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Piezotronic and Piezophototronic Effects

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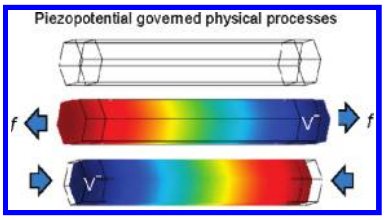
ABSTRACT Owing to the polarization of ions in a crystal that has noncentral symmetry, a piezoelectric potential (piezopotential) is created in the material by applying a stress. The creation of piezopotential together with the presence of Schottky contacts are the fundamental physics responsible for a few important nanotechnologies. The nanogenerator is based on the piezopotential-driven transient flow of electrons in the external load. On the basis of nanomaterials in the wurtzite semiconductors, such as ZnO and GaN, electronics fabricated by using a piezopotential as a gate voltage are called piezotronics, with applications in strain/force/pressure-triggered/controlled electronic devices, sensors, and logic gates. The piezophototronic effect is a result of three-way coupling among piezoelectricity, photonic excitation, and semiconductor transport, which allows tuning and controlling of electro-optical processes by a strain-induced piezopotential.



Piezoelectricity is a well-known effect that involves the production of an electrical potential in a substance as the pressure on it changes. This effect has been widely used for fabricating electromechanical sensors, actuators, and energy converters. The most well-known material that has a piezoelectric effect is $Pb(Zr,Ti)O_3$ (PZT). However, PZT is an electric insulator, and it is less useful for building electronic devices. Piezoelectric materials that are used for fabricating electronic and optoelectronic devices are required to be semiconductors, such as ZnO, GaN, InN, and ZnS.

One of the most common electronic devices is a single-channel field effect transistor (FET) based on a semiconductor nanowire, in which a source and drain are located at the two ends of the device and a gate voltage is applied to the channel and the substrate. By applying an external gate voltage, V_{ds}, at the source and drain, the charge carrier transport process in the semiconductor device is tuned/gated by the gate voltage V_g. We first suggested that the gate voltage can be replaced by the piezopotential in a piezoelectric nanowire, such as ZnO, so that the charge carrier transport process in FET can be tuned/gated by applying a stress to the device.[1,2] This type of device is called a piezotronic device as triggered or driven by a mechanical deformation action.[3,4] Alternatively, for a device with Schottky contacts at either or both the source or drain, by introducing a laser excitation at the source/drain, a coupling has been demonstrated among piezoelectricity, photoexcitation, and semiconductor characteristics, leading to the piezophototronic effect.[5] This Perspective is to introduce the principle and potential applications of the devices fabricated based on piezotronic and piezophototronic effects.

Piezopotential. We now use ZnO to elaborate on the piezopotential. For a crystal that lacks a center symmetry, the Zn^{2+} cations and O^{2-} anions are tetrahedrally coordinated. Under a strain-free condition, the center of the positive charges and the center of negative charges overlap, with zero dipole moment. If a stress is applied at an apex of the tetrahedron, the center of the cations and the center of the anions are relatively displaced, resulting in a dipole moment. A constructive addition of the dipole moments created by all of the units in the crystal results in a macroscopic potential drop along the strain direction in the crystal. This is the piezoelectric potential (piezopotential).[5,6] The piezopotential is created by the nonmobile, nonannihilative ionic charges, and the piezopotential remains in the crystal as long as the stress remains, although its magnitude depends on the density of doping.

The principle of the nanogenerator is a transient flow of electrons in an external load as driven by the piezopotential.

