www.MaterialsViews

A Review of Mechanical and Electromechanical Properties of Piezoelectric Nanowires

Horacio D. Espinosa,* Rodrigo A. Bernal, and Majid Minary-Jolandan

Piezoelectric nanowires are promising building blocks in nanoelectronic, sensing, actuation and nanogenerator systems. In spite of great progress in synthesis methods, quantitative mechanical and electromechanical characterization of these nanostructures is still limited. In this article, the state-of-the art in experimental and computational studies of mechanical and electromechanical properties of piezoelectric nanowires is reviewed with an emphasis on size effects. The review covers existing characterization and analysis methods and summarizes data reported in the literature. It also provides an assessment of research needs and opportunities. Throughout the discussion, the importance of coupling experimental and computational studies is highlighted. This is crucial for obtaining unambiguous size effects of nanowire properties, which truly reflect the effect of scaling rather than a particular synthesis route. We show that such a combined approach is critical to establish synthesis-structureproperty relations that will pave the way for optimal usage of piezoelectric nanowires.

1. Introduction

ADVANCED MATERIAL

Nanowires are envisioned as fundamental building blocks of future electronic, electromechanical, optoelectronic, sensing and actuation nanosystems.^[1] Given the remarkable progress in their synthesis in the last two decades,^[1,2] researchers have been able to demonstrate unique and novel nanosystems with unprecedented functionality; for example, high-mobility single-nanowire transistors,^[3] strain-controlled logic gates,^[4] single-nanowire lasers^[5] and strain sensors.^[6] The majority of these and other new applications of nanowires are largely possible as a result of the enhancement of the material properties at the nanoscale (such as size effects) including mechanical^[7] and electromechanical^[8–10] properties.

Among nanowires, those that exhibit piezoelectricity, for example, semiconducting wurtzite compounds (e.g., ZnO and GaN) or ferroelectrics (e.g., PZT, BaTiO₃), are technologically relevant and have received increased attention because usage

Prof. H. D. Espinosa, R. A. Bernal,^[+]
Dr. M. Minary-Jolandan^[+]
Department of Mechanical Engineering
Northwestern University
2145 Sheridan Road, Evanston, IL60208-3111, USA
E-mail: espinosa@northwestern.edu
[+] These authors contributed equally to this work

DOI: 10.1002/adma.201104810



of piezoelectric properties often results in nanosystems with high functionality. For instance, the combination of semiconducting and piezoelectric properties is important in core-shell optoelectronic heterostructures where a direct bandgap, combined with piezoelectric polarization fields created by lattice mismatch, are critical for the operation of the devices.^[11] Strain sensors with increased sensitivity, provided by the piezoelectric effect, are also possible.^[6] Another example, which perhaps has received the most attention, are nanogenerators^[12] where piezoelectricity is employed to convert mechanical energy to electrical energy for the operation of low-power electronics.^[13] Initial demonstrations of these devices were based on atomic force microscopy (AFM)induced bending of individual and arrays of semiconducting nanowires.[12] More recently, nanogenerators have been manu-

factured from systems consisting of millions of nanowires.^[14] Furthermore, nanogenerators employing traditional piezoelectric materials such as lead-zirconate-titanate (PZT)^[15] and flexible piezoelectric polymers such as poly(vinylidene fluoride) PDVF^[16] have also been demonstrated.

Although all these applications are very promising, they are still years away from being commercially available, mostly due to issues of reliability and robustness,^[17] as well as performance optimization, which remain to be addressed. For performance optimization it is desirable to know which set of nanowire morphological (diameter, length), structural (crystal structure, defect type and density, etc.), and electrical properties (conductivity, polarizability) gives the best performance for a particular application. Likewise, the effect such features have on their reliability is important. Furthermore, given that the size-induced enhancement of properties, e.g., mechanical^[7] and electromechanical,^[8] have been primarily reported for nanowire diameters below 100 nm, their detailed characterization in this size range is critical to the development of optimized nanosystems.

Characterizing and developing a mechanistic understanding of mechanical and electromechanical properties in nanostructures with characteristic dimensions below 100 nm has been challenging and required the development of new experimental, computational, and theoretical approaches. As it will be shown in this article, measurement of properties through a particular experimental technique is not sufficient to fully understand the behavior of nanostructures.



www.MaterialsViews.com

The challenging nature of experimentation and modeling at the nanoscale requires comparison between measurements and first-principles atomistic calculations in order to discard methodological artifacts and bridge the gap between theoretical and experimental investigations. Unambiguous property characterization can then emerge. Additionally, experimental approaches are usually not sufficient to establish mechanistic explanations for a particularly measured material behavior. Moreover, thorough structural characterization of the specimens must be performed in order to identify and quantify the presence of defects and impurities (e.g., dopants) and their influence on measured properties. This is of critical importance in nanoscale research because different synthesis routes can produce nanostructures that, although made of the same material and with similar morphological characteristics, may display different properties because of defects and impurities introduced (either intentionally or unintentionally) during synthesis.

For the particular case of mechanical and electromechanical characterization of piezoelectric nanowires, a combined experimental-theoretical methodology is provided in Figure 1. For structural and elemental characterization of nanostructures, high-resolution transmission electron microscopy (HRTEM) and atom probe tomography (APT)^[18] are employed because of their high resolution in the identification of defects, crystalline structure, and chemical composition. The outcomes of these characterizations are used as inputs for atomistic studies where first-principle calculations are directly employed or used to validate semi-empirical force fields employed in molecular mechanics (MM) and molecular dynamics (MD) simulations. The results of these simulations are compared with experimental measurements, and complemented by thorough structural and elemental characterization of the tested specimen, allowing the establishment of synthesis-structure-property relationships. The continued development of these different techniques, as will be shown in the following sections, has allowed the discovery of several size effects in mechanical and electromechanical behavior of piezoelectric nanowires. Nevertheless, additional research remains to be pursued in order to gain a fundamental understanding of these properties in nanostructures. In turn, this fundamental understanding should pave the way to design optimized nanowire systems for electronic, electromechanical, and optoelectronic applications.

This review article is divided into three sections. In the first section, the relevance of atomic characterization of nanowires with TEM and APT is briefly outlined. In the second section, a discussion of the mechanical properties of several piezoelectric nanowires, emphasizing recent results on semiconducting ZnO and GaN nanowires and other wurtzite compounds, is presented. In the third section, nanoscale techniques for the measurement of the piezoelectric coefficients in individual nanowires, as well as data reported in the literature for several materials, are presented. As it will be shown, accurate measurement of mechanical and electromechanical properties in the size range of a few nm to 100 nm is quite challenging and requires development of novel experimental techniques and methods of analysis. As a result, some of the findings are still subject of debate.



Prof. Horacio Espinosa is the chair and director of the Theoretical and Applied Mechanics program, and a Professor in the Department of Mechanical Engineering at Northwestern University. He received his PhD degree from Brown University in 1992. Prof. Espinosa has made contributions in the areas of dynamic failure of

advanced materials, computational modeling of fracture, and multiscale experiments and simulations of micro- and nanosystems.



Rodrigo Bernal is a Ph.D. student in the department of Mechanical Engineering at Northwestern University. He received bachelor's degrees in Mechanical and Electronics Engineering from Los Andes University in Bogotá, Colombia. His undergraduate work focused on powder metallurgy and development of low-cost Scanning

Probe Microscopes. He joined Prof. Espinosa's Lab in the fall of 2008. His current research interests include the mechanical and piezoelectric properties of semiconducting nanowires, in situ testing of nanostructures and nanomanipulation.



Dr. Majid Minary is a Postdoctoral Fellow in the Department of Mechanical Engineering at Northwestern University. He received a bachelor's degree in Mechanical Engineering from Sharif University of Technology in Iran in 2003 and a M. Sc. degree from the University of Virginia in 2005. He holds a PhD

degree in Mechanical Engineering from the University of Illinois at Urbana-Champaign, 2010, with a focus on nanoscale biomechanics and scanning probe microscopy of biomaterials.

