks to these properties, this material has numerous potential applications in energy harvesting, photonics, sensing, biomedical science, actuators, spintronics and optoelectronics (Yang et al 2002, 2012, Özgür et al 2005, Wang et al 2010, Wang 2012, Murillo et al 2017a, Kang et al 2019). One of the most useful nanostructures that can be utilized to generate energy is the NW (Xu et al 2010, Espinosa et al 2012). These nanostructures are commonly referred to as nanogenerators, which have the advantage of being more flexible and less sensitive to fracture than generators based on thin films. It was already demonstrated that a single ZnO NW can generate a piezoelectric potential along it when strained. The generated energy output by one NW in one discharge event is about 0.05 $\mu$J, and the output voltage on the load is around 8 mV, for a 5 nN force applied by an atomic force microscopy (AFM) tip (Wang and Song 2006; Riaz et al 2011).

One of the main hindrances in the expression for the piezoelectric properties in semiconductor materials is the screening effect of the available carriers, concealing any piezoelectric voltage (Morozovska et al 2007). The entanglement between conductivity and piezoelectricity conceals the determination of net piezoelectric coefficients as measured by electromechanical sensing techniques such as piezoresponse force microscopy (PFM), which on the other hand, is an ideal tool since it is able to measure this piezoelectric coefficient in a single nanostructure. In this work, we have developed a general model to describe nanoscale piezoresponse in piezoelectric semiconductors that deconvolutes the experimental effective piezoelectric response from the semiconductor screening effect. Moreover, we show how this entanglement leads to experimental non-linear piezoresponse signals and we demonstrate the emergence of multifrequency nanoscale electromechanical responses in the presence of Schottky barriers.

Due to the dual nature of ZnO, acting as semiconductor and piezoelectric material, in 2007, prof. ZL Wang introduced the fundamental principle of piezotronics (Zhong and Wang 2007, Wang 2010, 2012, Wang et al 2010). Piezotronic effect is based on the influence of the piezoelectric potential with the electronic bands in the semiconductor, creating electronic components that can be triggered with strain. Also, the opposite effect can be found, where an external voltage applied to the material can affect its electronic bands and therefore affecting the generated strain due to the piezoelectric effect. Here, we demonstrate that these dual properties of a ZnO nanostructure have to be taken into account because they directly affect the piezoresponse at the nanoscale measured by PFM.

2. Methods

ZnO can be grown by different bottom-up approaches such as vapor–liquid–solid, chemical vapor deposition or hydrothermal method. However, a crystalline substrate with a similar lattice constant is the best choice to obtain aligned and high-quality NWs (Vayssieres 2003, Jin et al 2005, Kwon et al 2012). Here, we use a hydrothermal method which is one of the most powerful low-cost, low-temperature and simple approaches to grow c-axis-aligned NWs. This method is based on an aqueous solution chemical reaction at low temperature ($<$80 $^\circ$C) directly on the silicon substrate covered by a seed layer (Murillo et al 2016, 2017b). The height and diameter of the NWs is determined by the growth time, temperature and concentration. For the ZnO NW growth, a silicon wafer with a seed layer of evaporated gold with a chromium adhesion layer (50 nm Au/20 nm Cr) is commonly used to favor the nucleation. Every chip is then placed floating face down inside a wide-mouth jar containing the aqueous solution consisting of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine [1:1] 5 mM each purchased from Sigma-Aldrich. Subsequently, the pot is closed and introduced in an oven at 70 $^\circ$C for 16 h. A scheme of this process is shown in figure S2 and a more detailed description is presented in the supplementary information. Figure 1 shows scanning electron microscopy (SEM) and AFM images of the ZnO NWs. As can be seen, the gold activation method ensures a well orientation of ZnO NWs (Vayssieres 2007). The entanglement between conductivity and piezoelectricity conceals the determination of net piezoelectric coefficients as measured by electromechanical sensing techniques such as piezoresponse force microscopy (PFM), which on the other hand, is an ideal tool since...
and it is based on the converse piezoelectric effect of the material under test. A conductive AFM probe tip is used as a top electrode to simultaneously measure the mechanical response when an electrical voltage is being applied to the sample surface. Then, in response to the electrical stimulus, the sample locally expands or contracts linearly according to the material piezoelectric coefficient. Usually an ac voltage ($V_{ac}$) is used to excite the sample, because it allows the use of a lock-in amplifier to read-out the tiny motion generated by the converse piezoelectric effect. In this case, if $V_{ac}$ is the voltage applied by the tip and $d_{33}$ is the piezoelectric coefficient in the z-axes, the amplitude of the vibration as measured by an AFM tip in the vertical direction is described by equation (1):

