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Electrostatic potential in a bent flexoelectric semiconductive nanowire

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Abstract: Flexoelectricity presents a strong size effect, and should not be ignored for nanodevices. In this paper, the flexoelectric effect is taken into account to investigate the electrostatic potential distribution in a bent flexoelectric semiconductive nanowire, and the numerical solution is obtained by using the finite difference method. The effect of donor concentration on the electrostatic potential are also investigated. The results show that, the flexoelectricity increases the value of the voltage on the cross section. The flexoelectric effect is varied with the size, i.e. when the radius of the nanowire is small the flexoelectric effect is significant. It is also shown that a lower donor concentration can increase the value of the voltage on the cross section. The results indicated that one can use the flexoelectricity to modify the transfer efficiency from mechanical energy to electric energy through doping and strain engineering.

Keywords: Flexoelectricity; Piezoelectricity; Semiconductivity; Nanowire

1 Introduction

For a dielectric, in the original undeformed state, there is no polarization because of the local compensation of the inherent electric dipole moment in the molecule, but the infliction of nonuniform strain can break this kind of local compensation and induce the polarization, which is called the flexoelectric effect (Tagantsev, 1986). Inversely, the gradient of polarization can lead to deformation (Catalan et al., 2004). In nanoscale, the flexoelectric effect is significant and the research on it is necessary. Actually compared with the piezoelectric effect, the flexoelectric effect exists in all dielectrics, that Askar et al. (1970) has confirmed by lattice dynamics. Recently, the flexoelectricity fascinates many researchers and plays a very important role in nanotechnology. Fousek et al. (1999) have proposed the possibility of fabricating the piezoelectric composite without using piezoelectric materials based on

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the flexoelectricity. Catalan et al. (2004) presented a phenomenological model considering the effect of flexoelectricity on the dielectric constants and polarization for ferroelectric thin films. Maranganti et al. (2006) reviewed the flexoelectricity theory and developed a complete mathematical framework for it. Majdoub et al. (2008) found the flexoelectricity has an obvious size effect and influences the piezoelectric and elastic behavior of the nanostructures. A theory is developed for nanosized dielectrics with both the flexoelectricity and surface effect, which provides an underlying framework for the analysis and computation of electromechanical problems in nanodielectrics (Shen and Hu, 2010; Hu and Shen, 2009).

Piezoelectric semiconductor has been used in high electron mobility transistors for a long time. As a kind of piezoelectric semiconductive material, zinc oxide (ZnO), with a hexagonal wurtzite structure, has extensional applications in nanodevices. For examples, it has been used as piezoelectric diode, piezoelectric field effect transistors and piezoelectric sensor (Wang, 2011). Based on the coupling piezoelectric and semiconductive property of ZnO nanowire, Wang and his colleagues (Wang and Song, 2006; Song, Zhou, Wang, 2006) proposed a nanogenerator which can convert the mechanical energy into the electric energy by mechanically bending a ZnO nanowire (NW). Both physical and mathematical investigations have been done by researchers to evaluate the piezoelectric potential generated in the bent NW. Gao and Wang (2007) utilized the perturbation theory to deduce an analytical solution for the piezoelectric potential distribution in the cross section of a bending NW. Shao et al. (2010) presented a continuum model to calculate the piezoelectric potential in a bending NW. To improve the electric efficiency, Momeni et al. (2010) designed a nanocomposite generator composed of an array of ZnO NWs and acquired an analytical solution. Gao and Wang (2009) analyzed the piezoelectric potential in a laterally bent piezoelectric ZnO nanowire by considering its semiconductivity. All the aforesaid papers are based on the classical piezoelectric theory, and neglect the flexoelectricity. However, for nanosized devices, the flexoelectric effect is significant. As discussed in Liu et al. (2012), the flexoelectric effect is very strong. Therefore, it will be reasonable to take the flexoelectric effect into account when one analyzes the piezoelectric potential induced by bending a NW, otherwise the classical piezoelectric theory cannot give the accurate result. There is a wide gap between the results from the classical piezoelectric theory and experiments. In that paper, Liu et al. (2012) showed that it is possible to fill the gap by means of the flexoelectricity.

