Effects of flexoelectricity and surface elasticity on piezoelectric potential in a bent ZnO nanowire

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Abstract. In this work, a rapid model is established to study the effects of flexoelectricity and surface elasticity on the piezoelectric potential of a bent ZnO nanowire. Based on the piezoelectric theory and core-surface model, the distribution of piezoelectric potential of the ZnO nanowire is investigated. The analytical solution shows that the flexoelectricity and surface elasticity both significantly influence the piezoelectric potential. However, the effect of flexoelectricity is longitudinal dependent, which vanishes on the top side of nanowire, but only left surface elasticity effect on the potential. Simulation results show that the maximum value of potential on the top side of nanowire is about ±220.5 mV, of which result is lower compared to other theoretical models, but it should be more reasonable.

1. Introduction
One-dimensional zinc oxide (ZnO) nanowire is an important semiconducting piezoelectric material that has been widely used as a biomedical [1], environment monitoring, and even personal electronic nanodevices and nanosystem. In recent years, ZnO nanowires are widely used as nanoscale power generating systems. Many theoretical papers are reported to analyze the electrostatic potential of ZnO nanowires. Gao and Wang [2] established a classical piezoelectric perturbation theory, which provides a way to estimate the potential generating in ZnO nanowire. Other groups [3, 4] also reported some similar studies to quantify the piezoelectric potential on a bent ZnO nanowire. It is well known that, with decreasing size of nanowire, strong size dependencies are displayed. Besides, flexoelectricity also becomes prominent at nanoscale, Liu et al. [5] took flexoelectric effect into account, analyzed the piezoelectric potential generated in a ZnO nanowire. Yan et al. [6, 7] utilized an extended linear theory of piezoelectricity to discuss the influence of flexoelectric effect on the electroelastic responses, and the bending and vibration behavior of piezoelectric nanobeams.

In this paper, with the consideration of the flexoelectricity and surface elasticity effect, a simple and comprehensive theoretical framework for bending ZnO nanowires will be established.

2. Theoretical Model And Derivation

2.1. Problem identification and flexoelectric equation
Based on the piezoelectricity of ZnO nanowires, Wang et al. [8] proposed a nanogenerator which can convert the mechanical energy into electrical energy by bending the ZnO nanowires. Figure 1 shows the configuration of a nanogenerator using an atomic force microscope (AFM) tip scanning over a ZnO nanowire. A lateral force $f_x$ from the AFM tip applied to the top side of nanowire, result in a
mechanical deflection and piezoelectric polarization. Flexoelectric polarization shows apparently in the nanoscaled material, and it should not be ignored. Liu et al [5] have set a model which describes the flexoelectricity affects electrostatic potential in a bent piezoelectric nanowire. However, the derivation process is complex, thus, it will be useful to simplify such a derivation process to establish a rapid model. In this research, for granting a most close realistic conclusion, the size dependent effect has been taken into consideration.

Figure 1. Sketch of nanogenerator based on ZnO nanowire.

Flexoelectricity describes the generation of electric polarization in dielectrics by the application of the strain gradient. For a wurtzite ZnO crystal, the constitutive equation for flexoelectricity from reference [5] takes the form

\[
P_i = e_{ijk} e_{jk} + \mu_{ijkl} e_{jk,l},
\]

where \(P_i\) (i=1, 2, 3) are components of the piezoelectric polarization vector \(P\), \(e_{ijk}\) is the piezoelectric stress constant, \(e\) is strain tensor, and \(\mu\) is fourth-order flexoelectric tensor. For simplicity, we give the constitutive relationship between the piezoelectric polarization vector \(P\) and stress tensor \(\sigma_{jk}\) as follow

\[
P_i = d_{jk} \sigma_{jk} + f_{ijkl} \sigma_{jk,l}.
\]

\(\sigma_{jk}\) (j, k=1, 2, 3) are the components of stress tensor. For a wurtzite crystal, the piezoelectric deformation constant matrix is

\[
d_{jk} = \begin{bmatrix}
0 & 0 & 0 & d_{15} & 0 \\
0 & 0 & 0 & d_{15} & 0 \\
d_{31} & d_{31} & d_{33} & 0 & 0
\end{bmatrix}
\]

\(f_{ijkl}\) is a so-called fourth-order flexoelectric tensor related to stresses. The transformed flexoelectric coefficients \(f_{ijkl}\) with the relation to \(\mu_{imnl}\) can be written as follow:

\[
f_{ijkl} = \mu_{imnl} c_{mnjk}^{-1}.
\]