$$A_{PFM} = d_{33} V_{ac}$$

3. Results and discussion

Following this relationship, it is possible to determine the effective $d_{33_{eff}}$ coefficient of a piezoelectric dielectric material by measuring the linear change in PFM amplitude as a function of the applied $V_{ac}$ voltage magnitude. Most of the materials that exhibit piezoelectricity are insulators for which the applied voltage between the AFM probe tip and sample substrate is fixed and well known. However, still quantification of piezoelectric coefficients by PFM is still a controversial issue due to several factors such as (i) the real distribution of electric field through the sample, (ii) undesired crosstalk between the tip and the sample due to electrostatic coupling, (iii) instrumental artifacts and (iv) possible flexoelectric effects due to the presence of strain and electric field gradients around the AFM tip (Abdollahi et al 2019). In fact, piezoelectricity can also be found in semiconductor crystals with non-central symmetry, especially those who have a wurtzite structure such as ZnO. One of the major issues when measuring piezoelectricity in semiconductors is that for an adequate charge separation generated by piezoelectricity during an applied stress, free carriers must not be allowed to travel through the semiconductor (in our case ZnO NW), otherwise the generated electric field across the semiconductor will be partly neutralized. On another hand, semiconductors under a voltage drop can indeed carry a current depending on the doping and the electrical connections or junctions. For the case of piezoelectric semiconductors, when a voltage is applied, current can flow through the NW reducing the effective electric field inside the nanostructure. Electronic characteristics of semiconductor materials such as $I–V$ curves can be measured by conductive AFM (C-AFM) thanks to the operational amplifier located in the tip holder that is used to measure the small currents passing through the tip-sample contact area (see supporting information for experimental details) (Wen et al 2019). In this sense, the simultaneous determination of the current profile as a function of the applied voltage will allow us to establish the effective voltage drop at the semiconductor that will promote the net effective electromechanical response.

The current–voltage ($I–V$) characteristic of a semiconductor device depends on a range of parameters of the semiconductor material, such as its resistivity, doping concentration and carrier mobility, but in our case we will specially focus on the dependence of the geometry and the electrical properties of its contacts. From the electronic point of view, our system is composed by a gold seed layer, a ZnO NW and
In the framework of the thermionic emission theory, the voltage drop across the Schottky barrier ($V_{\text{SC}}$) in a semiconductor is given by:

$$V_{\text{SC}} = \phi_b - kT \ln \left( \frac{I}{I_0} \right)$$

where $\phi_b$ is the barrier height, $k$ is the Boltzmann constant, $T$ is the temperature, and $I$ and $I_0$ are the current densities.

The forward current density ($I_F$) of a Schottky diode is given by:

$$I_F = I_0 \left( \frac{qV_F}{kT} \right) - \frac{1}{1 + \frac{V_F}{R_{\text{sh1}}}}$$

where $I_0 = A_1 A^* T^2 \exp \left( -\frac{q\phi_{01}}{kT} \right)$

and

$$I_R = I_0 \left( \frac{qV_R}{kT} \right) - \frac{1}{1 + \frac{V_R}{R_{\text{sh2}}}}$$

where $I_0 = A_2 A^* T^2 \exp \left( -\frac{q\phi_{02}}{kT} \right)$

The total current ($I_{\text{total}}$) is the sum of the forward and reverse currents:

$$I_{\text{total}} = I_F + I_R$$

In the forward bias condition, the voltage across the Schottky barrier decreases linearly with increasing current, whereas in the reverse bias condition, the voltage increases logarithmically with increasing current.