This paper is to investigate the flexoelectric effect on the piezoelectric potential in the bent ZnO NW when the flexoelectricity, piezoelectricity and semiconductivity are all taken into account. The effect of donor concentration on the electrostatic potential is also analyzed.

2 Modeling of ZnO NWs

A typical application of the piezoelectric semiconductor is a nanogenerator developed by Wang and Song (2006). This device relies on deflecting a ZnO NW by a conductive AFM tip, which results in polarization in the NW. It is the Schottky contact between the metal tip and the semi-conductive NW that plays a crucial role in controlling the accumulation and release of the piezoelectric energy (Song, Zhou, Wang, 2006). The model of a bent ZnO NW can be typically set up as applying a force f_y on the tip of a cantilever beam in a direction perpendicular to the nanowire (z-axis) as shown in Fig. 1. The objective of this paper is to acquire a relation between the lateral force f_y and the electric potential distribution in a bent semiconductive ZnO NW generated by both piezoelectricity and flexoelectricity. The following calculations are conducted under an infinite strain assumption in this model. We assume that the ZnO NW is a cylinder with diameter 2a and length l, and the substrate of the ZnO NW is also made of ZnO (Gao and Wang, 2009). To reduce the computational complexity of the electromechanical coupling, here we only consider the direct piezoelectric effect and the direct flexoelectric effect. Thus, the constitutive equations can be written as

$$\begin{cases} \sigma_{ij} = c_{ijkl}\varepsilon_{kl} \\ D_i = e_{ijk}\varepsilon_{jk} + \kappa_{ik}E_k + f_{ijkl}\varepsilon_{jk,l} \end{cases} \tag{1}$$

where σ_{ij} is the stress tensor, ε_{kl} is the strain tensor, E_k is the electric field, D_i is the electric displacement, c_{ijkl} is the elastic constant, e_{ijk} is the piezoelectric coefficient, κ_{ik} is dielectric constants, and f_{ijkl} is the flexoelectric coefficient.

For a wurtzite ZnO crystal, the linear piezoelectric coefficient matrix **e** is as follows:

$$e_{ijk} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \tag{2}$$

As discussed in Gao and Wang (2007), the zinc oxide can be approximated as an isotropic material. Thus, its elastic constants can be characterized by the isotropic elastic modulus with Young's modulus E and Poisson's ratio v. Therefore, the relationship between strain and stress can be written as

$$\begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{zx} \\ \varepsilon_{xy} \end{pmatrix} = \frac{1}{E} \begin{pmatrix} 1 & -\nu & -\nu & 0 & 0 & 0 \\ -\nu & 1 & -\nu & 0 & 0 & 0 \\ -\nu & -\nu & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(1+\nu) & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(1+\nu) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(1+\nu) \end{pmatrix} \begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} \tag{3}$$

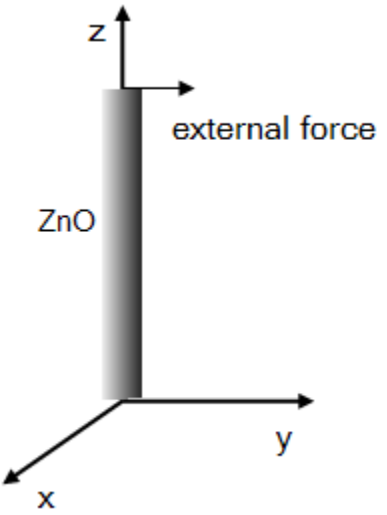

Figure 1: External force applied on the ZnO NW

Per Saint-Venant's principle, in the solution of pure bending problem of a beam in elasticity, the stress in the ZnO NW is (Soutas-Little, 1999)

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \tau_{yz} \\ \tau_{zx} \\ \tau_{xy} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ -\frac{f_y}{I} y(l-z) \\ \frac{f_y(3+2\nu)}{8I(1+\nu)} \left(a^2 - y^2 - \frac{1-2\nu}{3+2\nu} x^2\right) \\ -\frac{f_y(1+2\nu)}{4I(1+\nu)} xy \\ 0 \end{pmatrix} \tag{4}$$

where $I_x = \left(\pi/4\right) a^4$ is the cross-sectional inertia moment of the NW.

