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Investigating Output Voltage and Mechanical Stability of a Piezoelectric Nanogenerator Based on ZnO Nanowire

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ABSTRACT

The output of a piezoelectric nanogenerator based on ZnO nanowire is largely affected by the shape of nanowire. In order to obtain mechanically stable nanogenerator with high performance, the investigation of mechanical and electrical characteristics related to the nanowires and materials used in nanogenerators are of great interest and significance. This paper presents the various behavior of the conduction band, carrier concentration and the magnitude and distribution of the piezoelectric potential in cylindrical and conical shape ZnO nanowire (NW) by using finite element (FE) method. It is shown that symmetry reduction in nanowire shape and replacement the cylindrical NW with the conical NW, results in more advantageous both in terms of mechanical stability and piezoelectric potential. The large variation of the conduction band at the tip of conical nanowire results in receiving a large increase of maximum piezoelectric potential from -70 mv (cylindrical nanowire with radius of 30 nm) to -1750 mv (conical nanowire with tip radius of 5 nm and base radius of 30 nm). It is also shown that the insulating materials with lower Young's modulus and lower relative permittivity are the best options in nanogenerator device fabrication. This numerical study can provide a guideline to design of the piezoelectric nanogenerator with high performance.

Keywords: Conical nanowire; Piezoelectric nanogenerator; Piezoelectric potential; Insulating layer; ZnO.

1. INTRODUCTION

With the development of technology the size of systems and devices are getting smaller. They often are used in positions where there is very difficult to directly access them. Therefore using conventional battery for which must be replaced frequently is not a good option. Finding the low-size, low-weight, independent and sustainable power supply with continuous operation and long lifetime is a key challenge for powering [1].

The nature provides numerous potential power sources: light, thermal, mechanical, chemical, and biological energy, which must be converted to electrical energy [2]. Among them, harvesting the mechanical energy directly from the environment, using piezoelectric nanogenerator, is one of the useful and promising

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approaches [3]. The mechanism of the piezoelectric nanogenerator lies in the coupling of piezoelectric and semiconducting properties [4]. Among the known piezoelectric nanomaterials, Zinc Oxide (ZnO) has received broad attention due to three key advantages. First, ZnO exhibits both semiconducting and piezoelectric properties. Second, ZnO is nontoxic and biocompatible. Third, synthesize of the ZnO is easy and low-cost [2].

The first piezoelectric nanogenerator was introduced by Professor Zhong Lin Wang and Jinhui Song in 2006, which can convert mechanical forces to the voltage ,in nano scale, by bending a vertically grown ZnO nanowire when the atomic force microscopy (AFM)'s tip swept across the nanowire [2]. Science then, various kinds of nanogenerators has been demonstrated using piezoelectric effect. Recently the integrated nanogenerator based on vertically aligned ZnO nanowires has attracted much scientific interest because of its much simpler fabrication process than the bending type nanogenerators [5]. Xu et al. have fabricated the vertical nanowire array integrated nanogenerator (VING) which packaging with a layer of polymethyl-methacrylate (PMMA) [4]. In this structure, the output voltage of 80 mV and output current of 6 nA cm^{-2} can be extracted from the nanogenerator device [4]. The output voltage and current could be greatly enhanced by linearly integrating a number of VINGs [4]. The existence of PMMA layer can increase the stability and mechanical robustness of the nanogenerator device and also improve the efficiency of nanogenerator [4].

The current study has been focused on nanogenerator based on vertical ZnO NWs, which is compressed under certain pressure. The overall objective of this paper is to study how conical shape of the ZnO NW can affect the behavior of the free charge carriers and the piezoelectric potential distribution along the nanowire axis. The nanowire with conical structure offers more mechanical stability and more resistance against breaking, deflection and twisting than cylindrical nanowire, which helps to provide a piezoelectric nanogenerator with greater ability to withstand mechanical force. Applying an insulating layer among the ZnO nanowires augments the nanogenerator robustness [4]. Also in this work, a piezoelectric nanogenerator is simulated and investigated numerically. The obtained results show how to improve the nanogenerator performance. Designing the nanogenerator based on the conical nanowires with using the insulating layer can make an extremely stable device with high output.