The distribution of the piezopotential in a ZnO nanowire has been calculated using the Lippman theory.[7] For simplicity, we first ignore doping in ZnO, so that it is assumed to be an insulator. For a one-end fixed free-standing nanowire that is transversely pushed by an external force, the stretched side and the compressed side surfaces exhibit a positive and negative piezopotential (Figure 1a), respectively, which can act as a transverse voltage for gating the charge transport along the nanowire.[1] An alternative geometry is a simple two-end bonded single wire with a length of 1200 nm and a hexagonal side length of 100 nm (Figure 1b).[8] When a

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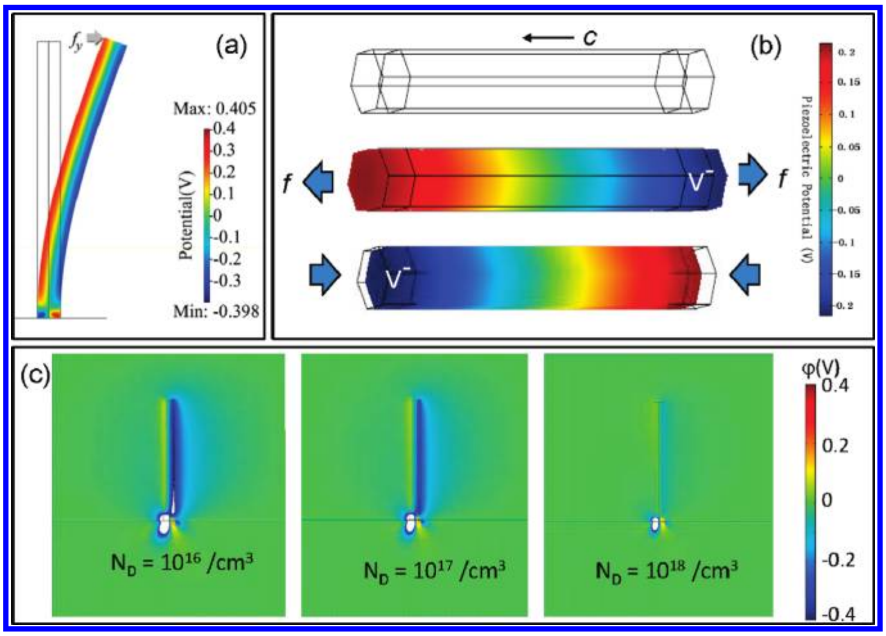

Figure 1. Numerical calculation of the piezoelectric potential distribution in a ZnO nanowire under transverse and longitudinal deformation. (a) A one-end fixed free-standing nanowire that is transversely bent without doping (from ref 7). (b) A two-end bonded nanowire under axial strain without doping (from ref 8). The growth direction of the nanowire is along the *c*-axis. (c) Color plot of the calculated piezoelectric potential at the side cross section of the nanowire with different donor concentrations. The dimensions of the nanowire are L = 600 nm and a = 25 nm; the external force is f_y = 80 nN (from ref 10).

stretching force of 85 nN is uniformly acting on the nanowire surfaces surrounded by electrodes in the direction parallel to the *c*-axis, it creates a potential drop of approximately 0.4 V between the two end sides of the nanowire with the +*c*-axis side of higher potential. When the applied force changes to a compressive, the piezoelectric potential reverses with the potential difference remaining 0.4 V but with the −*c*-axis side at a higher potential.

A common characteristic is that the piezoelectric potential continuously drops from one side of the nanowire to the other, which means that the electron energy continuously increases from the one side to the other. Meanwhile, the Fermi level will be flat all over the nanowire when equilibrium is achieved since there is no external electrical field. As a result, the effective barrier height and/or width of the electron energy barrier between ZnO and the metal electrode will be raised at one side and lowered at the other side, which can be observed experimentally as an asymmetric $I-V$ characteristic. This is the piezotronic effect.[8]

The piezopotential has several characteristics. First, the magnitude of the piezopotential depends on the degree of deformation. In the linear elasticity range, the piezopotential is proportional to the strain in the crystal. Second, the polarity of the piezopotential switches as the strain is changed from tensile to compressive. Finally, if the crystal has a finite doping or point defects, such as oxygen vacancies or Zn interstitials, the piezopotential could be partially or totally screened, depending on the density of the doping.[9]