The Schottky barrier height ($\phi_b$) is given by:

$$\phi_b = kT \ln \left( \frac{I}{I_0} \right)$$

where $I$ and $I_0$ are the current densities, $k$ is the Boltzmann constant, and $T$ is the temperature.

The carrier density in the semiconductor is given by:

$$n = \frac{qI}{qV_F + qV_R + qV_{\text{SC}}}$$

where $V_F$, $V_R$, and $V_{\text{SC}}$ are the voltage drops across the forward, reverse, and Schottky barriers, respectively.

The relationship between the current and voltage for a Schottky diode is given by the Shockley equation:

$$I = I_0 \left( \frac{qV}{kT} \right) - \frac{1}{1 + \frac{V}{R_{\text{sh1}}}}$$

where $I_0 = A_1 A^* T^2 \exp \left( -\frac{q\phi_{01}}{kT} \right)$ and $R_{\text{sh1}}$ is the series resistance.

The reverse current density of the Schottky diode results in:

$$I_R = I_0 \left( \frac{qV_R}{kT} \right) - \frac{1}{1 + \frac{V_R}{R_{\text{sh2}}}}$$

where $I_0 = A_2 A^* T^2 \exp \left( -\frac{q\phi_{02}}{kT} \right)$ and $R_{\text{sh2}}$ is the shunt resistance.

The voltage drop across the Schottky barrier ($V_{\text{SC}}$) is given by:

$$V_{\text{SC}} = \phi_b - kT \ln \left( \frac{I}{I_0} \right)$$

where $I$ and $I_0$ are the current densities, $k$ is the Boltzmann constant, and $T$ is the temperature.

The barrier height at the zero bias ($\phi_{01}$) is given by:

$$\phi_{01} = kT \ln \left( \frac{I_0}{I} \right)$$

where $I$ and $I_0$ are the current densities, $k$ is the Boltzmann constant, and $T$ is the temperature.

The barrier lowering due to the image force ($\Delta \phi_b$) is given by:

$$\Delta \phi_b = \frac{qE_0}{4\pi \varepsilon S}$$

where $E_0$ is the electric field strength, $\varepsilon$ is the dielectric constant, and $S$ is the contact area.

The barrier lowering due to the reverse bias ($\Delta \phi_{02}$) is given by:

$$\Delta \phi_{02} = \frac{qV_R}{kT}$$

where $V_R$ is the reverse voltage.

Finally, assuming that the undepleted part of the semiconductor is homogeneous and has a constant resistance, $R_{\text{SC}}$, the $I_{\text{SC}}$–$V_{\text{SC}}$ relationship for the semiconductor is simply:

$$I_{\text{SC}} = \frac{V_{\text{SC}}}{R_{\text{SC}}}$$

where $I_{\text{SC}}$ and $V_{\text{SC}}$ are the current and voltage across the Schottky barrier, respectively, and $R_{\text{SC}}$ is the series resistance.

Equation (2): according to the:

$$I_F = I_0 \left[ \exp \left( \frac{qV_F}{kT} \right) - 1 \right] + \frac{V_F}{R_{\text{sh1}}}$$

where

$$I_0 = A_1 A^* T^2 \exp \left( -\frac{q\phi_{01}}{kT} \right)$$

In this case, $\phi_{01}$ is the barrier height at the zero bias, $A^* = 4\pi e m^* k^2 / h^3$ is the Richardson constant, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $m^*$ is the effective mass.

