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Piezopotential Properties in Nanowire devices of ZnO

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Abstract : Polarization of ions in a crystal that has non-central symmetry, a piezoelectric potential (piezopotential) is created in the crystal by applying a stress. For materials such as ZnO, GaN, and InN in the wurtzite structure family, the effect of piezopotential on the transport behavior of charge carriers is significant due to their multiple functionalities of piezoelectricity, semiconductor and photon excitation. By utilizing the advantages offered by these properties, a few new fields have been created. Electronics fabricated by using innercrystal piezopotential as a ‘‘gate’’ voltage to tune/control the charge transport behavior is named piezotronics, with applications in strain/force/pressure triggered/controlled electronicdevices, sensors and logic units. Piezo-phototronic effect is a result of three-way couplingamong piezoelectricity, photonic excitation and semiconductor transport, which allows tuningand controlling of electro-optical processes by strain induced piezopotential. The objective of this review article is to introduce the fundamentals of piezotronics and piezo-phototronics and to give an updated progress about their applications in energy science and sensors.

Keywords: Piezoelectricity; ZnO ; Nanowire; wurtzite structure;Piezoresistance effect; Nanogenerator

Introduction

Piezoelectricity, a phenomenon known for centuries, is an effect that is about the production of electrical potential in a substance as the pressure on it changes. The most well known material that has piezoelectric effect is the provskite structured Pb(Zr, Ti)O3 (PZT), which has found huge applications in electromechanical sensors, actuators and energyenerators. But PZT is an electric insulator and it is less useful for building electronic devices. Piezoelectricity has itsown field and is being largely studied in the ceramic community. Wurtzite structures, such as ZnO, GaN, InN and ZnS, also have piezoelectric properties but they are not extensively used as much as PZT in piezoelectric sensors and actuators due to their small piezoelectric coefficient. Therefore, the study of wurtzite structures is mainly in the electronic and photonic communities due their semiconductor and photon excitation properties. In this review, we will explore the piezopotential [1—4] generated in the wurtzite structures and how to use it to serve as a ‘‘gate’’ voltage for fabricating new electronics [5,6]. One of the most common electronic devices is a single channel field effect transistor (FET) based on a semiconductor nanowire (NW), 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 [7,8]. By applying a source to drain driving voltage, VDS, the charge carrier transport process in the semiconductor device is tuned/gated by the gate voltage VG, which is an externally applied potential. Alternatively, the gate voltage can be replaced by the piezopotential generated inside the crystal (inner potential), so that the charge carrier transport process in FET can be tuned/gated by applying a stress to the device [9,10]. This type of device is called piezotronic device as triggered or driven by a mechanical deformation action. Alternatively, for a device with Schottky contacts at either or both of 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 piezo-phototronic effect [11]. This paper is to review the principle and potential applications of the piezotronics and piezo-phototronics. Piezoelectricity and piezopotential We now use ZnO to elaborate the structure and piezopotential in wurtzite family. Wurtzite crystal has a hexagonal structure with a large anisotropic property in c-axis direction and perpendicular to the c-axis. The crystal lacks of center symmetry, which is the core of piezoelectricity due to the intrinsic crystallographic structure. Simply, the Zn^{2+} cations and O^{2-} anions are tetrahedrally coordinated and the centers of the positive ions and negatives ions overlap with each other. Therefore, the crystal shows no polarization under strain-free condition. If a stress is applied at an apex of the tetrahedron, the center of the cations and the center of anions are relatively displaced, resulting in a dipole moment (Fig. 1A).