2. THEORETICAL FRAMEWORK

The piezoelectric equations in stress-charge form which represent the electromechanical interactions between the material stress and the electric field can be expressed by the constitutive relations [6]:

$$\begin{aligned} T &= C_E S - e^T E \\ D &= eS + \kappa E \end{aligned} \tag{1}$$

Where, S and T are the strain and stress tensor respectively. E is the electric field vector and D is the electric displacement. C_E is the elastic stiffness tensor, e is the piezoelectric constant tensor, κ is permittivity tensor, and e^T is the transpose of the tensor e. These material parameters are anisotropic tensors which have been taken from the C_{6V} symmetry of the ZnO crystal with wurtzite structure [6]. The ZnO is a piezoelectric material with semiconducting property. Thus in order to model the ZnO nanowire as a piezoelectric semiconductor material with a significant amount of free electrons, two electrostatic equations should be used. Equation 2 is a Gauss's law which links the electric displacement D to the volume charge density ρ_v [7]. Mechanical equation (Eq. 3) links the stress T to the applied force F. In Eq. 2, P and n are related to the hole concentration in the valance band and the electron concentration in the conduction band respectively, N_D^+ is the ionized donor concentration, N_A^- is the ionized acceptor concentration, and e is electron charge. It is mentioned that for ZnO NW under n-type doping concentration $P= N^-_A =0$ [7].

$$\nabla.D = \rho_V = e(p - n + N_D^+ - N_A^-) \tag{2}$$

$$-\nabla.T = F \tag{3}$$

The numerical values related to tensors for the ZnO

Table 1: *ZnO NW parameters with C_{6V} symmetry.*

Parameter	Magnitude [GPa]	Parameter	Magnitude [C/m^2]
C_{11}	207	e_{15}	- 0.45
C_{12}	117.7	e_{31}	- 0.51
C_{13}	106.1	e_{33}	1.22
C_{33}	209.5	κ_{11}	7.77 [1]
C_{44}	44.8	κ_{22}	7.77 [1]
C_{55}	44.6	κ_{33}	8.91 [1]

nanowire with the C_{6V} hexagonal symmetry are summarized in Table1. The Young's modulus and Poisson ratio are respectively Y= 129 GPa ν= 0.349 [6].

3. RESULTS AND DISCUSSION

The open circuit voltage is carried out based on the simulation of ZnO nanowire in static analysis. The geometry includes a ZnO nanowire, approximated as a cylinder, with radius and length of R= 30 nm, L= 700 nm. The ZnO nanowire is affixed on a gold substrate with thickness of 40nm. According to the Figure 1a, the geometry is surrounded by free space (air) and the nanowire is normally compressed by a vertical force F= 100 nN exerted at its top section. The ZnO nanowire is assumed with moderate conductivity and doped with initial donor concentration N_D= 1e17 C/m^3. At first, the simulation is carried out by considering the air as an insulating layer, but it is replaced with special dielectric materials to further study the influence of the insulating layer on piezoelectric potential.

The cylindrical nanowire is compressed by compressive forces, and the piezoelectric potential is distributed along the vertical axis (z-coordinate) of the ZnO nanowire. As seen in Figure 1b, the top part of the nanowire exhibits a negative potential (-66 mv) compared to the bottom part (+29 mv). Although by decreasing cylindrical nanowire diameter the piezoelectric potential has been improved; but structurally, narrow cylindrical nanowires are more fragile. Breaking the symmetry in ZnO nanowire geometry leads to the different procedure of carrier concentration in nanowire.

Generally, by applying the force, the conduction bands are deflected at the top part of the nanowire; charges are depleted from the upper part and created a depletion region at the nanowire tip. The results obtained by varying the nanowire shape from the cylindrical nanowire (30 nm base and tip circular radius) to the conical nanowire (circular base with 30 nm, circular tip with radii ranging from 30 nm to 5 nm) are presented in Figure 2. The behavior of the conduction band level and the charge carrier concentration along the z axis shows that, the depletion region width in the conical nanowires with smaller tip radius significantly increases and consequently the negative piezoelectric potential along the nanowire augments. Due to the conical shape of the nanowire, the free charge carrier depletion caused in conical nanowires with lower tip radius, is larger than cylindrical and conical nanowire with large tip radius. The depletion region width is 50 nm for nanowire in cylindrical shape and it reaches to 200 nm in conical nanowire with tip radius of 5 nm.