In this paper, we only consider the finite concentration of donors and free charge carriers in the ZnO. According to the Gauss's law, the divergence of the electric displacement can be written as

$$D_{i,i} = \frac{\partial}{\partial x_i} \left(e_{ikl}\varepsilon_{kl} + \kappa_{ik}E_k + f_{ijkl}\varepsilon_{jk,l}\right) = \rho_V = ep - en + eN_D^+ - eN_A^- \tag{5}$$

where ρ_V is the free charge volume density, p is the hole concentration in the valance band, e is the electron, n is the electron concentration in the conduction band, N_D^+ is the ionized donor concentration, and N_A^- is the ionized acceptor con-

centration. Generally, the ZnO NW is typically *n*-typed because of its unavoidable point defects[16], thus, we have $\mathrm{p} = \mathrm{N}_A^- = 0$ as in Gao and Wang (2009).

With Eqs. (1), (4), (5) and the geometrical compatibility equations, the electric field generated by the bent NW wire can be calculated when a proper boundary condition is given. We assume

$$D_k^R = e_{kij}\varepsilon_{ij} + f_{kijl}\varepsilon_{ij,l} \tag{6}$$

as the electric displacement vector in the polarization due to the piezoelectricity and flexoelectricity, and the corresponding piezoelectric and flexoelectric charge density is introduced as

$$\rho^R = -\nabla \cdot \mathbf{D}^R \tag{7}$$

which is the bound charge and cannot move freely like free charges. Then, Eq. (5) can be written as

$$\kappa_{ik}\frac{\partial^2}{\partial x_i \partial x_k}\varphi = -\left(\rho^R - en + eN_D^+\right) \tag{8}$$

where φ is the electric potential. For simplicity, we ignore the free charge on the surface due to the surface polarization. By now we have got Eq (8) as the governing equation for the electric potential in the bent ZnO NW under thermodynamic equilibrium.

Under the thermodynamic equilibrium state, the electrons concentration and ionized donor concentration will separately redistribute as

$$n = N_c F_{1/2}\left(-\frac{E_c(\mathbf{x}) - E_F}{kT}\right) \tag{9}$$

$$N_D^+ = N_D\frac{1}{1 + 2\exp\left(\frac{E_F - E_D}{kT}\right)} \tag{10}$$

where $N_c = 2\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2}$ is the effective state density of conduction band in semiconductor physics, which is only determined by the effective mass of conduction band electrons m_e and the temperature T according to this expression and independent on the thermodynamic equilibrium. $F_{1/2}(\eta)$ is the Fermionic-Dirac integral. N_D is the donor concentration. E_F is the Fermi energy which is flat all over the ZnO NW when the thermodynamic equilibrium is assumed (Gao and Wang, 2009). $E_c(\mathbf{x})$ is the position-dependent band edge energy, and $E_D(\mathbf{x}) = E_c(\mathbf{x}) - \Delta E_D$ is the position-dependent donor energy level, where ΔE_D is the activation energy of the donor. In addition, the electrostatic energy and the deformation potential make

up a shift ΔE_c between $E_c(\mathbf{x})$ and E_{c_0} which is the band edge energy of ZnO in free-standing undeformed state, i.e.

$$E_c - E_{c_0} = \Delta E_c = -e\varphi + \Delta E_c^{deform} = -e\varphi + a_c \frac{\Delta V}{V} \tag{11}$$

where a_c is the deformation potential constant. V is the volume, and ΔV is the change of the volume. We also define $\eta = -\frac{E_c(\mathbf{x})-E_F}{kT}$ which dictates how much the semiconductor degenerates to conductor and when $\eta >$ -3 it can be regarded as the highly degenerated case.

Eq. (8) is a second-order nonlinear partial differential equation of electric potential φ, and the boundary conditions are

$$\begin{cases} \varphi|_{r=a^-} = \varphi|_{r=a^+} \\ (D_i n_i)|_{r=a^-} - (D_i n_i)|_{r=a^+} = \rho_s = 0 \\ \varphi|_{r=\infty} = 0 \end{cases} \tag{12}$$

where $\mathbf{n}$ is the normal vector of the cylindrical surface, ρ_s is the density of free surface charge. Then, with the governing equation (8) and the boundary conditions (12), the electric potential in the bent ZnO NW considering the flexoelectric effect and the charge carrier density can be calculated.

