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Nanopiezotronics**

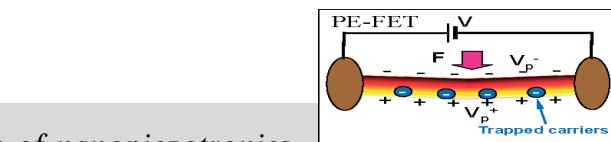
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This article introduces the fundamental principle of nanopiezotronics, which utilizes the coupled piezoelectric and semiconducting properties of nanowires and nanobelts for designing and fabricating electronic devices and components, such as field-effect transistors and diodes. The physics of nanopiezotronics is based on the principle of a nanowire nanogenerator that converts mechanical energy into electric energy. It is anticipated to have a wide range of applications in electromechanical coupled electronics, sensing, harvesting/recycling energy from the environment, and self-powered nanosystems.

1. Introduction

Today's nanoelectronics rely on the accumulation and movement of charge carriers to perform intelligence-bearing devices, such as transistors and diodes. Spintronics is an emerging field involving the detection and manipulation of electron spin for sensing, data memory, and functional devices. Molecular electronics (Moltronics) utilizes molecules as functional devices to achieve electronic performance. This article introduces a new field named nanopiezotronics,^[1] which utilizes the coupled piezoelectric and semiconducting property of nanowires and nanobelts for designing and fabricating electronic devices such as transistors and diodes. It is anticipated to have a wide range of applications in electromechanical coupled sensors and devices, nanoscale energy conversion for self-powered nanosystems, and harvesting/recycling of energy from environment.

Piezoelectricity (PZ) is a coupling between a material's mechanical and electrical behavior. When a piezoelectric material is squeezed, twisted, or bent, electric charges collect on its surfaces. Conversely, when a piezoelectric material is subjected to a voltage drop, it mechanically deforms. Many crystalline materials exhibit piezoelectric behavior, including



quartz, wurtzite-structured crystals, Rochelle salt, lead zirconate titanate ceramics, barium titanate, and polyvinylidene fluoride (a polymer film). When such a crystal is mechanically deformed, the positive- and negative-charge centers are displaced with respect to each other (Fig. 1). So while the overall crystal remains electrically neutral, the difference in charge-center displacements results in an electric polarization within the crystal. Electric polarization resulting from mechanical deformation is perceived as piezoelectricity.

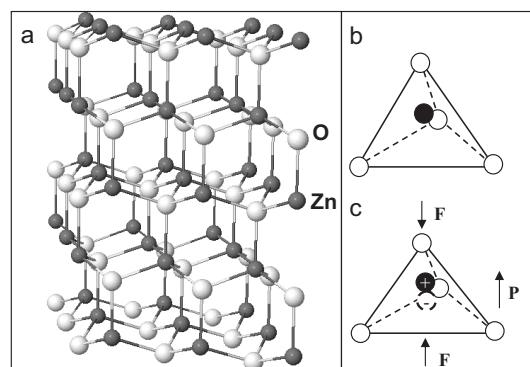


Figure 1. a) Structural model of wurtzite ZnO. b) Tetrahedral coordination between Zn and oxygen. c) Distortion of the tetrahedral unit under the compression of an external force, showing the displacement of the center of positive charge from that of the negative charge.

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To introduce nanopiezotronics, we first illustrate the piezoelectric behavior of a single nanowire (NW) or nanobelt (NB)^[2] of a piezoelectric material such as ZnO. For a vertical, straight ZnO NB (Fig. 2a), the deflection of the NB by an external applied force F results in (tensile) stretching of its outer surface (positive strain ϵ) and compressing of its inner surface