Nevertheless, a consistent picture is emerging in which both mechanical and electromechanical properties of nanowires are significantly enhanced below a critical dimension of \sim 100 nm.



www.MaterialsViev



Figure 1. Methodological approach to characterize mechanical and electromechanical properties of piezoelectric nanowires. Structural and elemental characterization provides information on defects and dopants that is used as input for atomistic calculations of realistic nanowires and helps establish the role of size, defects and dopants on mechanical and electromechanical properties. Atomistic calculations of these properties, where Density Functional Theory aids to validate empirical molecular mechanics/dynamics models, are compared against the results of experiments in order to establish unambiguous trends. The coupling of all these techniques allows establishment of synthesis-structure-property relations that lead to a fundamental understanding of the properties of nanowires.

2. Structural and Elemental Characterization of Piezoelectric Nanowires

2.1. The Role of Defects in Nanowire Behavior and their Characterization

Several types of defects have been identified in nanowires. Establishing their role on mechanical and electromechanical properties is of great importance. Stacking faults,^[19,20] inversion domain boundaries (IDB),^[21,22] screw dislocations or nanopipes,^[23] and surface defects^[24] have all been observed. The presence of such defects is highly dependent on the particular nanostructure synthesis method; for example, molecular beam epitaxy (MBE) has been reported to yield high crystalline perfection and few stacking faults,^[25] while the more extended vaporliquid-solid (VLS) method reportedly yields a higher density of such defects.^[20] Thus, to obtain measurements that probe the

effect of size and not the particular synthesis route, assessing the potential influence that defects have on the electromechanical and mechanical response, coupled with their direct identification in the tested nanowires, is imperative. Defects are known to affect, for example, mechanical,^[24] optical^[26] and electrical^[27] behavior of a material. The fact that defects play a role in mechanical behavior is widely accepted, although a quantification of their specific influence in the case of nanowires is still a subject of intense research (see section 3.2). On the other hand, the potential influence defects may have on the piezoelectric behavior of nanostructures is largely unknown.

Dislocations and inversion domain boundaries are known to have an effect on bulk piezoelectricity,^[28] while the role of stacking faults and surface defects is not clear (although stacking faults are known to affect the local band structure^[28]). As dislocations alter the local strain fields, they create a local piezoelectric polarization.^[28] This affects mostly the electric fields near surfaces or interfaces.^[29] As a result, the overall piezoelectric response may



www.MaterialsViews.com

change. However, the occurrence of dislocations in nanostructures is not as extended as in bulk or thin-films^[20,22] because they can migrate to the surface and disappear. For the case of inversion domain boundaries (IDB), they result in the inversion of the direction of the piezoelectric response. This defect consists of the coexistence of two inverted regions of the crystal separated by a single-atom boundary. As a result, applying, for instance, tension to such a structure would result in an electric field parallel to the stress in one region, while the other region would develop an anti-parallel field. There exists evidence that this type of defect appears in nanowires,^[21,22] although it is not clear to what extent. It is also noteworthy that published work on electromechanical properties of nanostructures has not reported whether this defect was present on the tested specimens.

The identification of the aforementioned defects in nanostructures has been mostly attempted using HRTEM,^[19–23] because of its resolution and suitability for examining singlecrystal specimens. Furthermore, development of in situ testing methods, where mechanical properties of nanostructures are simultaneously measured along with HRTEM observation, has garnered much attention recently^[30–33] because defect identification on the tested specimens is possible. Nevertheless, in situ TEM testing has been mostly applied for mechanical properties, while studies on piezoelectricity in nanostructures, where the atomic structure of the specific tested specimen is characterized, are lacking (See Section 4.1).

2.2. Characterization of Nanowire Dopants

Dopants in nanowires play a role in the conductivity of the specimen and therefore influence the electromechanical response, especially in the case of piezoelectricity.^[34–37] If the conductivity of a specimen is high, the direct piezoelectric response is quenched due to free charges (introduced by dopants) that screen the charges generated by the piezoelectric effect.^[38] Incorporation of intentional or unintentional doping^[39] is possible during the synthesis process; and given that even a small concentration of dopants can influence properties in nanowires, an elemental characterization method with high resolution is needed.^[40]

Atom probe tomography (APT) is a technique that allows both identification of the atomic species and its spatial distribution within a nanowire (NW) specimen with sub-nanometer resolution down to the single-atom level.^[18] However, application of this technique to piezoelectric materials, some of which display large wide band gaps is particularly challenging. A particular implementation of APT called local electrode atom probe (LEAP), which allows characterization of dopants in nanowires has recently been applied to GaN nanowires.^[41] In this technique, a high electric field is applied between a small-diameter sample (nanowire) and an electrode positioned directly in front of it (local-electrode). As a result of the high electric field and the energy transferred by a pulsed-laser focused on the tip of the sample, individual atoms are evaporated from the specimen and attracted to a detector positioned behind the local electrode. Spectroscopy is then performed by analyzing the time-of-flight and mass-to-charge state ratio of the evaporated atoms.

Using the LEAP technique, successful detection of Mg dopants and their spatial distribution in GaN nanowires was



Figure 2. Elemental mapping of a GaN nanowire using LEAP. (a) Experimental setup where an electric field applied between the specimen and an electrode, and a laser pulse, aid in the evaporation of individual atoms from the specimen. (b) Higher magnification image showing a nanowire positioned in the tungsten (W) probe in (a). Figure (c) and (d) show the identification of the material elements (gallium, nitrogen) and the dopant (magnesium) in the nanowire specimen. Reprinted with permission.^[41] Copyright 2011, American Chemical Society.

achieved (see **Figure 2**).^[41] As mentioned earlier, application of this technique in wide band gap materials is particularly challenging and requires further optimization of experimental parameters. As a result, only relatively high concentrations of dopants have been detected (6×10^{19} cm⁻³). These experiments suggest that Mg doping may distribute unevenly and preferentially on the nanowire surface, illustrating that indeed, synthesis may play a role on observed properties.

3. Mechanical Properties of Piezoelectric Nanowires

As stated above, nanowires made from piezoelectric materials are widely used for nanogenerators, optoelectronics and sensing/actuation devices. In these applications, especially in those where strain or displacement is needed to achieve functionality, knowledge of mechanical properties enables modeling, design and optimization of device functionality. Typically, one is interested in knowing the elastic moduli, failure properties (strength and strain), and the structural features that are responsible for both. These structural features are usually characterized in HRTEM, preferably in the same nanostructure that undergoes deformation–this is accomplished through *in situ* experiments.^[7,24,42] The final goal is to establish synthesis-structure-property relations that ultimately lead to device optimization.



The elastic moduli are critical to determine the deformation or strain that a nanostructure will undergo under an applied load or conversely, the stresses caused by a prescribed deformation. Knowledge of the strains or deformations is important in applications pertaining to piezoelectric materials since they will have a direct influence on the generated piezoelectric potential.^[36,37] On the other hand, knowledge of stresses, in conjunction with identification of failure mechanisms provides bounds for reliable design. Hence, failure or fracture strains and strengths are just as important as the elastic moduli because they determine the mechanical operational limits of the devices, and therefore have an influence over the reliability and robustness of the system.

In this section, an account of the state-of-the-art in mechanical characterization of piezoelectric nanowires is given. Particular focus is placed on wurtzite semiconductors, given that they are all piezoelectric. More specifically, Zinc compounds (ZnO, ZnS), the nitride series (AlN, AlGaN, GaN, InN), and CdS are reviewed here, due to their technological importance and also to the fact that nanogenerators using all these materials have been reported.^[43–46] Special emphasis is given to ZnO and GaN due to their importance not only in nanogenerators, but also to other applications, e.g., optoelectronics. In fact, it will be shown below that the mechanical properties of these two nanowire materials have been the most extensively characterized.

3.1. Summary of Nanomechanical Characterization and Modeling Methods

Many experimental and modeling approaches have been used to characterize the mechanical properties of piezoelectric nanowires. The experimental methods have been reviewed in detail in [31,32,47–50]. The methods are briefly discussed in this section and more extensively later in the context of the results presented. To provide appropriate background, a summary of the published reports on the mechanical characterization of the seven aforementioned materials, including the characterization techniques is given in **Table 1**.