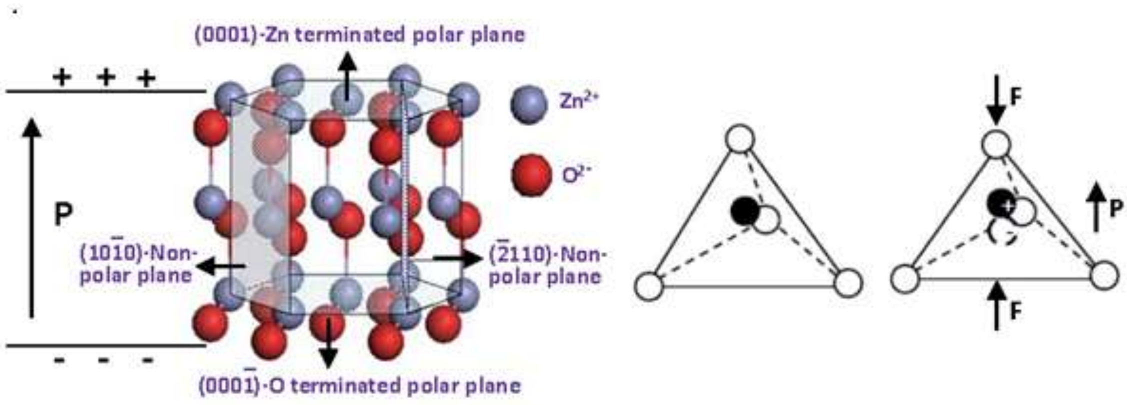

Figure 1A:Piezopotential in wurtzite crystal. Atomic model of the wurtzite-structured ZnO.

A constructive adds up of the dipolemoments created by all of the units in the crystal results ina macroscopic potential drop along the straining direction in the crystal. This is the piezoelectric potential (piezopotential).

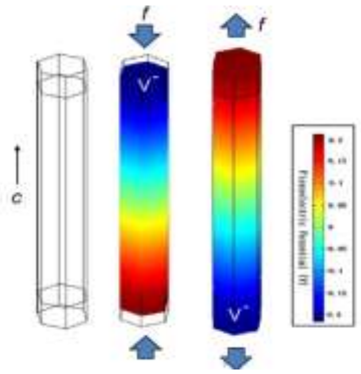

Figure :1BNumerical calculation of the piezoelectric potential distribution in a ZnO nanowire under axial strain. The growth direction of the nanowire is *c*-axis. The dimensions of the nanowire are L = 600nm and a = 25 nm; the external force is *fy* =80nN.

The piezopotential, an inner potential in the crystal, is created by the non-mobile, non-annihilativeionic charges, the piezopotential remains in the crystal as long as the stress remains. The magnitude of the piezopotential depends on the density of doping and the strain applied. The distribution of piezopotential in a ZnO NW has been calculated using the Lippman theory [12,13]. For simplicity, we first ignore doping in ZnO so that it is assumed to bean insulator. For a one-end fixed free-standing NW that is transversely pushed by an external force, the stretched side and the compressed side surfaces exhibit positive and negative piezopotential (Fig. 1B), respectively, which can act asa transverse voltage for gating the charge transport alongthe NW [1]. An alternative geometry is a simple two-end bonded single wire with a length of 1200nm and a hexagonalside length of 100nm [8]. When a stretching force of85 nN is uniformly acting on the NW surfaces surrounded by electrodes in the direction parallel to c-axis, it creates a potential drop of approximately 0.4 V between the two end sides of the NW 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. The presence of the piezo potential in the crystal has created a few new research fields. A nanogenerator has been developed for converting mechanical energy into electricity[1,14-17]. Once a strained piezoelectric crystal is connected at its two polar ends to an external electricload, the piezopotential creates a drop in the Fermi levels at the two contact ends, thus, the free electrons inthe external load are driven to flow from one side to the other to ‘‘screen’’ the local piezopotential and reach a new equilibrium. The generated current in the load is a result of the transient flow of electrons. An alternating flow of electrons is possible if the piezopotential is continuously changed by applying a dynamic stress across the crystal. This means that the nanogenerator gives continuous output power if the applied stress is varying, which means inputting mechanical work. The nanogenerator has been extensively developed and it is now gives an output of 3V,and the output power is able to drive a liquid crystal display(LCD), light emitting diode and laser diode [18-21]. The nanogenerator will play an important role in energy harvesting as the sustainable and self-sufficient power sources for the micro/nano-systems. We now introduce the electronic processes induced by the piezopotential in the next few sections.

Piezopotential gated electronic and photonic processes

Piezotronic and piezophotonic effects

A most simple FET is a two end bonded semiconductor wire, in which the two electric contacts at the ends are the source and drain, and the gate voltage can be applied either at the top of the wire through a gate electrode or at its bottom on the substrate. When a ZnO NW is strained axially along its length, two typical effects are observed. One is the *piezoresistance effect*, which is introduced because of the change in bandgap and possibly density of states in the conduction band. This effect has no polarity so that it has equivalent/ identical effect on the source and drain of the FET. On the other hand, piezopotential is created along its length. For an axial strained NW, the piezoelectric potential continuously drops from one side of the NW to the other, which means that the electron energy continuously increases from one side to the other. Meanwhile, the Fermi level will be flat all over the NW 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 metal electrode will be raised at one side and lowered at the other side, thus, it has a non-symmetric effect on the source and drain. This is the *piezotronic effect* [5]. A better understanding about the piezotronic effect is to compare it with the most fundamental structure in semiconductor devices: Schottky contact and p—n junction. When a metal and a n-type semiconductor forms a contact, a Schottky barrier (SB) ($e\ ø_{SB}$) is created at the interface if the work function of the metal is appreciably larger than the electron affinity of the semiconductor (Fig. 2A).