The above calculation assumes that there are no free charge carriers in ZnO, which may deviate from the practical case because ZnO is believed to have point defects caused by oxygen vacancies and/or Zn interstitials. The as-synthesized ZnO nanostructures are typically n-type with a typical donor concentration of $\sim 10^{17}\,\mathrm{cm}^{-3}$. Theoretical calculations based on statistical electron distribution in the conduction band show that the free electrons tend to accumulate at the positive potential side of the nanowire at thermal equilibrium.[9] Therefore, the effect of the free carriers is to partially, if not completely, screen the positive piezoelectric potential with no change to the negative piezoelectric potential. Figure 1c presents the calculated result of the donor concentration on the equilibrium piezoelectric potential.[10] As for a free-standing nanowire, the electric potential in the stretched side, showing a positive potential, is much more sensitive than the negative side to the increase of donor concentration N_D. The electric potential is almost completely screened for $N_D = 10^{18}$ cm^{-3}. The reason for the screening of the potential in the compressed side of the nanowire is that free electrons will be depleted in this region, while they will accumulate at the stretched side. Moreover, the decrease of the positive potential is due to the inflow of free electrons from the substrate reservoir, where free charges are abundant.

The creation of a piezopotential in the crystal can be applied to a few key applications. It can be used for converting mechanical energy into electricity, such as the nanogenerator.[6,11−14] A transient flow of electrons in an external load as driven by the piezopotential is the principle of the nanogenerator. A continuous alternating flow of electrons is possible if the piezopotential is continuously changed by applying a dynamic stress. This means that the nanogenerator gives continuous output power if the applied stress is varying, which means inputting mechanical work. The output voltage has been raised up to 1.2 V by integration of the contributions made by many nanowires.[15] The nanogenerator has been demonstrated to be able to power

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a nanosensor,[15] achieving a key step toward self-powered nanodevices/nanosystems.[6] We anticipate that the nanogenerator can play an important role in energy harvesting for the sustainable and self-sufficient micro/nanosystems.[16,17] Nanogenerators have also been demonstrated by other groups using different materials.[18−20] We now focus on the two new effects introduced by the piezopotential.

Piezotronics. When a semiconductor crystal is strained, two typical effects are observed. One is the piezoresistance effect, which is introduced because of the change in band gap and possibly density of states in the conduction band. This effect has no polarity; therefore, it has an equivalent effect on the source and drain of the FET. On the other hand, the piezopotential is created in the crystal if the material is also piezoelectric. Since the piezopotential has polarity, it can tune the effective heights of the Schottky barriers at the source and drain in opposite directions. This is a nonsymmetric effect. Devices fabricated by using the piezopotential as the gate voltage are called piezotronic devices.[3,4]

Electronics fabricated by using a piezopotential as a gate voltage are called piezotronics.

A simple piezotronic device is a polarity-switchable diode that is made of a ZnO nanowire contacted with silver paste at the two ends on a PDMS polymer substrate.[8,12,13] From the initial *I*−*V* curve shown in Figure 2a, the symmetric shape of the curve indicates that the Schottky barriers present at the two contacts are about equal in height. The equivalent circuit model of the device is a pair of back-to-back Schottky diodes, as illustrated in Figure 2b. Under tensile strain, the piezoelectric potential at the right-hand side of this nanowire was lower (denoted by blue color in Figure 2b), which raised the energy of the electrons in the conduction band; thus, the Schottky barrier height became higher (denoted by a large diode symbol in Figure 2b). Since the positive piezoelectric potential was partially screened by free electrons, the Schottky barrier height at the left-hand side remained almost the same. As a result, under positive bias voltage with the left-hand side positive, the current transport was determined by the reverse biased Schottky barrier at the right-hand side. While under the reverse biased voltage with the right-hand side positive, the current transport depended on the reverse biased Schottky barrier at the left-hand side, which had a much lower barrier height than the right-hand one. Experimentally, the device thus exhibited a rectifying behavior in the positive voltage region, and the *I*−*V* curve in the negative voltage region overlapped with that of the original curve without straining. By the same token, under compressive strain, the device exhibited a rectifying behavior in the negative voltage region, and the *I*−*V* curve in the positive voltage region overlapped with that of the original curve without straining, as shown by the green line in Figure 2a and c.