Figure 2. (a) Scheme of the PFM setup. (b) Schematic diagram of the equivalent circuit of the Pt/ZnO/Au corresponding to an M–S–M structure, where $R_{\text{sh1}}$ and $R_{\text{sh2}}$ are the shunt resistors associated with both Schottky contacts. $V_F$ is the voltage drop across the forward-biased Schottky barrier, $V_R$ is the voltage drop across the reverse-biased Schottky barrier, and $V_{\text{SC}}$ is the voltage on the semiconductor. This is the ZnO NW...
Figure 3. (a) I–V curve of a single ZnO NW as measured by C-AFM (red line) and simulated I–V curve for an M–S–M structure (black line) as explained in the text using parameters shown in table 1. The breaking point is not the same due to the difference between the Au–ZnO junction and the Pt–ZnO junction, producing the asymmetry in the I–V curve. The inset shows the scheme of the C-AFM setup, where the voltage is applied to the bottom electrode. (b) Transfer function of two different symmetric and asymmetric functions (shown in the inset) into the frequency space, showing their contribution to different harmonics. For an ideal sinusoidal function as used in excitation bias $V_{ac}$, there is only a contribution in the first harmonic (green line). Instead, for an asymmetric excitation voltage as that calculated for the semiconductor voltage drop $V_{SC}$ using equations (2)–(9) (potential difference along the ZnO NW), there is a relevant contribution to multiple higher harmonics (green line).

Table 1. List of parameters used in the simulations for the voltage drop at the semiconductor.

| Parameter                      | Symbol | Value |
|--------------------------------|--------|-------|
| Work function of the platinum  | $\Phi_{Pt}$ | 5.65 eV |
| Work function of the gold      | $\Phi_{Au}$ | 5.80 eV |
| Electron affinity of ZnO       | $\chi_{ZnO}$ | 3.70 eV |
| ZnO NW resistivity             | $R_{ZnO}$ | 60 MΩ |
| Electrical permittivity of ZnO | $\varepsilon_{ZnO}$ | 5.70 |
| Diffusion potential at the contact | $\varepsilon_{ZnO}$ | 5.70 |

Figure 3(a) shows the characteristic I–V curve of a single ZnO NW as measured by C-AFM using a Pt-coated tip as a mobile top electrode. Since in our configuration the voltage is applied to the sample, the I–V characteristics at the positive voltages corresponds to the Pt–ZnO junction, while at the negative voltages is assigned to the Au–ZnO junction. Computer simulations, using an ad-hoc MATLAB code, based on the M–S–M model were performed to calculate the real voltage drop at the semiconductor ZnO NW structure. First, the experimental I–V curve is simulated considering the M–S–M structure and equations (2)–(9). The parameters used in the simulations were initially taken from the literature and adjusted to our model based on the right fitting to the experimental I–V curves, and are listed in table 1. The fitting process was performed by using an ad-hoc routine to minimize the minimum square error. Figure 3(a) shows the simulated pseudo symmetrical total I–V curve resulting from our structure superimposed to the experimental measurement. The obtained asymmetry is due to the difference in the work function of the platinum ($\Phi_{Pt}$ = 5.6 eV) and gold ($\Phi_{Au}$ = 5.8 eV), non-identical area of contacts (the ZnO NW–Au substrate contact area corresponds to the NW diameter while the ZnO NW–PtIr tip contact area is smaller than the tip radius), shunt resistances, pinning of the Fermi energy levels by the surface states and the existence of the interfacial insulating layers at both electrode contacts. Notice that the simulation curves are in well agreement with the experimental measurements.

Assuming an ideal sinusoidal function for the $V_{ac}$ voltage applied to the tip (green line in figure 3(b) inset), and considering the I–V characteristics measured by C-AFM (as shown in figure 3(a)), the resulting simulated voltage along the piezo $V_{SC}$ is presented in figure 3(b) (inset, red line). As observed, the effective voltage drop in the NW is no longer symmetric but shows a threshold value together with a strong asymmetry. This fact is very relevant to the interpretation of the piezoresponse signal since (i) this will lead to non-linear piezoresponse as a function of the applied voltage and (ii) it will originate electromechanical responses at the higher harmonics of the excitation frequency leading to multiharmonic PFM response. As opposite to an ideal piezoelectric response under a symmetric applied voltage, where the electromechanical signal is only in the first harmonic, the frequency response of the signal shown in figure 3(b) will also show contributions into higher harmonics of the signal. Beyond the present case for a M–S–M structure, the multifrequency piezoresponse is indeed a general phenomenon that can be found in any piezoelectric
material arising from the application of asymmetric excitation voltages e.g. due to the use of non-equivalent electrodes.