Here, \(c_{mjkl}^{-1}\) is the transposition of linear elastic constant \(c_{mjkl}\). The number and types of all possible non-zero flexoelectric coefficients \(\mu_{imnl}\) was analyzed by Quang and He [9]. For cubic crystal, the non-zero flexoelectric coefficients are expresses as follow [10]:

\[
\mu_{111} = \mu_{222} = \mu_{333} = \mu_{11}
\]

\[
\mu_{113} = \mu_{223} = \mu_{122} = \mu_{212} = \mu_{323} = \mu_{313} = \mu_{111}
\]

\[
\mu_{221} = \mu_{133} = \mu_{213} = \mu_{321} = \mu_{312} = \mu_{113} = \mu_{111}
\]

(5)
It is well known that the polarization charges induced by piezoelectric effect and flexoelectric effect are bound charges rather than free charges. By Gauss’s law, it gives
\[ \nabla \cdot \mathbf{D} = \rho_s = 0. \] (6)

Where \( \rho_s \) is the cylinder surface free charge density in nanowire, and \( \mathbf{D} \) is the electric displacement, which is defined as
\[ \mathbf{D} = -\varepsilon \nabla \phi + \mathbf{P}. \] (7)

Here \( \varepsilon \) is the dielectric constant, and \( \phi \) is the electric potential.

### 2.2. Model derivation

The ZnO nanowire is a hexagonal prism in geometry. To simplify the process of analytical solution, we assume the nanowire has a cylindrical shape with a uniform cross section of diameter \( 2a \) and length \( l \). By Saint-Venant’s principle of pure bending in electricity [11], the stress induced in the nanowire is

\[
\sigma = \begin{bmatrix}
0 \\
0 \\
\frac{f_y}{I_z} y(l-z) \\
f_z \left( \frac{3+2\nu}{8(1+\nu)} \left[ a^2 - y^2 - \frac{1-2\nu}{3+2\nu} x^2 \right] + \frac{1+2\nu}{4(1+\nu)} xy \right)
\end{bmatrix}
\] (8)

where \( I_z = \frac{\pi a^4}{4} \) is the cross-sectional inertial moment of the nanowire.

Hence, non-zero stress gradients are derived as
\[
\sigma_{33,2} = -\frac{f_y}{I_z} (l-z); \quad \sigma_{33,3} = \frac{f_y}{I_z} y;
\]
\[
\sigma_{23,1} = \frac{f_z}{I_z} \left( \frac{2\nu-1}{4(1+\nu)} x \right); \quad \sigma_{23,2} = -\frac{f_z}{I_z} \left( \frac{3+2\nu}{4(1+\nu)} y \right);
\]
\[
\sigma_{13,1} = -\frac{f_y}{I_z} \left( \frac{1+2\nu}{4(1+\nu)} y \right); \quad \sigma_{13,2} = -\frac{f_y}{I_z} \left( \frac{1+2\nu}{4(1+\nu)} x \right).
\] (9)

It is known that the material elastic constants can be obtained by an isotropic elastic modulus \( E \) and Poisson ratio \( \nu \), hence, the non-zero flexoelectric coefficients \( f_{ijkl} \) can be derived from the equation (4) as

\[
\begin{align*}
 f_{2332} &= \frac{1}{E} \left[ (1-\nu) \mu_{44} - \nu \mu_{11} \right] = f_{23} \\
 f_{3232} &= f_{3313} = \frac{2}{E} \mu_{11} (1+\nu) = f_{31} \\
 f_{3333} &= \frac{1}{E} \left[ \mu_{11} - 2 \mu_{44} \nu \right] = f_{33}
\end{align*}
\] (10)

By solving the simultaneous equations (2), (3), (8), (9), and (10), we have
\[
\mathbf{P} = \frac{f_y}{I_x} \left\{ -d_{31} \frac{(1 + 2\nu)}{4 (1 + \nu)} x y - d_{15} \frac{(3 + 2\nu)(a^2 - y^2) - \frac{1 - 2\nu}{2\nu} x^2}{8(1 + \nu)} - f_{23} (l - z) \right. \\
\left. -d_{33} y (l - z) + \left[ f_{33} - 2 f_{31} \right] y \right\} .
\] (11)

Then we can easily get the piezoelectric charge density
\[
\rho_v = -\nabla \mathbf{P} = -\frac{f_y}{I_x} (d_{33} - d_{15}) y A y .
\] (12)

Where \( A = -\frac{f_y}{I_x} (d_{33} - d_{15}) \). This equation shows the polarization charges distribution is only dependent on \( y \). Combining the equations (6) and (7), the relationship between piezoelectric potential \( \phi \) and piezoelectric charge density \( \rho_v \) is derived as
\[
\nabla^2 \phi = -\frac{\rho_v}{\varepsilon} .
\] (13)