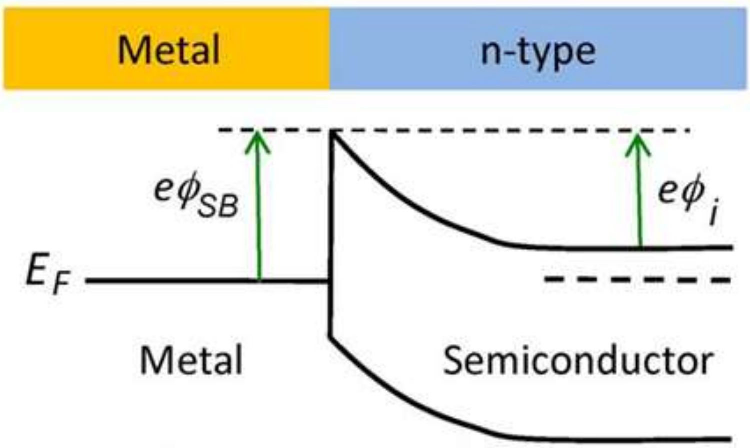

Figure 2A: Band diagram at a Schottky contacted metal—semiconductor interface.

Current can only pass through this barrier if the applied external voltage is larger than a threshold value (_*i*) and its polarity is with the metal side positive (for n-type semiconductor). If a photon excitationis introduced, the newly generated electron—hole pairs not only largely increase the local conductance, but also reduce the effective height of the SB as a result of charge redistribution (Fig. 2B).

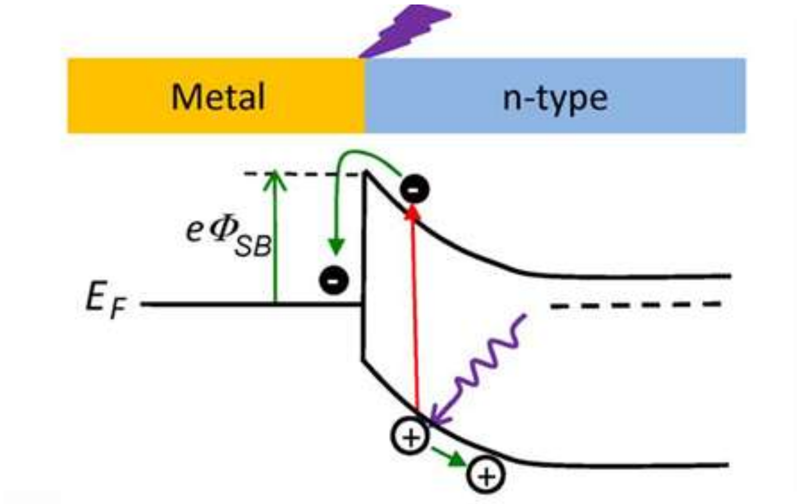

Figure 2B: Band diagram at a Schottky contact after exciting by a laser that has a photon energy higher than the bandgap, which is equivalent to a reduction in the Schottky barrier height.

Once a strain is created in the semiconductor that also has piezoelectric property, a negative piezopotential at the semiconductor side effectively increases the local SB height to *(e* ϕ_{SB}*)*(Fig. 2C), while a positive piezopotential reduces the barrier height.

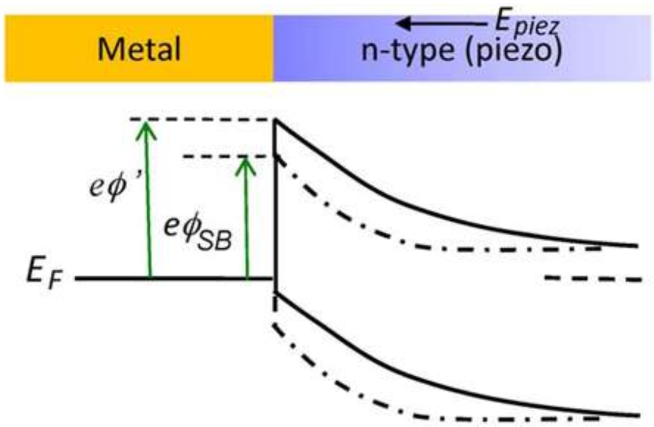

Figure 2C: Band diagram at the Schottky contact after applying a strain in the semiconductor. The piezopotential created in the semiconductor has a polarity with the end in contacting with the metal being low.