Table 1. Summary of the different methods (experimental and modeling) used to characterize the mechanical properties of ZnO, GaN and other wurtzite semiconductors (WZS). Acronyms: MEMS (Micro-Electromechanical Systems), SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy), AFM (Atomic Force Microscopy), LFM (Lateral Force Microscopy), MD (Molecular Dynamics), FEM (Finite Element Modeling), MST (Molecular Statistical Thermodynamics), DFT (Density Functional Theory).

Method	Loading mode		Material	
		ZnO	GaN	Other WZS
EXPERIMENTS				
MEMS in situ SEM/TEM	Tension	[7,24,66]	[42,52]	
Nanoindenter in situ TEM	Compression		[57]	
AFM Cantilever in situ SEM	Tension/buckling	[53–56]		
AFM Cantilever in situ TEM	Buckling	[67]		
AFM bending of cantilevered NW	Bending	[118,119]		
AFM-Instrument based				
AFM/LFM	Bending	[58]		InN:[120]
Three point bending	Bending	[59]	[64,121]	ZnS:[122]
Contact resonance	N/A	[123,124]		InN:[125]
Nanoindentation		[126]	[126]	ZnS:[127–129]
In situ SEM/TEM resonance	Bending	[60–62]	[130,131]	CdS:[132] AlGaN:[133]
Electrical resonator	Bending			CdS:[134]
SEM electrostatic bending	Bending			AlN:[135]
MODELING				
Atomistic				
MD	Tension/buckling	[7,24,53,73,74,136–138]	[42,139,140]	
MD/FEM	Tension			AlN:[78]
MST	Tension	[72]		
DFT	Tension	[75,141]	[42]	ZnS:[77]
DFT/surface elasticity	N/A	[142]	[143]	
Theoretical				
Bond-order-length correlation	N/A	[144]		
Core-shell modeling	N/A	[56,60,69]	[69]	
Surface elasticity	N/A	[145,146]		

PROGRESS REPORT



www.MaterialsViews.com

In the experimental domain, one can divide the methods based on the loading mode, namely uniaxial tension or compression, and bending-based, where bending (either static or in resonance) and buckling are employed. Uniaxial methods provide a means of applying a controlled deformation at one end of the specimen, while load measurement is performed at the other end. Strain is usually measured by imaging of the specimen, usually in situ an electron microscope. In situ TEM provides the highest resolution and enables characterization of the atomic structure of the specimen.^[24] Implementation of this loading mode has been carried out using Micro-Electromechanical Systems (MEMS) in situ the TEM^[7,24,42,51] or *in situ* the SEM^[52] where a thermal actuator applies the prescribed displacement to the specimen. The load-sensing mechanism is a capacitive displacement sensor.^[51] An alternative is to use a nanomanipulator as the actuator and an AFM cantilever as the load sensor. This later method has been used extensively in situ SEM.^[53-56] Likewise, in situ TEM nanoindentation has also been employed.^[57]

Bending and buckling methods are usually easier to implement but data interpretation is more complex. Nanostructure bending is achieved by means of atomic force microscopy, which also provides measurement of force, either in the lateral^[58] or vertical directions^[59] or by a nanomanipulator pushing the nanowire specimen until it buckles. Alternatively, bending can be induced by electrostatic resonance.^[60–62] In all cases, fixed boundary conditions at the nanowire end are difficult to ensure and this has led, e.g., in the case of ZnO nanowires, to significant data scatter, as reported in ref. [7].

Atomistic models, primarily molecular dynamics (MD) and first-principles density functional theory (DFT) calculations have been extensively used to predict nanowire properties (See Table 1). The most common investigated loading has been tension. These studies have provided important insight into the mechanisms leading to size effects. More discussion of the simulation methods and findings is provided in subsequent sections for both mechanical and piezoelectric nanowire properties.

3.2. Mechanical Properties of ZnO Nanowires

ZnO nanowires are, by far, the most extensively characterized among piezoelectric nanowires. This is partly because of the interesting properties exhibited by ZnO, such as relatively high piezoelectric constants and high exciton-binding energy, as well as the relative ease with which ZnO nanostructures can be synthesized.^[63] In fact, most of the techniques developed for mechanical characterization of one-dimensional nanostructures have been applied to ZnO, see Table 1. Currently, there is a general consensus pointing to the existence of a strong sizeeffect on the modulus of elasticity for nanowires oriented in the [0001] direction,^[7] in which the modulus increases as the diameters decrease below 100 nm. Their failure strength and strain, and their governing mechanisms, although known to be higher than in bulk, are still the subject of investigation. In this section we provide a summary of the identified mechanical properties of ZnO nanowires, namely elastic and failure properties.

The elastic properties of ZnO nanostructures have been studied by several experimental, computational and theoretical approaches. As shown in Table 1, the body of literature is vast, and until recently, conflicting accounts of the size dependence of the elastic modulus existed.

In terms of experimental results, as pointed out in ref. [7], several artifacts dominated the earlier reports, resulting in scatter and conflicting trends in the reported size effects. These artifacts were related to uncertainties in boundary conditions, metrology of the cross-section, instrument calibration and sample manipulation.^[7] For instance, in tests where an atomic force microscope was used to perform a three-point bending, the boundary conditions varied between fixed or pinned ends.^[64,65] Another source of boundary condition uncertainty was present when a compliant structure, such as a copper grid, was used to load the specimen.^[66]

Recently, Agrawal et al.^[7] used in situ TEM experiments and a MEMS testing platform, coupled with atomistic simulations to demonstrate unambiguously the size-dependence of the elastic modulus of [0001]-oriented ZnO nanowires. The combination of uniaxial loading condition, the use of selected area diffraction patterns to measure strains, and accurate measurement of the nanowire cross-sectional area together with atomistic simulation of nanowires with up to 20 nm in diameter, allowed identification of a consistent trend on elastic modulus. In particular, it was shown that the modulus increases as the diameters decreases below approximately 80 nm. Larger nanowires showed a modulus of elasticity that agreed well with the bulk value (140 GPa).

Subsequent reports (shown in **Figure 3**) have confirmed the existence of a size dependence on the elastic modulus of [0001]-oriented ZnO nanowires below a critical size. In particular, all the reports have shown that the modulus increases as the diameter decreases. This has been shown by in situ SEM uniaxial^[55,56] and buckling experiments.^[55,67] All these methods utilized AFM cantilevers to measure the applied load.

Among the recent results, one can highlight the work by Xu et al.,[55] which used the experimental setup shown in Figure 3(d) to test the size dependence of the modulus under uniaxial loading and under buckling. The uniaxial results agree well with the earlier results by Agrawal et al.^[7] The bending results demonstrated that different loading modes lead to a different size dependence of the modulus. This is a result of the greater influence of surface elasticity on the buckling loading mode given that the nanowire surface has a higher elastic modulus.^[7] This fact had been reported earlier, albeit with a more pronounced scatter and under different experimental setups for each loading mode.^[56] Theoretical estimations also predicted loading mode effects.^[68,69] The fact that surface elasticity plays a more pronounced role in the size dependence measured in bending was recently confirmed by the in situ TEM experiments performed by Asthana et al.^[67]

In summary, several experimental, computational and theoretical results have been applied to characterize or model the elastic behavior of ZnO one-dimensional nanostructures. Two important findings have become clear, namely: i) there is a sizedependence on the modulus along the [0001] orientation with the modulus increasing as the nanowire diameter decreases.



Makrials Views



Figure 3. (a) Recent reports on the elastic properties of [0001]-oriented (c-axis) ZnO nanowires as a function of the diameter. (b) and (c) illustrate the combined computational-experimental method employed by Espinosa and co-workers^[7] where a MEMS device and MD calculations were employed. See text for explanation of Figure (b). (d) Basic set up of the other experimental methods in which an AFM cantilever and a manipulator is used to load the specimen in tension or buckling. Figures (b) and (c) reprinted with permission.^[7] Copyright 2008, American Chemical Society. Figure (d) adapted with permission.^[55] Copyright 2010, Springer-Verlag.

ii) surface elasticity effects imply that the size-dependence measured in bending modes is more pronounced than the one measured under uniaxial loading.