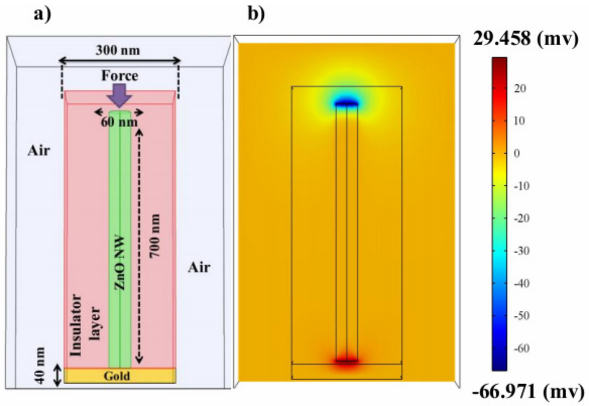

Figure 1: *a) The schematic of the considered ZnO nanowire b) The piezoelectric potential distribution along the cylindrical ZnO nanowire under compressive force F = 100 nm with donor concentration N_D= 1e17 C/m^3.*

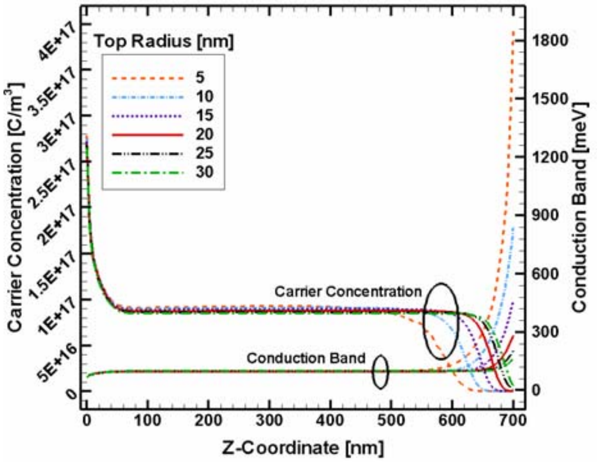

Figure 2: *The conduction band and the carrier concentaration along the ZnO nanowire in presence of the initial donor concentration* N_D*= 1e17 C/m*^{3}*. The tip nanowire radius sweeps from R= 30 nm to 5nm whereas bottom nanowire radius is R= 30 nm.*

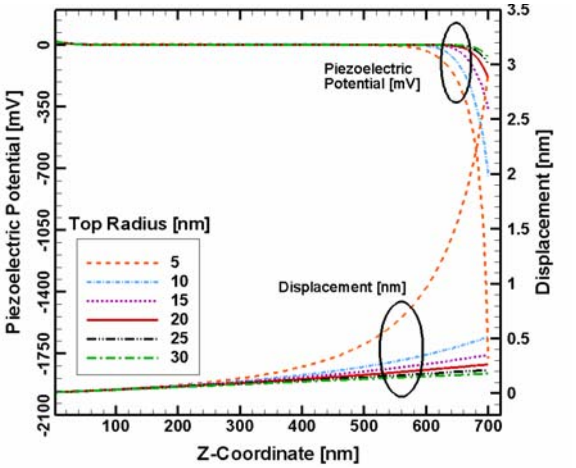

Figure 3: *The dissplacement and the piezoelectric potential along the ZnO nanowire in presence of the initial donor concentration* N_D*=1e17 C/m*^{3}*. The tip nanowire radius sweeps from R=30 nm to 5nm whereas bottom nanowire radius is R= 30 nm.*

By decreasing the nanowire tip radius, the conduction bands provide a strongly high potential barrier. The potential barrier height is 1800 mev for the conical nanowire with tip radius of 5 nm and 60 mev for the cylindrical nanowire.

The variations of the nanowire displacement and the piezoelectric potential distribution along the ZnO nanowire for different nanowire tip radius are shown in Figure 3. It is observed that the displacement along the nanowire, especially at the top part of the nanowire is increasing with decreasing the tip radius. In fact there is not a linear relation between the displacement and the applied force, due to the existence of the donor concentration N_D= 1e17 C/m^3 in ZnO NW. On the other hand, the lack of symmetry in the ZnO nanowire geometry (conical nanowire) leads to the parabolic displacement trend which is appeared especially in the conical nanowire with smaller tip radius. The curves related to the piezoelectric potential exhibit a significant increase in potential as well. The maximum piezoelectric potential is approximately V= -1750 mv at the tip of the conical nanowire (5 nm tip radius) compare to the cylindrical nanowire with V= -70 mv.