In cylindrical coordinates, the non-homogeneous differential equation (13) becomes
\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta^2} + \frac{\partial^2 \phi}{\partial z^2} = -\frac{\rho_v}{\varepsilon} = -\frac{A r}{\varepsilon} \sin \theta .
\] (14)

Then, we follow the solving steps of paper [4]. Finally, we can get the analytical solution of the piezoelectric potential distribution of the ZnO nanowire
\[
\begin{align*}
\phi_{in} &= \frac{f_y}{\pi} \left[ d_{15} - d_{33} \left( \frac{2\varepsilon + \varepsilon_0}{\varepsilon_0 + \varepsilon} - \frac{1}{a^2} - \frac{4 f_{23}}{a^4} \right) (l - z) \right] r \sin \theta & (r \leq a) \\
\phi_{out} &= \frac{f_y}{\pi} \left[ d_{15} - d_{33} \left( \frac{4 f_{23}}{\varepsilon_0 + \varepsilon} - \frac{1}{a^2} \right) (l - z) \right] \frac{1}{r} \sin \theta & (r > a)
\end{align*}
\] (15)

This equation is completely equal to the solution of paper [5].

As we known, when the characteristic sizes of materials shrink to nanometer, surface effects often plays an important role in their material properties due to the increasing ratio of surface area to volume. For the effect of surface elasticity, we adopt the core-surface model, which essentially assumes that a nanowire consists of a core with elastic modulus \( E_0 \) and a surface (zero thickness) with so-called surface elastic modulus \( E_s \) (the unit is N/m). We can use a concept of effective modulus \( E^* \) to describe the elasticity of nanowire with surface effect. Under bending, the expression of effective elasticity \( E^* \) with the bulk elasticity \( E_0 \) and surface elasticity \( E_s \) is written as follows [12]:
\[
E^* = E_0 + 4E_s a \left( \frac{E_s}{E_0} \right) = E_0(1 + \frac{4\gamma}{a}) .
\] (16)

Here, \( \gamma \) is a dimensionless elastic modulus ratio \( \gamma = E_s / E_0 \).
If the influence of surface elasticity is taken into account in our model, the solutions of potential (15) should be modified. Firstly, surface elasticity will affect the flexoelectric coefficients \( f_{ijkl} \), thus,
\[
f_{23}^* = \frac{1}{E^*} [(1 - \nu) \mu_{14} - \nu \mu_{11}] = \frac{a}{E_0 (a + 4\gamma)} [(1 - \nu) \mu_{14} - \nu \mu_{11}].
\]
(17)
Secondly, surface elasticity will affect the piezoelectric coefficients \( d_{ijk} \), the piezoelectric coefficients \( d_{ijk} \) with surface effect can be represented by \( d_{ijk}^* = \frac{E_0}{E} d_{ijk}^0 \), then,
\[
\begin{align*}
    d_{15}^* &= \frac{E_0}{E} d_{15}^0 = \frac{a}{a + 4\gamma} d_{15}^0 \\
    d_{33}^* &= \frac{E_0}{E} d_{33}^0 = \frac{a}{a + 4\gamma} d_{33}^0.
\end{align*}
\]
(18)
Therefore, if the effect of surface elasticity is taken into account, the solutions of piezoelectric potential are modified into
\[
\begin{align*}
    \varphi_m &= f_{\gamma} \frac{a}{\pi (a + 4\gamma)} \left[ \frac{d_{15}^0 - d_{15}^3}{2\varepsilon} \left( \frac{3\varepsilon_0 + \varepsilon_a}{\varepsilon_0 + \varepsilon} \frac{r^2}{a^2} \right) - \frac{4 f_{23}^0}{a^2 \varepsilon_0 + \varepsilon} (l - z) \right] r \sin \theta \\
    \varphi_{out} &= f_{\gamma} \frac{a}{\pi (a + 4\gamma)} \left[ \frac{d_{33}^0 - d_{33}^3}{2\varepsilon} \left( \frac{3\varepsilon_0 + \varepsilon_a}{\varepsilon_0 + \varepsilon} \frac{r^2}{a^2} \right) - \frac{4 f_{23}^0}{a^2 \varepsilon_0 + \varepsilon} (l - z) \right] \frac{1}{r} \sin \theta.
\end{align*}
\]
(19)
If the effect of surface elasticity is neglected, surface elasticity \( E_s = 0 \), namely, the dimensionless elastic modulus ratio \( \gamma = 0 \), the analytical solution can be reduced to the equation (15), which is the results without surface elasticity effect, but only with the effect of flexoelectricity.