The polarity of the piezopotential is dictated by the direction of the *c*-axis for ZnO. The role played by the piezopotential is to effectively change thelocal contact characteristics through an internal field, thus, the charge carrier transport process is tuned/gated at the metal—semiconductor (M—S) contact. By considering the change in piezopotential polarity by switching the strain from tensile to compressive, the local contact characteristics can be tuned and controlled by the magnitude of thestrain and the sign of strain. This is the core of piezotronics. When a p-type and a n-type semiconductors form a junction,the holes in the p-type side and the electrons in then-type side tend to redistribute to balance the local potential, the interdiffusion and recombination of the electronsand holes in the junction region forms a charge depletionzone (Fig. 3A).

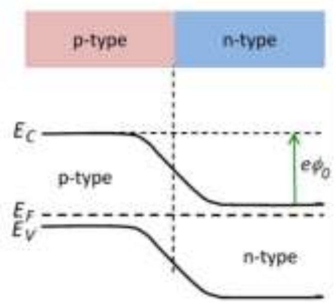

Figure 3A:Band diagram at a conventional pn junction made by two semiconductors have almostthe same bandgaps.

Once an external potential is applied across the junction with the n-type side positive, the width of the charge depletion zone is enlarged, thus, few charge carriers flow across it. But once the p-type side is applied with a positive bias and when the strength of the bias is high enough to overcome the barrier formed by the depletion zone, charge carrier can flow across the junction. This isthe working principle of the pn diode. With the creation of a piezopotential in one side ofthe semiconductor material under strain, the local band structure near the pn junction is changed/modified. For easy understanding, we include the screening effect of the charge carriers to the piezopotential in the discussion, which means that the positive piezopotential side in n-type material is largely screened by the electrons, while the negative piezopotential side is almost unaffected. By the same token, the negative piezopotential side in p-type material is largely screened by the holes, but leaves the positive piezopotential side almost unaffected. As shown in Fig. 3B for a case that the p-type side is piezoelectric and a strain is applied, the local band structure is largely changed, which significantly affects the characteristic of charge carriers flow through the interface.

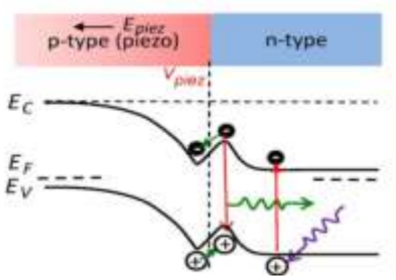

Figure 3B: Band diagram of the pn junction with the presence of a piezopotential at the p-type side with a polarityof higher potential at the junction side

This is the core of the piezotronic effect. In addition, the holes in the p-type side can drift to the n-type side to combine with the electrons in the conduction band, possibly resulting in an emission of photon. This is a process of piezopotential induced photon emission, e.g., *piezophotonics* [2]. The following conditions may need to be met in order to observe the piezophotonic process. The magnitude of the piezopotential has to be significantly large in comparison to *_i*, so that the local piezoelectric field is strong enough to drive the diffusion of the holes across the pn junction. The straining rate for creating the piezopotential has to be rather large, so that the charge carriers are driven across the interface within a time period shorter than the time required for charge recombination. The width of the depletion layer has to be small so that there are enough charge carriers available in the acting region of the piezopotential. Finally, a direct bandgap material is beneficial for the observation of the phenomenon. The fundamental working principles of the p—n junction and the Schottky contact are that there is an effective barrier that separates the charge carriers at the two sides to across. The height and width of the barrier are the characteristic of the device. In piezotronics, the role played by the piezopotential is to effectively change the width of p—n junction or height of SB by piezoelectricity.

1.1.2 Piezo-phototronic effect

For a material that simultaneously has semiconductor, photon excitation and piezoelectric properties, besides the well known coupling of semiconductor with photon excitation process to form the field of optoelectronics, additional effects could be proposed by coupling semiconductor with piezoelectric to form a field of piezotronics,and piezoelectric with photon excitation to form a fieldof piezophotonics. Furthermore, a coupling among semiconductor, photon excitation and piezoelectric is a field of *piezo-phototronics* [11], which can be the basis for fabricating piezo-photonic—electronic nanodevices. The piezo-phototronic effect is about the tuning and controlling of electro-optical processes by strain induced piezopotential (Fig. 4).