In addition, the effective electromechanical signal in the first harmonic will be reduced by this effect. Due to the asymmetrical $I$–$V$ curve and the modulated voltage applied in the NW, the real voltage drop at the NW is not linear. In order to calculate the voltage distribution along the M–S–M structure $(V_F, V_R$ and $V_{SC}$ from figure 2(b)) and their variation with the applied voltage, the equations (2–9) are numerically solved. The results are shown in figure 4(a), taking the parameters presented in table 1. Figure 4(a) shows that, as the excitation $ac$ bias voltage magnitude $(V_{ac})$ increases, the voltage drop across the reversed-biased Schottky barrier $(V_R)$ increases rapidly and becomes dominating until the voltage on the semiconductor bulk $(V_{SC})$ becomes notable. At the same time, the voltage drop across the forward-biased Schottky barrier $(V_F)$ remains negligible. It is clear that the range in which the voltage drop across the reverse-biased Schottky barrier $(V_R)$ is dominant depends on the value of the resistance of the semiconductor, in this case, the ZnO NW $(R_{ZnO/NW})$. As the $V_R$ increases, $R_{ZnO/NW}$ decreases and vice versa. At a large bias and in the case of a high value of $R_{ZnO/NW}$ the voltage drop $(V_R)$ starts to saturate, while the voltage drop across the semiconductor bulk increases almost linearly. Also, $V_F$ starts to increase slowly. In this large bias regime, the change of the voltage across the semiconductor bulk is responsible for the change of the bias.

Because the generated piezoelectric displacement $(\Delta_{PPM})$ is linearly related to the voltage applied to the piezoelectric material $(V_{SC})$ (equation 1), a PFM signal with two differentiated regions should also be expected. The PFM amplitude is simulated using equation (1) by substituting $V_{ac}$ by $V_{SC}$. As can be seen from figure 4(b), the real PFM signal in the first harmonic has a non-linear behavior, as expected from the effective voltage $(V_{SC})$ at the semiconductor (figure 4(a)). The linear part of the response has a lower slope as compared to the ideal signal obtained for a pure dielectric piezoelectric, leading to an apparent lower than real value. In addition, a measurable PFM signal appears in the second harmonic.

The multiharmonic response for the PFM amplitude as a function of $V_{ac}$ measured for ZnO NW is presented in figure 4(b). The effective piezoelectric coefficient has been calculated by fitting the experimental data with the simulations giving a value of $d_{33eff} = 9.6 \pm 2.5 \text{ pm V}^{-1}$. The variability on the experimental results is attributed to the tip damage, alteration of the surface states that may modify surface charge and carriers (Yang et al 2019) or the changes in the contact area between the tip and the NW, and is in good agreement with previously reported results using similar techniques (Tumvako et al 2015, Su 2017, Fortunato et al 2018, Lim et al 2018). This $d_{33eff}$ coefficient has been calculated by assuming a capacitor like structure in which the electric field can be taken as homogeneous. Still, this assumption is far from the real electric field lines around an AFM tip, which is closer to a radial distribution. In the limiting case of considering an electric field distribution as that created by a punctual charge, the voltage drop along the sample would differ by a factor of 2 with respect to the nominal one (Kalinin and Bonnell 2002, Stitz et al 2016). This leads to an effective piezoelectric coefficient that would double the one calculated here, that can be taken as a lower limit value.

Finally, in order to avoid the current flow through the NW thus cancelling the Schottky barrier effect, an insulator layer of 5 nm of alumina (Al$_2$O$_3$) was deposited over the NWs by atomic layer deposition. The presence of the alumina layer changes the configuration of the system breaking the M–S–M structure by adding a capacitor that eliminates the behavior of the two Schottky confronted diodes. Figure 4(c) shows the electronic configuration for this system and the measured PFM amplitude response as a function of the $V_{ac}$ for the ZnO NW under the alumina layer. In this case, the response recovers the linear behavior but the linear fitting gives a lower coefficient.
of $d_{33}^{\text{eff}} = 4.5 \text{ pm V}^{-1}$ (lower slope), probably due to effect of the insulating layer.