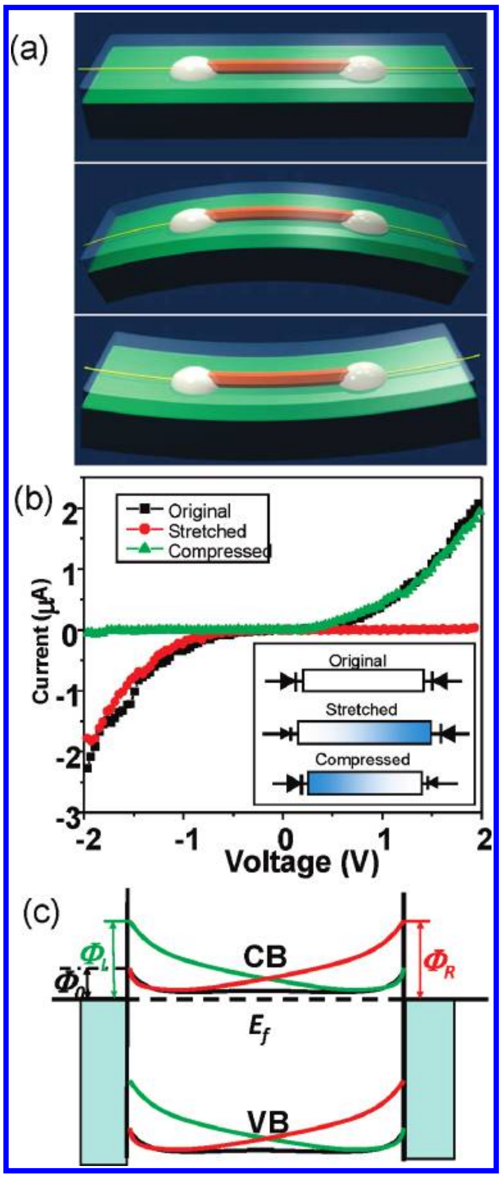

Figure 2. Piezotronic strain sensor/switch. (a) Schematic of a two-end bonded nanowire device on a polymer substrate. The bending of the substrate creates tensile or compressive strain in the nanowire. (b) Changes of transport characteristics of a Ag/ZnO nanowire/Ag device from symmetric *I*−*V* characteristic (black) to asymmetric rectifying behavior when stretching (red) and compressing (green) the wire. The inset is the equivalent circuit models of the device corresponding to the observed *I*−*V* curves; different sizes of diode symbol are used to illustrate the asymmetric Schottky contacts at the two ends of the nanowire. The blue side is the negative potential side, and the other side is the positive side. (c) Schematic energy band diagrams illustrating the changes of Schottky barriers from symmetric (black) to asymmetric under tensile strain (red) and compressive strain (green), corresponding to the *I*−*V* curves in (b) (from ref 10).

Piezophototronics. As demonstrated in Figure 2, strain can effectively increase the height of the Schottky barrier in a ZnO wire based device, allowing a fine-tuning of the electric transport property of the device. In contrast, the effective height of the Schottky barrier can be lowered by shining a laser beam at the local contact with the excitation energy larger than the band gap,[14] which increases the density of the local electron−hole pairs and the change of barrier profile due to charge separation/redistribution. By controlling the magnitude of the strain and the intensity of the laser beam, we can effectively tune the charge-transport property from Schottky to Ohmic or from Ohmic to Schottky. This study describes a new principle for controlling the coupling among mechanical, photonic, and electrical properties of ZnO nanowires, which can be the basis for fabricating piezophotonic−electronic nanodevices. Therefore, the piezophototronic effect involves the tuning and controlling of electro-optical processes by a strain-induced piezopotential.[5]

> **The piezophototronic effect is a result of three-way coupling between piezoelectricity, photonic excitation, and semiconductor transport, which allows tuning and controlling of electro-optical processes by a strain-induced piezopotential.**