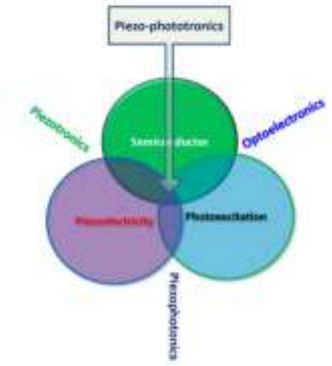

Figure 4: Schematic diagram showing the three-way coupling among piezoelectricity, photoexcitation and semiconductor, which is the basis of piezotronics

2.0 Piezotronic devices and applications

2.1 Piezodiode

A simple piezotronic device is a polarity switchable diode that is made of a ZnO NW contacted with metal contactsat the two ends on an insulator polymer substrate [22,23].From the initial *I*—*V* curve measured from the device before applying a strain as shown in Fig. 5A, the symmetric shape of the curve indicates that the SBs present at the two contacts are about equal heights. The equivalent circuit model of the device is a pair of back-to-back Schottky diodes, as illustrated in the inset in Fig. 5A.

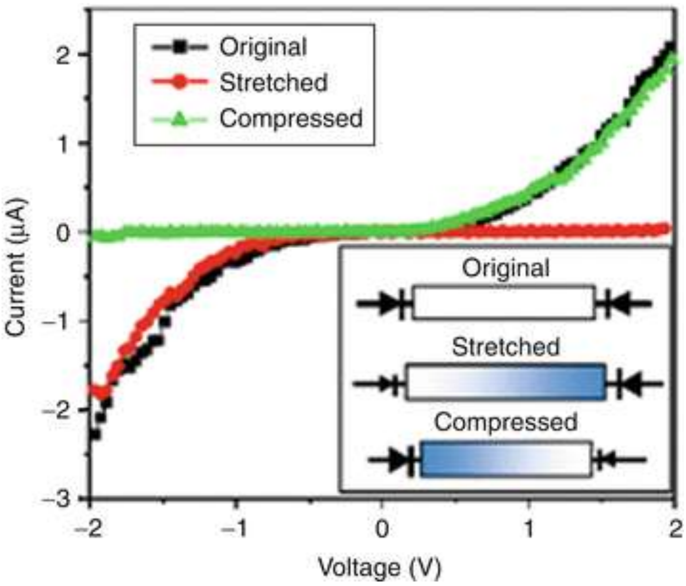

Figure 5A : Piezotronic strain sensor/switch. (A) Changes of transport characteristics of an Ag/ZnO-nanowire/Ag device from symmetric *I*—*V* characteristic (black) to asymmetric rectifying behavior when stretching (red) and compressing (green)the wire. The inset is the equivalent circuit models of the device in 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 thenegative potential side, and the other side is positive side

Under tensile strain, the piezoelectric potential at the right-hand side of this NW was lower (denoted by blue color in the inset in Fig. 5A), which raised the local barrier height (denoted by a large diode symbol in the inset). Since the positive piezoelectric potential was partially screened by free electrons, the SB height at the left-hand side remained almost unchanged. As a result, under positive bias voltage with the left-hand side positive, the current transport was determined by the reverse biased SB 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 SB at the left-handside, which had a much lower barrier height than the righthand side 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 Fig. 5A. Studies by others groups also support the proposed model [24—28].

Results and Discussion

Piezopotential is created in a piezoelectric material by applying a stress, and it is generated by the polarization of ions in the crystal. The introduction of this inner potential in semiconductor materials can significantly change/modify the band structure at a pn junction or metal—semiconductor Schottky barrier, resulting in significant change in the charge transport property.

Conclusion

This is the core science of piezoelectricity on electronic and photonic devices. Piezotronics is about the electronics fabricated by using piezopotential as a ‘‘gate’’ voltage for controlling the charge transport process. Its applications have been demonstrated as diode, strain/force/sensors, triggers, and logic gates. Although the response time of the piezotronics is slower than the conventional CMOS technology and it is mostly likely to work at lower frequencies, the functionality itoffers are complimentary to CMOS technology. An effective integration of piezotronic and piezo-phototronic devices with silicon based CMOS technology, unique applications can be found in areas such as human—computer interfacing, sensing and actuating in nanorobotics, smart and personalized electronic signatures, smart MEMS/NEMS.

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