To conclude, we have analyzed the dependence between the effective piezoelectric coefficient $d_{33}^{\text{eff}}$ and the geometry (Kim et al. 2012) and dimensions of the NW using the piezoelectric module of COMSOL Multiphysics to simulate the piezoelectric response for different ZnO NWs dimensions. The geometry of the simulated model is an hexagonal column of 500 nm of radius and 5 μm and 600 nm of height that represents the ZnO NW shown in figures 5(a) and (b) respectively. The Au substrate is designed as a block of $2 \mu m \times 2 \mu m \times 0.6 \mu m$ at the bottom of the NW and at the top of the NW a cylinder of 100 nm of height and 50 nm of radius emulates the Pt tip. Following the experimental configuration, the Au block is defined as a terminal and the tip as ground in the COMSOL piezoelectric module. Figures 5(a) and (b) show the total displacement of the NW due to the piezoelectric effect: after applying 10 V the NWs show a deformation of 108 pm and 75 pm respectively. Notice that the total displacement is higher for a long thin NW than for thick and short NW. To study the NW radius effect, we perform a sweep in the NWs dimensions. Figure 5(c) shows a 3D plot of the behavior of the effective piezoelectric coefficient as the length and the radius of the NW is changed and the color range shows the piezoelectric coefficient. For thick and short NW, the $d_{33}^{\text{eff}}$ is lower than for thin and long NW and the obtained piezoelectric coefficient values are in the range between 1 and 11 pm V$^{-1}$. The decrease of $d_{33}^{\text{eff}}$ for thicker geometries can be explained taking into account two different effects: (i) the radial distribution of the electric field due to the small tip size as compared to the NW geometry is bigger for higher radius, increasing the divergence of the real electric field distribution from that of a parallel plate capacitor, leading to a lower effective $d_{33}$ coefficient corresponding to a deformation in the NW axis direction; (ii) for bigger radius, there is stronger lateral constraint that prevents vertical expansion of the samples around the point of application of the electrical field. Moreover, since the piezoelectric coefficient is itself a tensor, one can observe that the sample deformation, after the application of a fixed voltage, stays constant over a fixed radius to length ratio.

This evidences the fact that the piezoelectric effect is indeed including the whole volume of the NW through the tensor proportionality between deformation and applied field. The obtained experimental results of $d_{33}^{\text{eff}} \sim 9 \text{ pm V}^{-1}$ for ZnO NW of 1.2 μm of length and 900 nm of radius falls within the expected range.

4. Conclusion

In summary, in this work we have developed a full electromechanical response model for piezoelectric semiconductorors with asymmetric electrodes based on an M–S–M piezotronic structure, also suitable for leaky ferroelectrics that behave as wide band-gap semiconductors. We have demonstrated that the apparent non-linearity in the piezoelectric coefficient is generated by (i) the asymmetry created by the Schottky barrier at the semiconductor–metal junctions and (ii) the effective voltage drop at the ZnO NW due to partial screening of the electric field by the semiconductor carriers. Moreover, this non-linearity leads also to multiharmonic electromechanical response generating a PFM signal at the second and higher harmonics. Multifrequency PFM response is indeed not restricted to piezoelectric semiconductor materials but is general phenomenon that can be found in any piezoelectric material arising from the application of asymmetric excitation voltages as those created by different top and bottom electrodes materials. By directly measuring the experimental $I$–$V$ characteristics of ZnO NWs with C-AFM together with the piezoelectric vertical coefficient by PFM, and comparing them with simulations, effective piezoelectric coefficients in the range $d_{33}^{\text{eff}} \sim 8.6 \text{ pm V}^{-1}$–12.3 pm V$^{-1}$ have been extracted for ZnO NWs which perfectly match the simulations resulting from the proposed theoretical model. Finally, a useful computational tool to predict the piezoresponse of semiconducting NWs measured by PFM has been generated, revealing the strong effect of tensor nature proportionality between electric fields and deformation in NW geometries, demonstrating...
the dependence of the piezoelectric coefficient with the radius to length ratio.