3 Results and discussions

We use the finite difference method to solve the nonlinear partial differential equation (8) in polar coordinates. For the bulk ZnO material, the material constants are taken the same value as in Gao and Wang (2009), i.e., an isotropic elastic Young's modulus $E = 129.0GPa$ and Poisson ratio $\nu = 0.349$; relative dielectric constants $\kappa_{\perp}^r = 7.77$, $\kappa_{||}^r = 8.91$, piezoelectric constants $e_{31} = -0.51C/m^2$, $e_{33} = 1.22C/m^2$, $e_{15} = -0.45C/m^2$. Additionally, for the flexoelectric constants of isotropic materials, one has that[6]

$$\mathrm{f}_{ijkl} = f_{12}\delta_{kl} + f_{44}\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right)$$

The flexoelectric constants can be obtained by experiments and atomic calculations. However, due to lack of such work, here as an approximation, we choose $f_{12} = f_{44} = -0.45 \times 10^{-9} C/m$, a reasonable value for flexoelectric coefficients. As discussed in Kogan (1963), the order of 10^{-9} C/m is an appropriate lower bound for flexoelectric coefficients. The external force is set to be $f_y = 80\,nN$. In our calculations, we choose the typical donor concentration $N_D = 1 \times 10^{17} Cm^{-3}$ and only a single donor level with $\Delta E_D = 35meV$ as in Gao and Wang (2009). For the geometric sizes of the NW, we assume that the radius $a = 25\,nm$ and the length

$l = 600\ nm$ (Wang and Song, 2006). In this paper, all the parameters required in the calculations are taken the values depicted in this paragraph unless specified.

The electric potential distribution on the cross section at the height $z = 400\ nm$ for $T = 300\ K$ is plotted in Fig. 2. The maximum of electric potential exist in the tensile area on the surface of the NW is 0.040 V, while the minimum is -0.367 V on the other side. To illustrate the flexoelectric effect, the electric potential distributions are calculated by changing the flexoelectric constants, and the corresponding electric potential distributions on the y-axis at $z = 400\ nm$ are shown in Fig. 3. In this figure, the black line presents the one without the flexoelectric effect where all of the flexoelectric constants are zero ($f_{12} = f_{44} = 0$), which is highly matched with the result obtained by using the finite element method in Gao and Wang (2009). It is noted that the flexoelectric effect changes the electric potential along the diameter obviously. Comparing the black and red lines in Fig. 3, the polarization caused by stain gradient decreases the minimum of the negative potential by 0.030V (about 8.9%), and increases the maximum of the positive potential by 0.006V (about 17.1%). With higher flexoelectric constants shown as the blue line in Fig. 3, the electric potential changes more obviously with a higher electric potential difference, i.e. the voltage, along the diameter. Additionally, the variation of the electric potential brought by the flexoelectricity is non-uniform along the diameter.

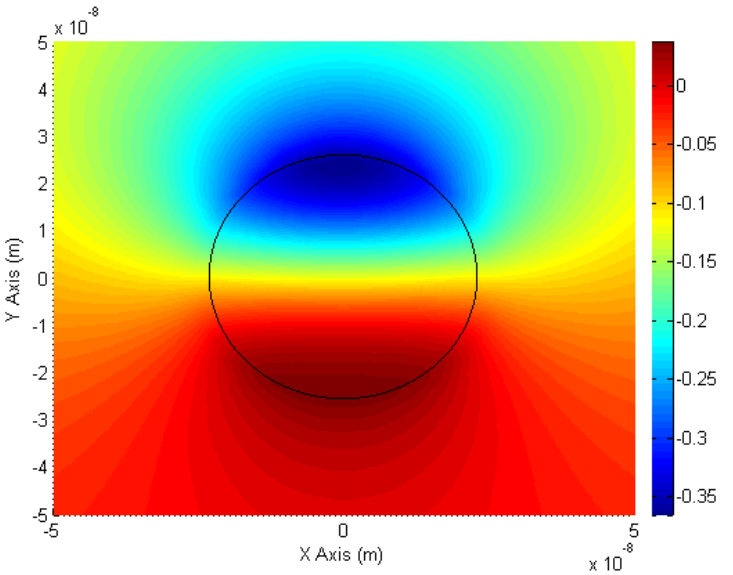

Figure 2: Cross section color plot of electric potential φ considering the flexoelectric effect