To illustrate the piezophototronic effect, we have fabricated a two-end bonded ZnO wire device. Owing to the variation in local contacts, the device shows an asymmetric $I-V$ transport property. Both the piezoelectric effect and photoexcitation intensity can tune the $I-V$ transport property of a ZnO microwire device, but they act in opposite directions. If we refer to one end of the device as A, by shining the laser at contact A of the device, as the relative intensity of the light is changed via optical filters from a transmission coefficient of $T = 0.001$ to 1, the $I-V$ curve is largely tuned (Figure 3a). Fine-tuning of the magnitude of mechanical strain and the intensity of the light illumination can produce a designed shape of the $I-V$ characteristic. Figure 3b shows the coupled tuning of the two effects on the $I-V$ shape. By choosing a strain of -0.2% and a relative light intensity of $T = 0.01$ (green curve), the observed $I-V$ curve matches the original $I-V$ curve obtained without applying a strain or laser excitation (dark curve) well. This experiment shows the possibility of controlling the $I-V$ characteristic of a nanowire device by the piezophototronic effect.[5]

The piezopotential is created in a piezoelectric material by applying a stress, and it is generated by the polarization of ions in the crystal. Following our first few studies,[1−4] the effect of the piezopotential on various electronic devices has also been studied by various groups.[21−26] The nanogenerator is based on the piesopotential-driven transient flow of electrons in the external load.[6,11−15] Mechanical energy has been converted into chemical energy by splitting water using a piezopotential stimulated redox reaction.[27] Electronics fabricated by using piezopotential as a gate voltage established a new approach for fabricating strain/force/pressure-triggered/controlled electronic devices, sensors, and logic gates (Figure 4).[4]

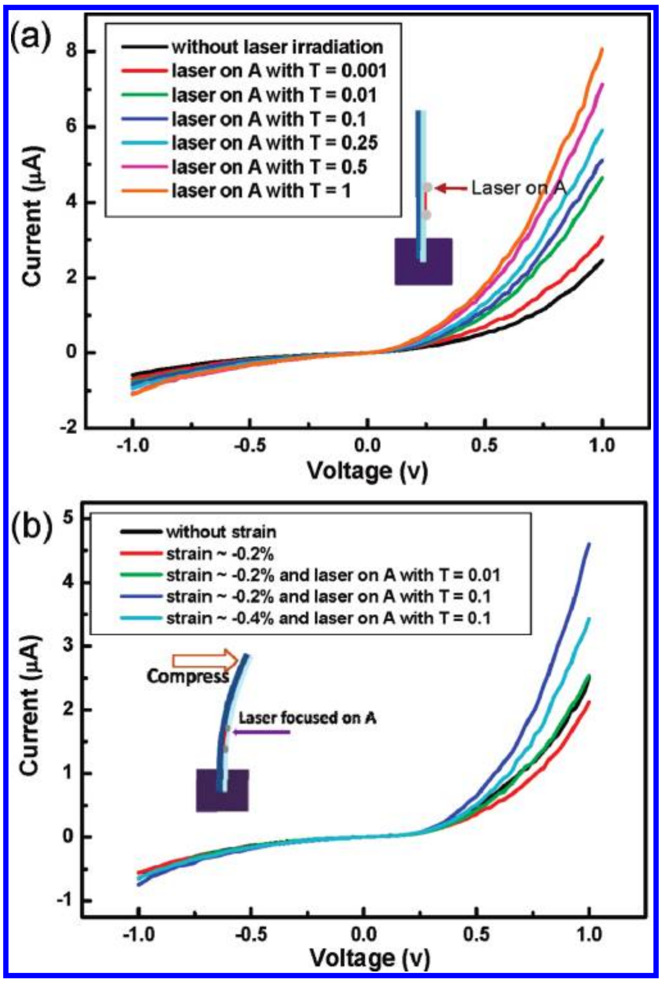

Figure 3. Piezophototronic effect by coupling among piezoelectric, photon excitation, and semiconductor properties. (a) Tuning the $I-V$ transport characteristic of a device by controlling the intensity of the excitation laser focused at contact A via optical filters from transmission coefficient $T = 0.001$ to 1, without strain. (b) Design and control of the transport properties of the device by coupling the intensity of the illuminating laser and the degree of strain in the microwire, showing the basic principle of piezophototronics (from ref 5). The insets are the corresponding configurations of the two-end bonded nanowire device.