Acknowledgments

Financial support was obtained under projects from the Spanish Ministerio de Economía y Competitividad (MINECO) under project FIS2015-73932-JIN, H2020 ECSEL-JU under EnSO project (Energy for Smart Objects) (Contract no. 692482) and La Caixa Foundation under the Junior Leader Retaining program (LCF/BQ/PR19/11700010). In addition, this work was partially funded by 2017-SGR-579 from the Generalitat de Catalunya. ICN2 is supported by the Severo Ochoa program from Spanish MINECO (Grant Nos. SEV-2017-0706).

Conflict of interest

The authors declare no competing financial interest.

ORCID iDs

Helena Lozano https://orcid.org/0000-0002-8609-003X
Gustau Catalán https://orcid.org/0000-0003-0214-4828
Jaume Esteve https://orcid.org/0000-0001-9440-7984
Neus Domingo https://orcid.org/0000-0002-5229-6638
Gonzalo Murillo https://orcid.org/0000-0002-0368-1900

References

Abdollahi A et al 2019 Converse flexoelectricity yields large piezoresponse force microscopy signals in non-piezoelectric materials Nat. Commun. 10 1266
Choi M et al 2017 Mechanical and electrical characterization of PVDF-ZnO hybrid structure for application to nanogenerator Nano Energy 33 462–468
Duque M et al 2019 Optimization of a piezoelectric energy harvester and design of a charge pump converter for CMOS-MEMS monolithic integration Sensors 19 (B) 1895
Elhaddid H, Sikula J and Franc J 2012 Symmetrical current–voltage characteristic of a metal–semiconductor–metal structure of Schottky contacts and parameter retrieval of a CdTe structure Semicond. Sci. Technol. 27 015006
Espinosa H D, Bernal R A and Minary-Jolandan M 2012 A review of mechanical and electromechanical properties of piezoelectric nanowires Adv. Mater. 24 4656–75
Fortunato M et al 2018 Piezoelectric thin films of ZnO-nanorods/nanowalls grown by chemical bath deposition IEEE Trans. Nanotechnol. 17 311–9
Harb A 2011 Energy harvesting: state-of-the-art Renew. Energy 36 2641–54
Janotti A and Van De Walle C G 2009 Fundamentals of zinc oxide as a semiconductor Rep. Prog. Phys. 72 126501
Jin C et al 2005 Epitaxial growth of zinc oxide thin films on silicon Mater. Sci. Eng. B 117 348–54
Kalinin S V and Bonnell D A 2002 Imaging mechanism of piezoresponse force microscopy of ferroelectric surfaces Phys. Rev. B 65 125408
Kalinin S V, Karapetian E and Kachanov M 2004 Nano electromechanics of piezoresponse force microscopy Phys. Rev. B 70 1–24
Kang Z et al 2019 Interface engineering for modulation of charge carrier behavior in ZnO photoelectrochemical water splitting Adv. Funct. Mater. 29 1808032
Keil P et al 2017 Piezotronic effect at Schottky barrier of a metal-ZnO single crystal interface J. Appl. Phys. 121 155701
Kim D Y et al 2018a Floating buoy-based triboelectric nanogenerator for an effective vibrational energy harvesting from irregular and random wave waves in wild sea Nano Energy 45 247–254
Kim H S, Lee D, Kim D, Kong D, Choi J, Lee M, Murillo G and Jung J 2018b Dominant role of Young’s modulus for electric power generation in PVDF–BaTiO3 composite-based piezoelectric nanogenerator Nanomaterials 8 777
Kim S M et al 2012 Radially dependent effective piezoelectric coefficient and enhanced piezoelectric potential due to geometrical stress confinement in ZnO nanowires/nanotubes Appl. Phys. Lett. 101 13104
Kwon B J et al 2012 Synthesis of vertical arrays of ultra long ZnO nanowires on nanocrystalline substrates Mater. Sci. Eng. B 177 132–9
Lee J A et al 2016 Schottky nanocant of one-dimensional semiconductor nanostructures probed by using conductive atomic force microscopy Nanotechnology 27 425711
Lee M et al 2012 A hybrid piezoelectric structure for wearable nanogenerators Adv. Mater. 24 1759–64
Li Y et al 2017 Analysis on the piezoelectric effect in a strained piezo-Schottky junction with AC impedance spectroscopy Nano Energy 36 118–25
Lim T et al 2018 Crystal growth and piezoelectric characterization of mechanically stable ZnO nanostructure arrays CrystEngComm 20 5688–94
Lord A M, Ramasse Q M, Kepaptsoglou D M, Perival P, Ross F M and Wilks S P 2017 Stability of Schottky and Ohmic Au nanocatalysts to ZnO nanowires Nano Lett. 17 6626–36
10.1021/acs.nanolett.7b02561
Morozovska A N et al 2007 Piezoresponse force spectroscopy of ferroelectric-semiconductor materials J. Appl. Phys. 102 114108
Murillo G et al 2017a Electromechanical nanogenerator–cell interaction modules cell activity Adv. Mater. 29 1605048
Murillo G, Lozano H, Cases-Utrera J, Lee M and Esteve J 2017b Improving morphological quality and uniformity of hydrothermally grown ZnO nanowires by surface activation of catalyst layer Nanoscale Rev. Lett. 12 1–8
Murillo G, Rodríguez-Ruiz I and Esteve J 2016 Selective area growth of high-quality ZnO nanosheets assisted by patternable AuN seed layer for water-level integration Cryst Growth Des. 17 5059–66
Özgür Ü et al 2005 A comprehensive review of ZnO materials and devices J. Appl. Phys. 98 041301
Panda; S K, Sant S B, Jacob C and Shin H 2013 Schottky nanocant on single crystalline ZnO nanorodusing conductive atomic force microscopy Nano Energy 21 628–33
Stitz N et al 2016 Piezoelectric templates – new views on biomimeralization and biomimetics Sci. Rep. 6 26518
Su T 2017 Origin of surface potential in undoped zinc oxide films revealed by advanced scanning probe microscopy techniques RSC Adv. 7 42393–7
Tamvakos D et al 2015 Piezoelectric properties of template-free electrochemically grown ZnO nanorod arrays Appl. Surf. Sci. 356 1214–20
Torah R et al 2018 Energy-harvesting materials for smart fabrics and textiles MRS Bull. 43 214–9
Vayssieres L 2003 Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions Adv. Funct. Mater. 13 662–66
Wang Z L 2007 Nanopiezotronics 19 889–92
Wang Z L 2009 ZnO nanowire and nanobelt platform for nanotechnology *Mater. Sci. Eng. R: Rep.* 64 33–71