3.2.2. Mechanical Failure Properties

Among several of the characterization techniques for mechanical properties of nanowires, only a limited number have the capability of characterizing failure properties such as fracture strain and fracture strength. As a result there is less data available on failure of ZnO nanowires. Furthermore, there is no current consensus about strength size-dependence, although some attempts to explain the phenomenon have been made. Strength of ZnO nanowires was first measured using the AFM/LFM technique where a suspended nanowire is subjected to a three-point bending test by lateral bending using an AFM tip.^[58] More recently, uniaxial fracture experiments carried out *in situ* TEM, with MEMS devices,^[24] and in situ SEM tests, with nanowires clamped between a nanomanipulator and an AFM cantilever, were reported.^[53–55] These results are presented in **Figure 4**.

The data shown in Figure 4 clearly reveals the existence of size effects in the fracture strength and strain of ZnO nanowires. ZnO nanowires display fracture strengths of a few GPa, several times the fracture strength of the bulk and approaching the theoretical strength ($E/10 \sim 14$ GPa) at the smallest nanowire



Figure 4. Fracture properties of ZnO Nanowires. (a) Fracture strains as a function of nanowire diameter, plotted from data in Ref. [53,55] (b) Fracture strength as a function of diameter.^[54,55,58] (c) Fracture strengths as a function of nanowire surface area.^[24]



www.MaterialsViews.com



Figure 5. Alternative Weibull statistics to quantify the fracture in ZnO nanowires (a) illustrates the fracture from a surface-defects perspective^[24] (thus using surface area), while (b) shows the Weibull statistics from a point-defect perspective.^[53] Figure (a) reprinted with permission.^[24] Copyright 2008 American Chemical Society, (b) Reprinted with permission.^[53] Copyright 2011, American Institute of Physics.

diameter. Consequently, the fracture strain is relatively high, usually higher than 2% even for the larger nanowire-diameters. Two mechanisms have been proposed to explain the results based on surface defects and point defects (vacancies). The first mechanism based on surface defects was proposed by Agrawal et al.^[24] and correlates strength with surface imperfections (as imaged in HRTEM), which are inherent to many of the synthesis processes employed in the manufacturing of nanowires. These surface irregularities induce stress concentrators that lead to fracture. Weibull statistics using the nanowire surface area as the physical parameter lead to the results shown in **Figure 5**b. Clearly, there is a correlation between surface area and fracture strength, meaning that surface defects do play a role in nanowire fracture, albeit the regression coefficient is rather low, likely due to the somewhat limited number of performed experiments.^[24]

The second mechanism was proposed by He et al.^[53] and correlates failure with vacancies existing in nanowires. This mechanism was first postulated by Pugno for carbon nanotubes.^[70,71] Under certain assumptions, quantized Weibull statistics was fitted to the experimental data. However, the physical meaning of this exercise remains somewhat questionable since He et al. did not report unambiguously absence of surface defects or quantification of vacancy cluster size, e.g., through highresolution transmission electron microscopy in the tested specimens.

In principle, the fracture behavior of ZnO nanowires may be the result of a combination of surface defects and point defects. However, the quantification of the specific role each one plays in fracture remains challenging because it is still quite difficult to identify the largest surface defect or vacancy cluster size for a particular sample. Identification of the role of these defects is more amenable to be investigated using atomistic methods, in which precise control of the starting atomic structure of the nanowire is achieved. Indeed, failure properties of ZnO nanowires were investigated using Molecular Dynamics and First-Principles atomistic calculations.

Most molecular dynamic simulations of ZnO nanowires have employed the pairwise Buckingham potential (see references in Table 1). Although this potential has been able to yield appropriate results for elastic properties,^[7] researchers

trying to study failure properties found that at large strains a phase transformation from the wurtzite phase to a body centered tetragonal occurs. This phase transformation has been observed computationally by several researchers,^[24,53,72–74] yet it has not been realized in experiments. It occurs at around 5–7% strain and is accompanied by a sudden stress drop, followed by a reloading and subsequent failure at strains of around 17%.^[24] Recently, this phase transformation accompanied by subsequent reloading was deemed an artifact of the Buckingham force field as demonstrated by large scale first principles DFT calculations.^[75] These simulations revealed that the phase transformation occurs, but as a precursor to fracture. Indeed, a nonlinear stress-strain curve with brittle failure was predicted for nanowires up to 3.6 nm in

diameter. This result is not surprising in view of the pairwise nature of the Buckingham potential as well as the neglect of changes in electronic structure at high strains.

Even when the existence of the wurtzite to body-centertetragonal phase transformation has been elucidated, the computationally predicted failure strains and stresses are higher than those observed in experiments. Two reasons can be given to explain such a discrepancy: temperature effects and initial defects in the atomic structure of the nanowires. The introduction of defects in DFT calculations remains challenging because even a few atomic defects lead to unrealistically high defect densities.^[75] Further understanding calls for development of multiscale methods that can simulate nanowires with realistic sizes, yet avoiding the artifacts introduced by semi-empirical potentials.^[75]

3.3. Mechanical Properties of GaN

GaN nanowires are the second most-studied material among wurtzite semiconductors. Similar to ZnO, several methods have been applied to its elastic characterization. However, very little has been reported on failure properties.

Recently, Bernal et al.^[42] summarized elasticity results reported in the literature, which, similarly to ZnO, exhibited significant scatter. The authors concluded that the sources of such scatter is primarily the result of experimental artifacts, as pointed out previously for ZnO.^[7] Using a combined methodology of DFT, MD, and in situ TEM testing, Bernal et al. presented a consistent trend for the mechanical properties of c-axis, a-axis, and m-axis GaN nanowires. One of the main conclusions of the study was that GaN nanowires exhibit bulk elastic properties for diameters greater than 20 nm, which is in contrast to the stronger size effect, at around 80 nm, observed in ZnO nanowires.^[7] This can be explained by differences in the reduction of interatomic spacing near the surfaces, which is more prominent for ZnO than for GaN. Comparison of Figure 3b and Figure 6b shows that for nanowires of the same diameter, surface atoms are displaced more with respect to their pristine crystal positions in ZnO.

www.advmat.de



Figure 6. a) Elastic Properties of [0001]-oriented (c-axis) GaN nanowires, b) Atomic displacements from the bulk crystal positions as obtained from MD simulations. Reprinted with permission.^[42] Copyright 2011, American Chemical Society.

Much less is known about fracture, either from experimental or computational studies. Recently, Huang et al.^[57] reported uniaxial compression experiments on GaN nanowires, using an in situ TEM nanoindenter. Their results indicate that the failure is brittle, with some instances of incipient, localized plasticity in the vicinities of the nanoindenter. They identified failure planes that correspond to the major slip systems in wurtzite GaN. It should be noted that the tested nanowires were not c-axis orientation [0001] but rather a-axis $[1\overline{2}10]$. The failure strength of GaN nanowires, as measured by this method, is on the order of 1–2 GPa for diameters between 100-200 nm. Given the identified failure strength of ZnO, it is expected that the failure strength of GaN should be of the order of a few GPa for sub-100 nm diameter nanowires. Future characterization studies should shed light on this issue.

A feature that may be important in the mechanical characterization of failure properties of GaN is the presence of planar defects, such as stacking faults. The precise extent to which these defects are widespread among the different synthesis methods is unknown, although they seem to be less important in molecular beam epitaxy,^[76] while they have been clearly observed for CVD synthesis.^[20] The characterization of the mechanically-tested structures for this type of defects, preferably in situ the TEM, will be critical in unambiguously characterizing the failure properties of GaN nanowires.

3.4. Mechanical Properties of ZnS, CdS, InN, AlN and AlGaN **Piezoelectric Nanowires**

The mechanical properties of these semiconductors have been studied less extensively when compared to ZnO and GaN. Their characterization is of technological relevance, especially the nitrogen-containing semiconductors, in view that it has been reported that transition from Al to In in the nitride series improves the characteristics of nanogenerators.^[43]

The mechanical properties available in the literature for these semiconducting nanowires are summarized in Table 2. The bulk mechanical properties are also given in the table for comparison and future reference. It is expected that, just as it has been shown for GaN and ZnO, nanowire properties should converge to the bulk values at some critical dimension.