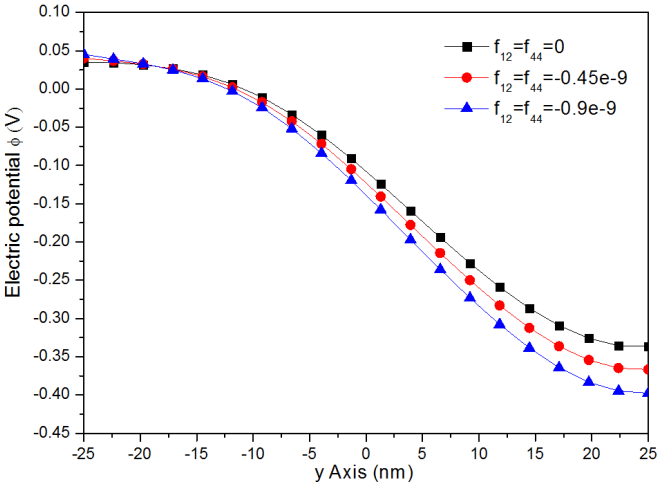

Figure 3: Line plot of φ with different flexoelectric constants along the diameter

Fig. 4 and Fig. 5 present the distributions of ionized donor concentration and electron concentration on the y-axis (z=400 *nm*) with different flexoelectric constants, respectively. It is indicated that the flexoelectricity changes N_D^+ and n obviously in the tensile area of the bent nanowire. In these 2 figures, the black line presents the one without the flexoelectric effect where all the flexoelectric constants are zero ($f_{12} = f_{44} = 0$), which agrees very well with the result obtained by using the finite element method in Gao and Wang (2009).

To investigate the variation of the effect of flexoelectricity on the voltage with diameters, we define V_f and V_0 to be the voltage, i.e. the potential difference, on the cross section with and without flexoelectricity respectively. We define the relative difference between the voltage with and without flexoelectricity as $(V_f - V_0)/V_0$ (at z=300 *nm*) and plot the corresponding curve in Fig. 6 to analyze the effect of flexoelectricity on the voltage in bent ZnO NWs with different wire diameters and flexoelectric constants. It is obvious that the relative difference between the voltage with and without flexoelectricity decreases with the increase of wire diameters, and the flexoelectric solution approaches to the classical piezoelectric one for large diameter. The results clearly show that the flexoelectricity should not be ignored for bending or inhomogeneously stretching a NW. By comparing the red and black lines, it is indicated that the larger absolute value of the flexoelectric constants are, the larger the influence range of the flexoelectricity is.

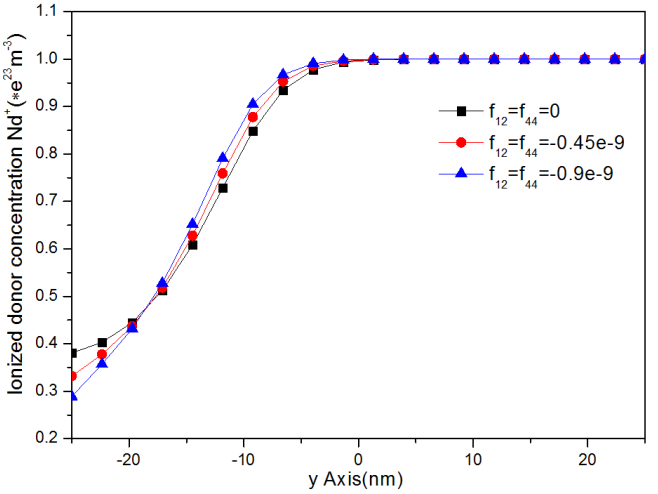

Figure 4: Line plot of N_D^+ with different flexoelectric constants along the diameter