Piezophototronics are a result of three-way coupling among piezoelectricity, photonic excitation, and semiconductor transport.[5] This effect allows tuning and controlling of the electro-optical process by a strain-induced piezoelectric potential, with potential applications in light-emitting diodes, photocells, and solar cells (Figure 4).

Materials that are candidates for piezotronics and piezophototronics are mainly the wurtzite family, including but not limited to ZnO, GaN,[28,29] InN, and CdS.[30] Among these materials, ZnO is probably the only nanomaterial that can be grow at a large scale by a chemical approach at <100 °C. The remaining nanomaterials have to be grown in the vapor phase, which usually requires a high temperature. We anticipate that the research in nanogenerators, piezotronics, and

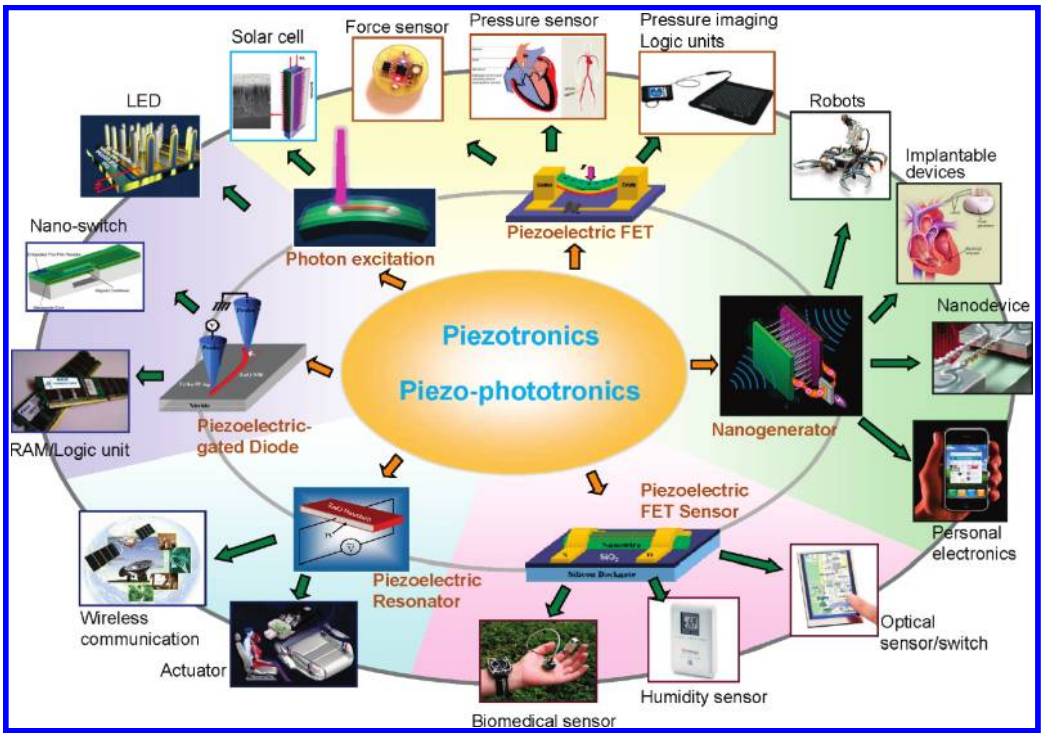

Figure 4. Potential applications of piezotronic and piezophototronic devices.

piezophototronics will not only impact the energy harvesting technologies for micro/nanosystems but also inspire the inventions of new electronic devices.

> We anticipate that research in nanogenerators, piezotronics, and piezophototronics will impact energy harvesting technologies for micro/nanosystems and inspire the invention of new electronic devices.

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