Inspection of the table reveals that further characterization efforts are necessary to achieve certainty on the properties of these nanostructures; nevertheless, some trends can be readily identified. For ZnS, the first-principles results of Chen et al.^[77] are noteworthy, since they predict that nanowire with sizes of ~20 nm would probably display the elastic properties of the bulk ZnS. The same can be said for the results of Mitrushchenkov et al.,^[78] which predict convergence to bulk properties at small diameters.

Inspection of the other results reported in Table 2 reveals either a significant scatter or insufficient information to draw conclusions. Based on the understanding and insight gained through mechanical characterization of GaN and ZnO nanostructures, it is evident that some of the scatter reported for these semiconducting nanowires arises from limitations and drawbacks of the employed experimental approaches. Thus, it is imperative that future characterization efforts draw from past experience and are based on protocols with well-defined boundary conditions and unambiguous metrology. It is noted that any mechanical characterization method should achieve convergence to bulk properties at large nanowire diameters.

4. Characterization of Piezoelectricity in Nanowires

Piezoelectricity is a linear electromechanical coupling, which manifests itself as a direct effect ($P_i = d_{iik} \sigma_{ik}$) and a converse effect ($\varepsilon_{ii} = d_{iik} E_k$), where *P* is the polarization vector, σ is the stress tensor, ε is the strain tensor, E is the electric field vector, and d is the piezoelectric third rank tensor.^[79] In a particular coordinate system, the third rank tensor is given by a piezoelectric matrix having several independent constants, whose numerical values depend on the crystallographic structure of the material. In direct piezoelectricity, application of mechanical stress on a piezoelectric material results in generation of electrical charges (voltage) on its surface. This charge can be utilized in sensing and energy harvesting. In the converse piezoelectric mode, an electric field applied across the material generates strain or deformation in the material, which can be employed, for example, in actuators.^[8] Accordingly,

Table 2. Results available in the literature for mechanical properties of ZnS, CdS, InN, AlN and AlGaN one-dimensional nanostructures. Bulk properties were calculated using elastic constants in references^[147] (ZnS),^[148] (CdS) and^[149] (InN, AlN). The moduli of any basal-plane orientation have the same value in bulk wurtzite so only one of them is reported.

Material	Method	Orientation	Diameter [nm]	Modulus [GPa]	Ref.	Orientation	Modulus in bulk [GPa]
ZnS	AFM Three-Point Bending	[0001] [100]	Not reported	52 ± 7	[122]	[0001]	116.8
	Nanoindentation	Not reported	100	55.2 ±5.6	[127]		
	Nanoindentation	[0001]	50–100	35.9 ±3.5	[129]	[100]	91
	DFT	[0001]	~0.5–2.4	~125	[77]		
CdS -	In situ TEM Resonance	[10-10] (m-axis)	50–300	20–200	[132]	[10–10]	47.8
	Electrical Resonator	Not reported, pos- sibly [0001]	60 ± 10	62 ± 17	[134]	[0001]	62.8
InN	AFM/LFM	Not reported	Not reported	150	[120]	[0001]	174
	AFM Contact Resonance	[110]	88.6	260	[125]	[110]	153
AIN	SEM Electrostatic Bending	[0001]	175	67	[135]	[0001]	329.2
						Any basal plane direction	334.1
	DFT-based FEM modeling	[0001]	<10 nm	C ₃₃ ~400	[78]	C ₃₃	373
AlGaN	In situ SEM Resonance	[12-10] (a-axis)	Not reported	185 ± 20	[133]		Not available for specific alloy

piezoelectricity can be experimentally characterized in both direct and converse modes.

The most common methods for characterization of direct piezoelectricity in nanostructures usually involve tensile loading or lateral bending of the material with simultaneous measurement of generated charge or electric potential. This is challenging because the charges or voltages tend to be small, which requires ultra-sensitive electronics.^[80] On the other hand, the measurement of converse piezoelectricity in nanostructures is mostly performed by means of piezoresponse force microscopy (PFM). This method takes advantage of the scanning and cantilever deflection measurement capabilities of the AFM. By applying a local electric field on the material of interest and measuring the induced displacements (often in the pico-meter range), the components of the piezoelectric matrix are measured. PFM is by far, the most employed method for characterization of piezoelectricity in nanostructures.

In the context of computational methods, typically the direct piezoelectric effect is quantified. This involves the application of prescribed strains to the model and subsequent calculation of the change in polarization.^[81] Typically, full first-principles calculations using density functional theory (DFT) are employed, although recently a modified version of molecular dynamics (referred to as core-shell MD) has been proposed.^[82]

In this section, we review the literature on characterization of piezoelectricity in nanowires using experimental and computational approaches. In contrast to the characterization of mechanical properties, where atomic structural characterization, experimental measurements, and simulations have been performed, much remains to be done in establishing synthesis-structure-properties relations in the context of piezoelectricity. The experimental method most widely used (piezoresponse force microscopy–PFM–explained below) has relatively high throughput but does not allow *in situ* characterization of the specimen under test. Furthermore, due to coupling between mechanical and electrical effects, these experiments are even more challenging than nanomechanical ones, and as a result the number of studies focusing on characterization of piezoelectricity in nanowires is much smaller when compared to those on mechanical characterization. Furthermore, the majority of computational results are still limited to nanowire sizes smaller than 5 nm. Notwithstanding all these challenges, recent experimental results point to an enhancement of piezoelectricity for nanowires below 100 nm.

4.1. Experimental Investigation of Piezoelectricity in Nanowires

4.1.1. Converse Piezoelectric Characterization by Piezoresponse Force Microscopy

Piezoresponse force microscopy (PFM) has been employed to characterize the converse piezoelectric properties of several materials.^[83–86] Due to its high resolution and insensitivity to topographic features, PFM has been extensively used in imaging domain structure and domain evolution in thin ferroelectric films,^[87,88] and in characterization of ferroelectric and piezoelectric nanowires.^[89,90] The PFM setup is shown in **Figure 7**a. It consists of the AFM system, extended electronics including a lock-in amplifier, and a function generator. In PFM







Figure 7. (a) Schematic of the PFM setup, including the AFM system and extended electronics, for measurement of the converse piezoelectric effect at the nanoscale. (b) Two common modes of PFM: lateral and vertical PFM for measurement of in-plane and out-of-plane deformation in the material, respectively.

a conductive cantilever is brought into contact with the surface of the material of interest under a controlled constant force. The conductive probe is often obtained by coating commercial AFM probes with a thin layer (~10-20 nm) of Au or Pt. An AC voltage, $V_0 \sin(\omega t)$, is then applied between the cantilever and the grounded substrate. Due to the piezoelectric effect, a local AC strain is generated by the application of the AC voltage. The deformation of the surface of the sample, arising from the converse piezoelectric effect, is detected through the optical beam path and four-quadrant photodetector of the AFM. The induced signal on the cantilever $(d_0 \sin (\omega t + \phi))$ is deconvoluted in a lock-in amplifier to measure amplitude (d_0) and phase (ϕ) with respect to the input AC voltage. Amplitude of the PFM response is indicative of the strength of the piezoresponse and the phase signal is indicative of the polarization direction underneath the probe tip.

The AFM cantilever can undergo bending and torsion similar to a regular cantilevered beam. Consequently, complementary information about the deformation of the sample surface is acquired. To take advantage of this effect, PFM can be operated in the vertical and lateral modes, (Figure 7b). In the lateral PFM mode, the electric-field-induced shear deformation of the sample surface causes torsional twist of the cantilever, similar to friction measurements with AFM. For full transfer of the shear response to the probe, the cantilever should be scanned laterally with respect to its long axis (90-degree scan). On the other hand, in the vertical PFM mode, the out-of-plane deformation of the surface is registered through the deflection of the cantilever.