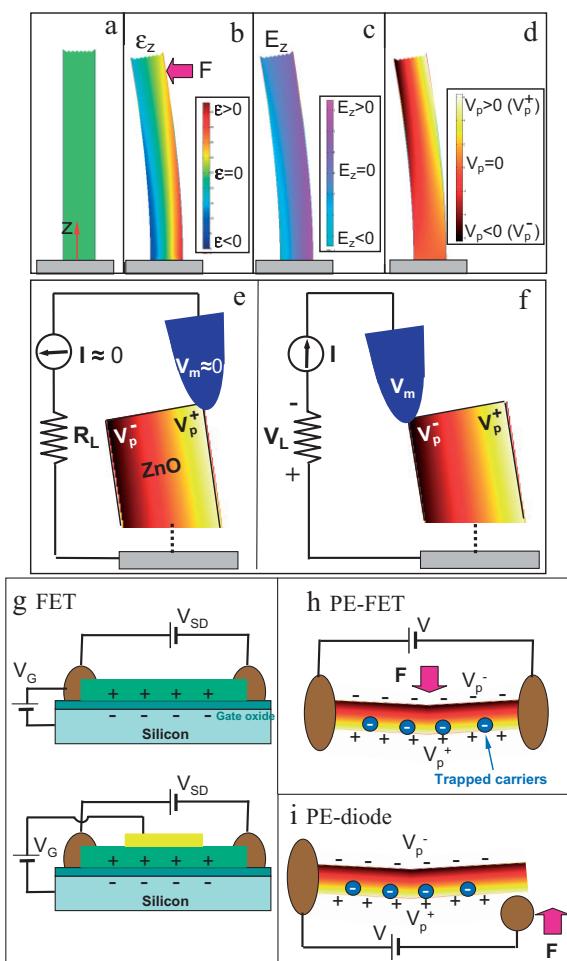


Figure 2. The physical principle of nanopiezotronics. a–d) The principle of the piezoelectric nanogenerator [3]: a) schematic definition of a nanobelt (NB) and the coordination system; b) longitudinal strain ε_z distribution in the NB after being deflected by an atomic force microscope (AFM) tip from the side; c) the corresponding longitudinal piezoelectric-induced electric field E_z distribution in the NB; d) potential distribution in the NB as a result of the piezoelectric effect; e) metal–semiconductor Schottky contact between the AFM tip and the semiconductor ZnO NB at reverse bias, which is responsible for separating and preserving the piezoelectric charges; f) metal–semiconductor Schottky contact between the AFM tip and the semiconductor ZnO NB at forward bias, which is responsible for releasing the accumulated piezoelectric charges. g) Schematics of conventional field-effect transistors (FETs) using a single nanowire/nanobelt, with gate, source, and drain. h) The principle of the piezoelectric field-effect transistor (PE-FET) [4], in which the piezoelectric potential across the nanowire created by the bending force F replaces the gate in a conventional FET. The contacts at both ends are Ohmic. i) The principle of the piezoelectric gated diode [6], in which one end is fixed and enclosed by a metal electrode, and the other end is bent by a moving metal tip. Both have Ohmic contact with ZnO. The piezoelectric potential V_p^+ at the tensile surface acts like the p–n junction in a conventional diode.

(negative strain ε ; Fig. 2b). An electric field E_z along the NB (z -direction) is then created inside the NB through the PZ effect, $E_z = \varepsilon_z/d$, where d is the PZ coefficient^[3] along the NB direction that is normally the positive c -axis of ZnO. The

PZ-field direction is closely parallel to the z -axis (NB direction) at the tensile surface and antiparallel to the z -axis at the compressed surface (Fig. 2c). Under the first-order approximation, as a result of flipping of the PZ field across the width of the NB, the electric potential distribution from the compressed to the stretched side surface is approximately between V_p^- (negative) to V_p^+ (positive). The electrode at the base of the NB is grounded. Note V_p^+ and V_p^- are the voltages produced by the PZ effect. The potential is created by the relative displacement of the Zn^{2+} cations with respect to the O^{2-} anions because of the PZ effect in the wurtzite crystal structure (see Fig. 1); thus, these ionic charges cannot freely move and cannot recombine without releasing the strain (Fig. 2d). The potential difference is maintained as long as the deformation is in place and no foreign free charges (such as from the metal contacts) are injected. The process shown in Figure 2a–d is the fundamental principle of piezotronics for creating functional devices such as the nanogenerator, piezoelectric transistor, and piezoelectric diode.

2. Results

2.1. Nanogenerators

The physical principle for creating and separating the PZ charges in the NB (see Fig. 2a–d) is the first half of a nanogenerator^[4] for converting mechanical energy into electricity. Then, the preserving and discharging is the second half of the nanogenerator, which is a coupling process of piezoelectric and semiconducting properties.

We now consider the discharge process. In the first step, the atomic force microscope (AFM) conductive tip that induces the deformation force F is in contact with the stretched surface of positive potential V_p^+ (Fig. 2e). The metal tip has a potential of nearly zero, $V_m=0$, so the metal tip/ZnO interface is negatively biased for $\Delta V = V_m - V_p^+ < 0$. Considering the n-type semiconductor characteristic of the as-synthesized ZnO NBs, the metal/ZnO semiconductor (M/S) interface in this case is a reverse-biased Schottky diode (Fig. 2e), and little current flows across the interface. This is the process of preserving and accumulating charges.

In the second step, when the AFM tip is in contact with the compressed side of the NB (Fig. 2f), the metal tip/ZnO interface is positively biased for $\Delta V = V_L = V_m - V_p^- > 0$. The M/S interface in this case is a positively biased Schottky diode, and it produces a sudden increase in the output electric current. The current is the result of ΔV driven flow of electrons from the semiconductor ZnO NB to the metal tip. The flow of the free electrons from the loop through the NB to the tip will neutralize the ionic charges distributed in the volume of the NB and thus reduce the magnitude of the potentials V_p^- and V_p^+ . This is the process of outputting piezoelectric charges. The principle demonstrated in Figure 2 is the fundamental of nanopiezotronics.