The doping levels in ZnO, as a semiconducting and piezoelectric material, have a large influence on the piezoelectric polarization charges in nanowire and on the output potential of the nanogenerator. According to the growth conditions [7], the donor concentration ranging from N_D= 1e15 C/m^3 to N_D= 1e18 C/m^3. So in the following, a comparative investigation is carried out on n-type ZnO nanowire to study the screening effect on the piezoelectric potential in ZnO conical nanowires. The donor concentration ranging from ND= 1e15 C/m^3 to ND= 1e18 C/m^3. It is found that the maximum piezoelectric potential decreases as doping level increases (Figure 4). The conical structure of nanowire reveals that by increasing the nanowire tip radius and closing the nanowire to the cylindrical

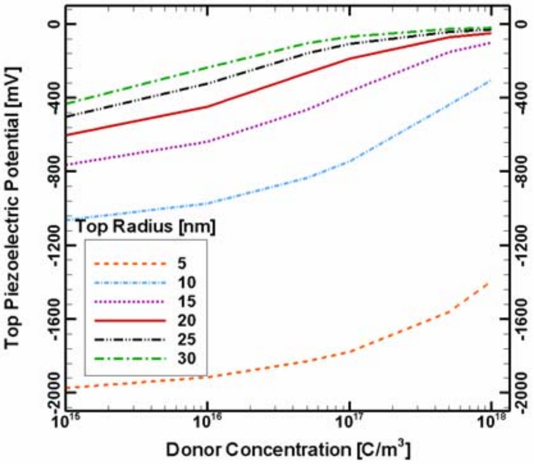

Figure 4: *The maximum piezoelectric potential at the tip of the ZnO nanowire as a function of the donor concentration from* N_D*=1e15 C/m*^{3} *to* N_D*= 1e18 C/m*^{3}*. The tip nanowire radius sweeps from R=30 nm to 5nm whereas bottom nanowire radius is R=30 nm.*

shape, the potential becomes less effective to the donor concentration augmentation. The reduction of the output potential for low donor concentrations is more relevant.

Finally, the influence of the dielectric material around the nanowire is investigated. For this purpose, the ZnO nanowire is immerged in an insulating layer. The insulating layer not only leads to robust nanogenerator but also protects the nanowires from the short circuits which occur because of the semiconducting properties of ZnO nanowires [8]. The relative dielectric constant as an electrical parameter, Young's modulus and Poisson's ratio as mechanical parameters of insulating layer between ZnO nanowires, are separately investigated with keeping constant all the other parameters. As shown in Figure 5, the dashed lines indicate the maximum piezoelectric potential at the top surface of insulating layer and solid lines reveals the potential at the tip of nanowire versus the electrical and mechanical parameters for conical nanowire with tip radius equal to 10 nm, and donor concentration N_D= 1e17 C/m^3. All extracted results from insulating layer surface are few orders of magnitude lower than the nanowire tip. According to the results, the Young's modulus and relative dielectric constant have significantly affected the potential. The value of Young's modulus spans from 1GPa to 400GPa, the potential decreases from -600 mv to -40 mv; and by varying the relative dielectric constant from 1 to 10, the potential decreases from -700 mv to -195 mv. In contrast, the effect of the Poisson's ratio is less significant on piezoelectric potential and almost becomes negligible. The potential variation is less than 5 mv for the Poisson's ratio ranging from 0.1 to 0.45 (the potential is increased by increasing the Poisson's ratio).