Overall, PFM allows for acquiring five different signals simultaneously, including topography, vertical PFM amplitude, vertical PFM phase, lateral PFM amplitude, and lateral PFM phase. These signals can then be used to construct the local strain state under the tip. PFM can be operated in imaging mode as well as spectroscopy mode for single point measurements. In imaging mode, the tip is scanned over the surface of the sample, often at a very low speed (<1 Hz), while the harmonic voltage is continuously applied between the tip and the sample. In this manner a continuous map of piezoelectricity on sample surface is obtained with sub-nm resolution. In point measurement mode, the scan size is set to zero and the strain state in the local area directly beneath the tip is collected. To obtain the piezoelectric constant, the amplitude of the applied AC voltage is swept between zero and several volts, and the slope of the response curve vs. applied voltage is used to extract the corresponding piezoelectric constants. In this review we focus on the piezoelectric characterization of nanowires, without going into details on the theoretical description of piezoresponse force microscopy. There are comprehensive reviews in the literature that could be referred to for complete theoretical description of PFM.^[91,92]

PFM is a common method for characterization of piezoelectricity in 2D materials such as thin films ferroelectrics. However, for one-dimensional nanostructures such as nanowires, it is rather challenging in practice. The probe has to be precisely positioned

on the top of the nanowire, often under 100 nm in diameter. This is rather difficult especially for nanowires with circular cross sections. The system should be thermally stabilized prior to the experiment to limit the thermal drift between the probe and the sample. Furthermore, often the cantilever and the nanowire should align at a specific angle with respect to each other in order to probe the desired piezoelectric constant. Often the nanowire tends to move under the probe during mapping of the PFM response.

Since piezoelectricity is a first order linear effect, care must be taken to distinguish higher order terms arising from electrostatic and electrostrictive effects. The lateral PFM is not susceptible to electrostatic interactions due to the symmetric nature of the electrostatic interactions in PFM setup, and therefore, often soft cantilevers could be used. In vertical PFM, rigid cantilevers are used to screen for weak electrostatic interactions in order to avoid possible interference of the electrostatic forces in the PFM signal,^[86,93] The stiff cantilevers, however, apply larger forces on the sample and could induce nanoindenation into the nanowire. Therefore, soft cantilevers are preferred as long as the electrostatic response does not dominate the deflection of the cantilever.

4.1.2. PFM Applied to Piezoelectric Nanowires

PFM has been widely used for probing the converse piezoelectric effect at the nanoscale.^[83,84] Specifically, piezoelectricity in ZnO nanobelts,^[94] PZT nanowires,^[95] BaTiO₃ nanowires,^[89,96] sodium niobate nanowires,^[97] potassium niobate nanowires,^[98] GaN nanowires,^[9] ferroelectric nanoribbons,^[99] and PZT ribbons^[100] has been characterized.

The earliest applications, and most of the reported results for PFM deal with ferroelectric materials. PFM on BaTiO₃ nanowires was reported in 2002^[96] where Yun et al. demonstrated that nonvolatile electric polarization could be reproducibly induced and manipulated in BaTiO₃ nanowires, as small as 10 nm, by an external electric field.^[96] For single crystal BaTiO₃ nanowires a shear piezoelectric constant of d₁₅ ~ 16.5 pm/V was obtained using a modified PFM that allowed for direct axial polarization of the nanowire.^[90] In addition, it was shown that the stable and one-dimensional ferroelectric mono-domain polarization in these nanowires could be switched under axial electric biasing, indicating the ferroelectric nature of the nanowires.^[89]



www.MaterialsViews.com

Monocrystalline lead zirconate titanate $Pb(Zr,Ti)O_3$ nanowires also showed piezoelectric hysteresis and ferroelectric switching behavior.^[95] Further studies with this material, on nanowires with diameter of ~45 nm^[101] revealed that the piezoresponse for the PZT nanowires was larger than in thin films of the same material. In addition to nanowires grown in conventional bottom-up approach, PZT nanowires fabricated via lithography and electrochemical etching methods were also characterized.^[102] For PFM characterization, an 80 nm Pt film was deposited prior to PZT film growth as the bottom electrode. Unpoled PZT nanowires obtained in this manner were shown to display a piezoelectric constant of 114 pm/V, which increased to 145 pm/V after poling for 30 minutes under 10 V. This value represents the highest value of piezoelectric constant reported for nanostructures.^[102]

Other materials, namely Niobates, have also been characterized by PFM. KNbO₃ nanowires with diameter of ~100 nm, mechanically clamped and electrically biased in the axial direction showed a piezoelectric constant of 7.9 pm/V.^[98] In this configuration, the substrate is left floating and the bias is applied between the lithographically fabricated electrodes on the clamped ends of the nanowire and the AFM tip. Nanowires of crystalline orthorhombic sodium niobate (NaNbO₃) of ~100 nm in diameter displayed a vertical piezoelectric constant of a few pm/V, much smaller than that of the polarized and doped bulk NaNbO₃. This was attributed to the unknown and unfavorable crystal orientation in the nanowire and its interaction with the electric field.^[97]

In the context of piezoelectric, semiconducting materials, PFM was applied to individual ZnO nanobelts in the (0001) surface where the piezoelectric constant was measured to be $d_{33} \sim 14.3$ to 26.7 pm/V, higher than its bulk counterpart (~9.9 pm/V).^[94] It was observed that the effective piezoelectric constant was frequency dependent, and decreased by increasing the frequency of the applied electric field. It was speculated that

such frequency dependence may be due to the surface charge effect or imperfect electrical contact between the bottom of the nanobelts and the conductive layer. Another study was reported on pillars of ZnO.^[103] In this method the pillars are templategrown on a highly doped substrate functioning as the bottom electrode, while their top facet is in contact with the AFM tip, which acts as the top electrode. In this method, the PFM map could be simultaneously obtained from several nanopillars. Figure 8 depicts the experimental setup for this type of measurement. For ZnO nanopillars with typical diameters of ~300 nm, a piezoelectric constant d_{33} ~7.5 pm/V was obtained. In this study, the AFM cantilever was in contact with the pillars on their (0001) surface, as opposed to nanowires laying on the substrate. Figure 8b shows the simultaneously acquired PFM map (left) and the topography image (right) in which correspondence between the bright area in the PFM image and the top surface of the individual pillars can be observed. Figure 8c shows the linear behavior of the obtained piezoresponse amplitude vs. applied electric potential.

A similar study, for ZnO nanorods with diameters in the range of 150–500 nm, and length of 400 nm to 600 nm, reported a variation of piezoelectric constant from 0.4 to 9.5 pm/v.^[35] Interestingly, a direct correlation was found between the piezoelectric coefficient and the resistivity of the nanorods. Nanorods with low piezoelectric response display low resistivity, with variation from 0.1 to 155 Ω .cm. This observation was explained by the reduction of the Madelung constant due to free electrons^[35] and confirmed earlier results pointing to the fact that conductivity does in fact quench piezoelectric response.^[38]

Another way of revealing the converse piezoelectric effect is by direct application of an electric field in a freestanding nanowire and then observing the induced displacement. Electric field induced transverse deflection of freestanding nanowires was demonstrated in ZnO.^[104] When an electric field was applied along the *a*-axis of a *c*-axis nanowire, a shear stress



Figure 8. Piezoelectric characterization of pillars. (a) Schematic of the measurement setup. (b) PFM amplitude (left) and topography image (right) showing that the bright spots in PFM amplitude image correspond to the top face of the ZnO pillars. (c) Piezoresponse vs. applied potential revealing linear behavior. The slope corresponds to the d₃₃ piezoelectric constant. b) and c) reprinted with permission.^[103] Copyright 2006, Wiley-VCH.

MATERIA



was induced in the a-c plane causing transverse deflection of the nanowire, which was imaged in situ an SEM. It was found that under 100 V electric bias, the nanowire deflected by an angle of $\sim 0.18^{\circ}$.

PFM was also recently applied to individual c-axis GaN nanowires as small as 65 nm in diameter.^[9] Nanowires with hexagonal structure grown by catalyst-free molecular beam epitaxy method showed a piezoelectric constant (d_{15} ~10 pm/V) of three times that of the bulk value.

An AFM topography image of a 64 nm GaN nanowire is shown in **Figure** 9a. Figure 9b,c show the simultaneously acquired piezoresponse amplitude and phase image obtained under $10V_{pp}$ and scanning speed of 0.25Hz. As shown in the high magnification image, Figure 9(e), only the top facet of the NW exhibits a strong piezoelectric signal due its proper orientation with the AFM tip. The lateral facets, identified mainly from the deflection image, show minimal to no piezoresponse. Furthermore, the piezoresponse amplitude signal is fairly uniform over the length of the NW (2 µm).

