4 Nanopiezotronics and Nanogenerators

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Abstract Today’s nanoelectronics rely on the transport of charge carriers under the driving of externally applied voltage to perform specific functionality, such as transistors and diodes. Recently, Piezotronics was introduced as a new field in nanoelectronics[1,2]. It utilizes the coupled piezoelectric and semiconducting property of nanowires (NWs) and nanobelts (NBs) for designing and fabricating electronic devices such as transistors and diodes. Piezoelectricity is a coupling between a material’s mechanical and electrical behavior. When a piezoelectric crystal is mechanically deformed, the positive- and negative-charge centers are displaced with respect to each other. Therefore, 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. Once the piezoelectric materials are also semiconductors, such as ZnO, their electronic characteristic can be affected by the piezoelectric potential. This phenomenon becomes more obvious when the crystal size is in nanometer regime and so it is also called nano-Piezotronics. 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.

In this chapter, ZnO, as a typical and widely studied piezotronic material, is reviewed in detail from the origin of its piezoelectric property to the novel nanodevices made from piezotronic ZnO NWs.

Keywords ZnO nanowire, nanogenerator, piezopotential, piezotronics

4.1 Piezotronic Property of ZnO Nanowires

4.1.1 Crystal Structure of ZnO

Zinc oxide has a Wurtzite hexagonal structure (space group P63mc) with lattice
parameters $a=0.3296$, and $c=0.52065$ nm. The structure of ZnO can be simply described as a number of alternating planes composed of $\text{O}^{2-}$ and $\text{Zn}^{2+}$ ions, stacked alternatively along the c-axis (Fig. 4.1(a)). The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(0001) polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis. Such spontaneous polarization leads to the self-assembly of novel nanostructures like nanorings and nanosprings, which are driven by the minimization of electrostatic energy coming from the ionic charges on the polar surfaces. Inside the crystal, $\text{O}^{2-}$ and $\text{Zn}^{2+}$ ions are tetrahedrally coordinated, which results in a non-central symmetric structure. The lack of a center of symmetry, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in actuators$^{[3]}$, piezoelectric sensors$^{[4,5]}$, piezoelectric diodes$^{[6]}$ and nanogenerators (NGs)$^{[7]}$. To illustrate the piezoelectric effect, consider a zinc atom with positive charge that is surrounded tetrahedrally by negatively charged oxygen anions (Fig. 4.1(b)). Strong piezoelectric effect can be observed along ZnO [0001] crystal direction. Once the {0001} is the biggest surface of a ZnO nanobelt, the effective piezoelectric coefficient $d_{33}$ has been measured 14 pm/V, which is larger than that of the bulk (0001) ZnO, 9.93 pm/V$^{[8]}$.

![Figure 4.1](image)

*Figure 4.1* (a) Wurtzite structure model of ZnO. (b) The tetrahedral coordination of Zn-O and the corresponding Polarization of ions under stress (see color figure at the end of this book)

### 4.1.2 Piezoelectricity of ZnO Nanowire

A ZnO NW is a beam-like structure that always grows along its [0001] direction.