3. Numerical Results And Discussion
We established a rapid model which simplifies the derivation process, and also incorporating the effects of flexoelectricity and surface elasticity on the electric potential of ZnO nanowire. For a bulk ZnO, the Young’s modulus \( E_0 = 129 \text{GPa} \), Poisson’s ratio \( \nu = 0.349 \) [2, 4], relative dielectric constant \( \varepsilon/\varepsilon_0 = 7.7 \) [13], and the surface elastic modulus \( E_s \) takes the value of 235N/m [12]. The piezoelectric constants \( d_{15}^0 = -8.3 \text{pC/N} \) and \( d_{33}^0 = 12.3 \text{pC/N} \) [4]. And the strain-related flexoelectric coefficient \( \mu_{14} = \mu_{11} = 10^{-9} \text{C/m} \) [5], by the values of \( \mu_{11} \) and \( \mu_{14} \), we can get the flexoelectric coefficient \( f_{23}^0 \). Figure 2 gives the potential distribution along the y-axis direction at \( z = 300 \text{nm} \) for a nanowire with \( a = 25\text{nm} \) and \( l = 600\text{nm} \) bent by a force of 80 nN under different effect conditions. It is shown that flexoelectric effect strengthens the value of electric potential, and this curve with flexoelectric effect is consistent with the previous work [5]. However, the effect of surface elasticity weakens the value of electric potential. It is found from the curve that the value of potential decreases when the effects of flexoelectricity and surface elasticity are both taken into consideration. The curve with no surface elasticity and flexoelectricity comes to the classic result of piezoelectric polarization [2, 4].

Moreover, we simulate the side and top cross-sectional potential distribution at an applied force of 80nN on the nanowire, of which the effects of flexoelectricity and surface elasticity are both taken into account, shown in figure 3(a) and 3(b). It is clearly found that the electric potential due to flexoelectricity is dependent on \( z \). More closely to the top side, more weak effect of flexoelectricity. According to the equation (19), the effect from flexoelectricity is vanished on the top side. Therefore, on the top of nanowire, the main effect is only from surface elasticity. The maximum output of potential on the top side of nanowire is about \( \pm 220.5\text{mV} \), but at the bottom side is \( \pm 312\text{mV} \). In Gao and Wang’s model [2] the calculated potential value is \( \pm 284\text{mV} \), and Shao et al. obtained the voltage...
theoretically is $\pm 271$ mV [4]. Though our theoretical result is decreased but still has a wide gap from the experimental value. However, our theoretical result should be more reasonable, for the reason that, firstly, actually, in the process of experimental operation, the primary captured voltage comes from the top side or its vicinity of the ZnO nanowire when the AFM tip scanning over the nanowire, that is to say, the influence of flexoelectricity is almost zero or very weak. Secondly, most researches have proved that surface effects become the important effect for the nanoscale elements [14–16]; especially the effect of surface elasticity cannot be ignored. Thus, it is possible that surface elasticity becomes one of key factors influencing the piezoelectric potential.

![Figure 2](image)

**Figure 2.** The electric potential distribution on the y-axis with different conditions for a nanowire of $a=25$ nm at $z=300$ nm.

**Figure 3(a).** Side cross-sectional output of the piezoelectric potential for the nanowire with $a=25$ nm and $l=600$ nm by a lateral force of 80 nN, due to both flexoelectric and surface elastic effects.

**Figure 3(b).** Top cross-sectional output of the piezoelectric potential of the nanowire, due to both flexoelectric and surface elastic effects.
4. Conclusions
In summary, we discuss a rapid theoretical model to describe the effects of flexoelectricity and surface elasticity on the piezoelectric potential generated in a bent ZnO nanowire. An analytical solution of potential distribution is deduced, and the results indicate that the effect of flexoelectricity is longitudinal dependent, which vanishes on the top side of nanowire, but surface elasticity demonstrates significant effect on the captured potential. Therefore, the primary contribution to the piezoelectric potential of ZnO nanowire comes from surface elasticity. Simulation result show that the maximum output of potential on the top side of nanowire is about $\pm 220.5\text{mV}$, which is more reasonable than other theoretical models. Though our result still has a wide gap between the experimental data, there must be other influencing factors for further study in the future.

Acknowledgements
This paper is supported by the Inner Mongolia National Science Foundation (Grant No. 2014BS0102), Scientific Research Program for Higher Schools of Inner Mongolia (Grant No. NJZY16371) and College Student Innovative Training Program of Inner Mongolia University (Grant No. 201519004).

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