Figure 9(d) shows the obtained piezoresponse as a function of applied potential. The response is reproducible, and as expected, linear. The slope of the obtained response represent the shear piezoelectric constant of the NW, as $d_{15} = 2\varepsilon_{13}/E_1$.^[105] From the lateral sensitivity calibration, the obtained shear piezoelectric constant of the NW was $d_{15} = 10 \pm 0.7$ pm/V.

In addition to the previous results, it has recently been shown that the full piezoelectric tensor can be characterized using PFM. As previously stated, piezoelectricity is a third rank tensor. Hence, the piezoelectric tensor for most crystals has a number of non-zero independent constants. For example, for wurtzite GaN and ZnO nanowires, which exhibit hexagonal symmetry, the piezoelectric matrix has three independent coefficients (d_{33} , d_{13} , and d_{15}),^[79,106] where under a complex deformation mode all three constants contribute to charge (voltage) generation. The strain-electric field relationship for piezoelectric material with 6mm symmetry is expressed as:

$$\begin{pmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2\varepsilon_{23} \\ 2\varepsilon_{13} \\ 2\varepsilon_{13} \\ 2\varepsilon_{12} \end{pmatrix} = \begin{pmatrix} 0 & 0 & d_{31} \\ 0 & 0 & d_{31} \\ 0 & d_{15} & 0 \\ d_{15} & 0 & 0 \\ d_{15} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix}$$
(1)

The induced strain due to electric fields in different directions is therefore expressed as:

$$\varepsilon_{11} = \varepsilon_{22} = d_{31}E_3, \ \varepsilon_{33} = d_{33}E_3,$$

$$2\varepsilon_{23} = d_{15}E_2, \ 2\varepsilon_{13} = d_{15}E_1, \ \varepsilon_{12} = 0$$
(2)

It is noteworthy that nearly all studies on piezoelectric characterization of nanowires provide only one piezoelectric constant, often the one related to the out-of-plane deformation measured from the bending of the cantilever in the PFM setup (vertical PFM). However, a full characterization of piezoelectricity in these one dimensional nanostructures requires quantification of all three independent piezoelectric constants. For example, for a-axis $[1\bar{2}10]$ and m-axis $[1\bar{1}00]$ GaN nanowires, due to their crystallographic orientation, even in pure bending or tension all three constants contribute to the generated voltage. In order to probe piezoelectricity in *3D*, the torsional twist and flexural



Figure 9. (a) AFM topography image of a H = 64 nm nanowire, along with (b) PFM piezoresponse amplitude image, and (c) phase image. It is clear from the image that the top facet of the NW shows strong piezoresponse due to its alignment with the AFM probe, while the side facets show weak to no response. (d) Lateral piezoresponse amplitude vs. applied AC voltage peak-to-peak amplitude; four responses measured on different points on the same nanowire are overlaid showing the reproducibility of the measurement. The average slope of the response is d_{15} ~10 pm/V. (e) A higher magnification image of the area marked in (b). Reproduced with permission from.^[9] Copyright 2011 Cambridge University Press.



www.MaterialsViews.com



Figure 10. Extension of PFM to 3-dimensional measurement of piezoelectricity in individual nanowires. (a) A nanowire is clamped by metallic contacts at its two ends, and the electric field is applied in the axial direction of the nanowire. The vertical and lateral responses of the cantilever measure the axial and lateral piezoelectric response of the nanowire. (b) The common PFM method where the nanowire is placed on a conductive substrate and a lateral electric field is applied between a conductive AFM cantilever and the grounded substrate. The lateral and vertical piezoelectric response of the nanowire is detected by the cantilever torsion and bending, respectively. Reproduced with permission from.^[10] Copyright 2012 American Chemical Society.

bending of an AFM cantilever was employed to measure the harmonic in-plane and out-of-plane displacements induced by applying AC voltage on the piezoelectric nanowire. Through the application of an electric field in various directions (axial and transverse) and by physical rotation of the nanowire with respect to the AFM cantilever (parallel or perpendicular), the three piezoelectric constants in individual c-axis GaN nanowires were measured.^[10]

For the c-axis GaN nanowires, the coordinate system can be defined such that the 3-axis is aligned with the long axis of the nanowire (c-axis [0001]), and 1-2 axes are in its cross-sectional plane, with the 1-axis being normal to the facet of the NW (Figure 10). To obtain the three piezoelectric constants in the defined coordinate system, axial (E_3) and lateral $(E_1 \text{ and } E_2)$ electric fields must be applied on the nanowire. By applying a voltage in the axial direction, the piezoelectric constants d_{13} and d_{33} are obtained by measuring the corresponding displacements. The d_{15} constant is obtained by applying a transverse electric field (E_1) across the nanowire and measuring the strains ε_{23} or ε_{13} .^[105,107] Figure 10 schematically shows the experimental setup for the measurement of the 3D piezoelectric matrix of an individual nanowire. In Figure 10(a), the nanowire is shown on an insulating surface with its two ends clamped by electric contacts, which are used to apply an axial electric field. In Figure 10b, the nanowire is shown on top of a conductive substrate acting as an electric ground, as in the conventional PFM setup. An electric voltage is applied between a conductive AFM probe and the grounded substrate to induce a transverse electric field in the nanowire. The displacement along the nanowire axis is measured in this case. For nanowires with diameters in the range of 64 nm-190 nm, piezoelectric coefficients $d_{33} =$ 12.8 pm/V, $d_{13} = 8.2$ pm/V, and $d_{15} = 10.2$ pm/V were measured, which reveal that the piezoelectric constants of the GaN nanowires are up to six times that of the bulk values.^[10]

4.1.3. Direct Piezoelectric Measurement

In the literature, the direct piezoelectric measurement is most often presented in the context of piezoelectric nanogenerators. The generated electric charges or the produced electric potential under a mechanical deformation, such as tensile^[80] or bending,^[12] is reported as the outcome of direct piezoelectricity. Two common methods for direct piezoelectric measurement include tensile testing and lateral bending experiments, much similar to nanomechanical characterization.

In the tensile test, the specimen is placed on a precision tensile apparatus and fixed at two ends by conductive electrodes wired to a charge amplifier, **Figure 11**. Direct tension induces electric polarization in the specimen due to the piezoelectric effect and the induced electric charges are measured. Using a precision mechanical testing stage, Wang et al. measured direct piezoelectric effect in suspended and doubly clamped single crystal BaTiO₃ nanowire (~280 nm in diameter) under periodic tensile strain in high

vacuum.^[80] The charge response from the nanowire was measured with a high sensitivity fast-response charge amplifier and it was directly proportional to the applied strain rate. A charge constant of ~45 pC/N for the BaTiO₃ nanowire was measured. Considering that the charge constant for bulk BaTiO₃ is $d_{33} = 190 \text{ pC/N}$,^[79] it shows that part of the generated charge is dissipated or leaked into the measurement system.