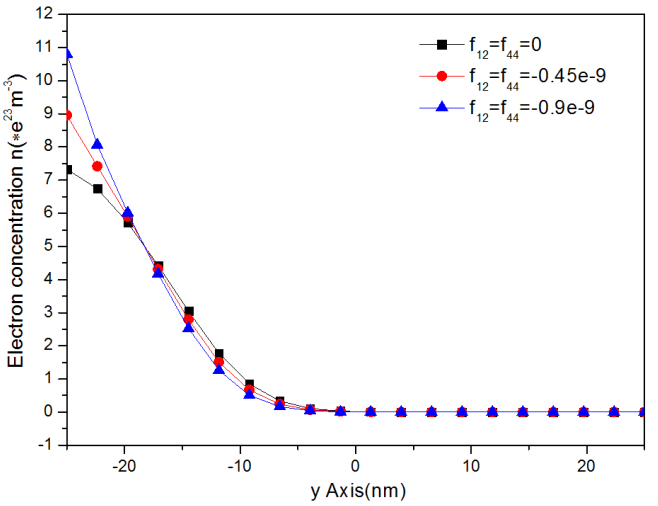

Figure 5: Line plot of n with different flexoelectric constants along the diameter

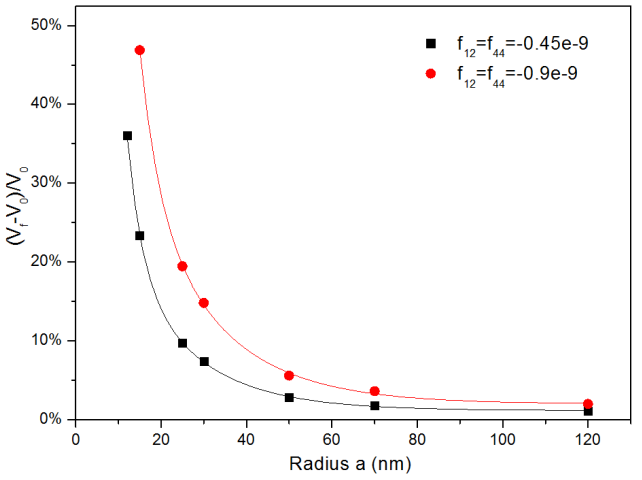

Figure 6: Values of $(V_f - V_0)/V_0$ with radius

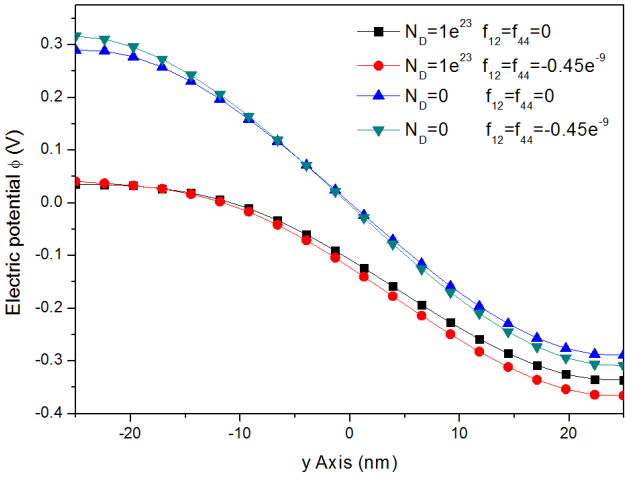

Figure 7: Electric potential along diameter with different donor concentration and flexoelectric constants

Fig. 7 describes the electric potential distributions along the y-axis with different sets of flexoelectric constants and different donor concentrations. No matter the flexoelectricity is considered or not, the effect of the doping is significant, the electric potential along the diameter decreases obviously after doping.

It is apparently shown in this section that the flexoelectricity plays an important role in changing the magnitude of voltage, the electrons concentration and ionized donor concentration, even though the flexoelectric coefficients are set to be the minimum. It means that one can use the flexoelectricity to modify the transfer efficiency from mechanical energy to electric energy through doping and strain engineering.

4 Conclusions

In this paper, the effect of flexoelectricity on the polarization and semiconductivity is taken into account and the numerical solutions for electrostatic potential and semiconductivity in a bent ZnO nanowire are obtained by using the finite difference method. The solution shows that the size-dependent electromechanical coupling due to inhomogeneous strain is significant. The flexoelectric effect also changes the distributions of the electron concentration and ionized donor concentration in the tensile area to some extent. The numerical results indicated that the flexoelectric effect is size-dependent and cannot be neglected when the radius of the ZnO nanowire is in nanoscale. In addition, a lower donor concentration can increase the voltage on the cross section.

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