2.2. Piezoelectric Field-Effect Transistors

Field-effect transistors (FETs) based on nanowires/nanotubes are one of the most studied nanodevices. A typical NW FET is composed of a semiconducting NW that is connected by two electrodes at the ends and placed on a silicon substrate covered by a thin layer of gate oxide. A third electrode is built between the NW and the gate oxide (Fig. 2g). The electric signal output from the drain electrode of the NW is controlled by a gate voltage applied between the gate and the NW. An NW-based sensor is a source–drain structured NW FET without a gate, thus, a large portion of the NW is exposed to the environment. The mechanism of NW sensors for sensing gases, biomolecules, or even viruses relies on the creation of a charge depletion zone in the semiconductor NW by the surface adsorbed sensing targets.^[5]

By connecting a ZnO NW across two electrodes that can apply a bending force to the NW, the electric field created by piezoelectricity across the bent NW serves as the gate for controlling the electric current flowing through the NW (Fig. 2h).^[5] Once deformed by an external force F , a piezoelectric potential is built across the bent NW, and some free electrons in the n-type ZnO NW may be trapped at the surface of the positive side and become nonmovable charges, thus, lowering the effective carrier density in the NW. On the other hand, even though the positive-potential side could be partially neutralized by the trapped electrons, the negative potential side remains unchanged. The free electrons will be repulsed away by the negative potential and leave a charge depletion zone around the compressed side surface. Consequently, the width of the conducting channel in the ZnO NW becomes smaller and smaller while the depletion region becomes larger and larger with the increase of the NW bending. Therefore, the role played by the piezoelectric-induced field across the width of the NW (Fig. 2h) is analogous to the case of applying a gate voltage across the width of the ZnO NW as for a typical NW FET (Fig. 2g). The process shown in Figure 2h gives a good explanation of the transport property of a ZnO NW as observed by Lin et al.^[6]

2.3. Piezoelectric Nanosensors

As illustrated in the last section, the PE-FET can be turned “on” or “off” by applying mechanical force/pressure to bend a NW/NB. A nanometer-sized force/pressure sensor has been demonstrated for measuring forces in the nanonewton range and even smaller.^[7] Since the bending curvature of the NW is directly related to the force applied to it, the mechanical force can be retrieved from its bending shape, which is the principle of the force sensor. Based on the principle shown in Figure 2, a zero-power sensor can also be designed.

2.4. Piezoelectric-Gated Diodes

A piezoelectric-gated diode^[8] was demonstrated using a two-probe technique.^[6] The difference between a PE diode

from a PE-FET is that only one side of the bent NB is in contact with the probe. One probe holds the stationary side of the NB, and the other probe bends the NB from the tensile side (Fig. 2i).

The observed diode effect may be explained using the mechanism demonstrated in Figure 2a–d. When the probe pushes a NB and bends it, a positive potential is produced at the stretched side of the NB due to the piezoelectric effect. As a result, a potential barrier V_p^+ is produced at the interface between the tip and the NB with the NB being at the higher potential. Such an energy barrier may effectively serve as a p–n junction barrier at the interface that resists the current flow from the tip to the NB, but current can flow from the NB to the tip. The magnitude of the barrier increases with the increase of the degree of NB bending, resulting in a drastic increase of the rectifying effect. This is a simple piezoelectric field gated diode.^[6]

3. Perspectives

Based on the semiconducting and piezoelectric coupled properties, several important prototype devices, such as nanogenerators, PE-FETs, piezoelectric diodes, and piezoforce/pressure sensors, have been demonstrated. These devices are the fundamental components of nanopiezotronics.

Piezotronics based on nanowires/nanobelts as the fundamental building blocks have the following unique advantages: First, the NW-based nanogenerators can be subjected to extremely large deformation, so they can be used for flexible electronics as a flexible/foldable power source. Secondly, the large degree of deformation that can be withstood by the NWs is likely to result in a larger volume density of power output. Third, ZnO is a biocompatible and biosafe material;^[9] it has great potential as an implantable power source within the human body. Fourth, the flexibility of the polymer substrate used for growing ZnO NWs/NBs makes it feasible to accommodate the flexibility of human muscles so that we can use the mechanical energy (body movement, muscle stretching) in the human body to generate electricity.^[10] Fifth, ZnO NW/NB nanogenerators can directly produce current as a result of their enhanced conductivity with the presence of oxygen vacancies. Finally, ZnO is an environmentally “green” material. The phenomena we have demonstrated for ZnO can also be applied to other wurtzite-structured materials, such as GaN and ZnS.

The future in nanotechnology research lies in the area from single devices, to arrays of devices with multifunctionality, to an integrated nanosystem. It is important to find various approaches that are feasible for harvesting energy and recycling energy from the environment to self-power a nanosystem so that it can operate wirelessly, remotely, and independently with a sustainable energy supply. It is also important to develop zero-power sensors that respond to a change in the environment. The principle demonstrated for the piezoelectric nanogenerator could be the foundation for self-powered

nanosystems. It also has the potential to harvest/recycle energy from the environment and/or recycle energy that is wasted, such as the energy when walking.

The piezoelectric FETs and diodes are outstanding examples of devices made using piezoelectric NWs and NBs. Based on the electromechanical coupled properties of the nanostructures, novel and unique applications will be explored in areas of sensors, actuators, switches, and microelectrochemical systems (MEMS).

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