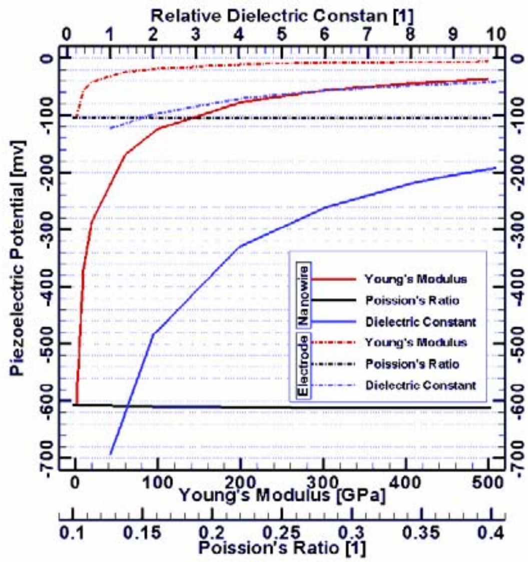

Figure 5: *Variations of piezoelectric potential in respect to Young's modulus, Poisson's ratio and relative dielectric constant of insulating layer.*

From the application point of view, finding the optimal insulating material is of vital importance in nanogenerators output. Dielectric material surrounding the nanowire does not have all ideal terms such as large Young's modulus, Poisson's ratio and low relative permittivity. Therefore some different dielectric mate-

Table 2: *Different insulating materials with various mechanical and electrical parameters.*

Parameter / Material	Electrical parameters	Mechanical parameters	
	Relative dielectric constant [1]	Poisson's ratio [1]	Young's modulus [GPa]
PVC	2.9	0.37	2.9
Nylon	4	0.4	2
PMMA	3	0.4	3
SiO_2	4.2	0.17	70
Glass	4.2	0.3	74
Si_3N_4	9.7	0.23	250
Al_2O_3	5.7	0.22	400
SiC(6H)	9.7	0.45	748

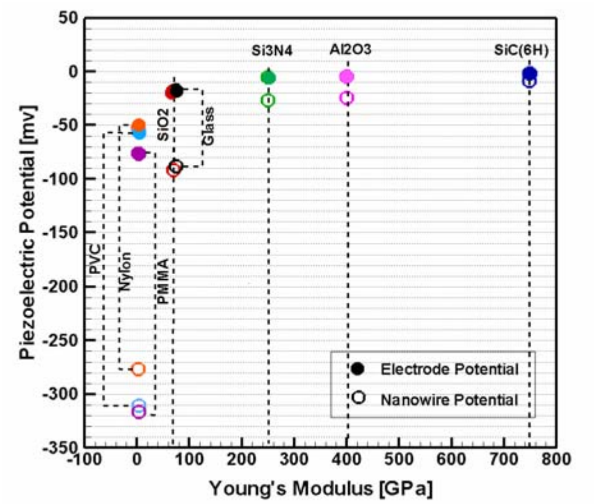

Figure 6: *The maximum piezoelectric potential at the tip of the ZnO nanowire with conical shape (tip nanowire radius 10 nm) and at the top surface of insulating layer by using the insulating materials with different Young's modulus. The initial donor concentration is* N_D*= 1e18 C/*m^3.

rials are considered around the nanowire and simulation is carried out by considering the influence of both electrical and mechanical parameters simultaneously. Mechanical and electrical parameters of materials are listed in Table 2.

According to simulation results, PVC, Nylon and PMMA, with low Young's modulus and low relative dielectric constant, are better suited for a nanogenerator device than the other insulating materials tested. The greater part of the applied forces can be transmitted to the nanowires, so more piezoelectric potential transfer to the surface of the nanogenerator through the insulating layer with low Young's modulus. The maximum piezoelectric potential variations at the tip of nanowire versus mechanical and electrical parameters of insulating layer are more important than the potential variations exerted from insulating layer (nanogenerator output) surface (Figure 6).

4. CONCLUSIONS

In present paper, the strong dependence of the piezoelectric potential on the nanowire shape is investigated. The different behaviors of free charge carriers in vertically compressed conical n-type ZnO nanowire, through reducing symmetry in the nanowire shape, more increases the piezoelectric potential compared to the cylindrical nanowire. The undesirable effect of donor concentration on piezoelectric potential is compensated by decreasing the conical nanowire tip radius. Moreover, the influence of electrical and mechanical properties of insulating layer around the ZnO nanowire on improving the nanogenerator device strength and performance is studied. The materials with low Young's modulus and low relative dielectric constant are the best candidate in order to high pressure transmission to the nanowire and reception of large amount of piezoelectric potential from nanogenerator.

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