Wang Z L *et al* 2010 Lateral nanowire/nanobelt based nanogenerators, piezotronics and piezo-phototronics *Mater. Sci. Eng. R: Rep.* 70 320–9

Wang Z L 2010 Piezotronic and piezophototronic effects *J. Phys. Chem. Lett.* 1 1388–93

Wang Z L 2012 From nanogenerators to piezotronics—a decade-long study of ZnO nanostructures *MRS Bull.* 37 814–27

Wang Z L and Song J H 2006 Piezoelectric nanogenerators based on zinc oxide nanowire arrays *Science (New York, N.Y.)* 312 242–6

Wen C *et al* 2019 *In situ* observation of current generation in ZnO nanowire based nanogenerators using a CAFM integrated into an SEM *ACS Appl. Mater. Interfaces* 11 15183–8

Xu S *et al* 2010 Self-powered nanowire devices *Nat. Nanotechnol.* 5 366–73

Yang F *et al* 2019 The high-speed ultraviolet photodetector of ZnO nanowire Schottky barrier based on the triboelectric-nanogenerator-powered surface-ionic-gate *Nano Energy* 60 680–8

Yang P *et al* 2002 Controlled growth of ZnO nanowires and their optical properties *Adv. Funct. Mater.* 12 323–31

Yang Y *et al* 2012 Pyroelectric nanogenerators for harvesting thermoelectric energy *Nano Lett.* 12 2833–8