In lateral bending experiments, a conductive AFM probe bends the nanowire and the generated electric potential across the nanowire is measured with the same conductive probe.^[12] It has been shown that in lateral bending by an AFM tip, the maximum potential produced at the NW surface has an inverse relationship with the cube of its length/diameter aspect ratio and a direct relationship with the lateral displacement by the probe.^[108] Theory has shown that for a ZnO NW with a diameter of 50 nm and length of 600 nm, the piezoelectric voltage is on the order of 0.3 V, enough to drive the metal-semiconductor Schottky diode at the interface of the AFM probe and the NW.^[108] This method was applied to ZnO nanowires and CdS nanowires grown on a substrate.^[46] By scanning the tip



Figure 11. Direct measurement of piezoelectricity in an individual $BaTio_3$ nanowire. (a) Schematic of the experimental setup for charge measurement and SEM image of the fixed-fixed nanowire, and (b) acquired signal from the charge amplifier under periodic tensile loading. Reproduced with permission from.^[80] Copyright 2007 American Chemical Society





Figure 12. Direct piezoelectric measurement by lateral bending. (a) The experimental setup, including a high impedance preamplifier, and AFM probe. (b) Measured electric potential from an individual GaN nanowire vs. applied force. The inset is an AFM topographic image of the nanowires. Reproduced with permission.^[111] Copyright 2011, IOP Publishing Inc.

across the sample surface with standing nanowires in contact mode AFM, the output voltage was detected across an external load. Similarly, piezoelectricity in single GaN nanorods was demonstrated.^[109] The coupling between the piezoelectric and the semiconducting properties of the sample and the Schottky contact between the semiconducting nanowire and the conductive AFM probe govern the mechanism of measurement in this method. In slightly different configuration, direct bending of PZT nanofibers spanned over a trench under bending using a tungsten probe in a nanomanipulator was presented by Chen et al.[110] A piezoelectric voltage constant of 0.079 Vm/N was measured.^[110] Recently, an improved method was introduced using AFM direct bending of individual nanowires.^[111] This new method (Figure 12) allows for more precise selection of a nanowire including its state before and after the experiment. It also provides precise control of the applied force and its point of application. Due to the anticipated high tip-sample contact resistance, a high input impedance preamplifier was required to improve the voltage measurement accuracy. In bending, the electric potential is positive on one side and negative on the other side. By precise force control, the relationship between the applied force and generated potential was established.

4.2. Computational Investigation of Piezoelectricity

Computational investigations of piezoelectricity are limited mainly due to the computational cost associated with simulating large size (length and diameter) nanowires. As a result, the majority of the available studies are limited to nanowires with diameters below 4 nm. Espinosa and co-workers studied the size-dependence of piezoelectricity in GaN and ZnO nanowires, for diameters ranging from 0.6 to 2.4 nm, based on first principle-based density functional theory (DFT) calculations.^[8] The generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional and the revised PBE functional with double- ζ polarization (DZP) orbital basis sets was used for the calculations. The length of the nanowires along the polar axis was set to one lattice constant, with periodic boundary conditions applied. In order to obtain the piezoelectric constant d₃₃, each nanowire was strained along the polar axis up to 4% strain, with steps of 0.5%. After energy minimization, polarization was calculated using the Berry-phase approach. The



slope of the polarization per unit volume vs. the applied strain provided the piezoelectric constant.^[8] A giant piezoelectric size effect was observed for both nanowires, with GaN exhibiting larger and more extended size dependence than ZnO. The results presented in Figure 13 show that for both ZnO and GaN nanowires, approximately two orders of magnitude enhancement in piezoelectric coefficient could be achieved if the diameter of the nanowire reduces to less than 1 nm. Since the output charge in piezoelectric nanogenerators scales with piezoelectric coefficient, the strong piezoelectricity in smaller nanowires is promising for energy harvesting for selfpowered nanodevices. In order to under-

stand the underlying size-dependence, the authors performed an analysis of distribution of charges and dipole moments. One of the observations from the computational modeling was that the absolute value of polarization in nanowire was smaller than the bulk value. However, when normalized for volume, the nanowires exhibited larger values. For the same number of atoms, the nanowire had smaller volume respect to the bulk material due to radial contraction caused by surface relaxation. This observation asserted that reduction of volume due to surface reconstruction in nanowires play an important role in the enhancement of the piezoelectric constants.^[8]

Similar enhancements, although of lesser magnitude, were identified for [0001] ZnO nanowires, using similar density functional theory calculations, carried out in nanowires up to 2.8 nm in diameter.^[112] In this work, it was found that ZnO nanowires have larger effective piezoelectric constant respect to their bulk counterparts due to their free boundary. For nanowires with diameters larger than 2.8 nm, the effective piezoelectric constant was almost constant. It was found that the effective piezoelectric constant in small nanowires did not depend monotonically on the radius due to two competitive effects of the increase of the lattice constant with reduction in the radius.

For the case of ZnO, the aforementioned computational studies, along with other similar reports are summarized in **Figure 14**. It is evident from the plot that computational studies still need to reach a larger size, and that there is a gap in the characterization of piezoelectricity between 10 nm and 100 nm. This size range is very relevant as the advantages of scaling usually appear below 100 nm and nanowire diameters, achievable with current synthesis methods, are typically above 10 nm.

Along this vein, there are noteworthy efforts being done in order to expand the range of computational studies of piezoelectricity. Specifically, simulation of larger models has become possible when molecular dynamics (MD) is modified to capture the effects of polarization.^[82] This formulation was used to study strain effect on the polarization distribution, piezoelectric coefficient, and hysteresis behavior in BaTiO₃ nanowires.^[113] In the core-shell MD method, two charged particles, a massive ion core and a mass-less ion-shell were used to describe each atom. This phenomenological model enabled capturing the dipolar moment within each unit cell. It was found that the axial polarization changed linearly with the strain over a relatively large range, such that it increased with tensile strain and decreased



Figure 13. (a) Cross-sections of GaN nanowires after minimization of energy. (b), (c) Diameter-dependence of piezoelectric coefficient d_{33} , for ZnO and GaN nanowires; (b) is the absolute values and (c) is the normalized with respect to the respective bulk value. Reproduced with permission.^[8] Copyright 2011, American Chemical Society.

with the compressive strain. Surprisingly it was found that as the size of the nanowire increased, the piezoelectric coefficient increased and approached the bulk value ($e_{33} = 6.71 \text{ C/m}^2$) when the diameter of the nanowire was larger than 2.4 nm.^[113]



Figure 14. Plot showing the scatter in piezoelectric coefficients for different characteristic sizes, obtained using experimental and computational techniques.^[8,35,94,103,112,115–117] Values are normalized with respect to the corresponding value for bulk ZnO, indicated by a horizontal line.

More recently this method has been proposed for piezoelectric semiconductors, namely ZnO.^[82] The piezoelectric constants were calculated for bulk wurtzite ZnO with $10 \times 10 \times 10$ unit cells in 3-dimension for a total of 4000 atoms, with periodic boundary conditions imposed. Small strains between -1% and 1% were applied to extract the three piezoelectric constant e₃₃, e₃₁, and e₁₅. It was shown that the classical core-shell potentials are sufficiently accurate for large scale atomistic simulation of the piezoelectricity in ZnO, as compared to benchmark DFT calculations. The authors reported ongoing efforts to extend these calculations for ZnO nanostructures such as nanowires.

As an overall conclusion to this section, a summary of the available data for piezoelectric nanowires is provided in **Table 3**. Furthermore, the available results, computational and experimental, available for ZnO nanowires are plotted in Figure 14. An inspection of these data reinforces the fact that further characterization efforts are needed to reduce the existing scatter and identify size-effects trends in the piezoelectricity of nanowires. Evidently, coupling of improved experimental techniques, which allow in situ structural characterization, and enhanced computational methods, are needed before reaching a unified set of values and more understanding of the physics behind the observed effects.

5. Concluding Remarks and Outlook

The widespread and relatively high yield synthesis of nanowires achieved in the past two decades offers great promise to their application in next generation electronics and energy harvesting devices. However, a better understanding of mechanical

ADVANCED MATERIALS

www.advmat.de

 Table 3. Electromechanical properties of piezoelectric nanowires.



Material	Piezoelectric Properties	electric Properties Size [nm]		Reference	
ZnO nanorods	d ₃₃ = 0.4–9.5 pm/V	d = 150–500 nm	PFM on nanorods	[35]	
ZnO nanorods	$d_{33} = 4.41 \pm 1.73 \text{ pm/V}$	d = 150–500 nm	PFM on nanorods	[150]	
ZnO nanobelt	14.3–26.7 pm/V	w = 360 t = 65	PFM	[94]	
ZnO pillars	d ₃₃ = 7.5 pm/V	d~300 nm	PFM on pillars	[103]	
ZnO	$e_{33} \sim 1.27 - 1.29, e_{31} \sim 2.16 - 2.28, e_{15} \sim 3.176 - 3.219$	10 ³ unit cells	Atomistic simulations	[82]	
ZnO	e ₃₃ ~1453–2025 (10 ⁻¹⁶ μC Å/ion)	d = 2.8 nm	Density functional calculations	[112]	
NaNbO3 nanowire	0.85–4.26 pm/V	d = 100	PFM	[97]	
KnbO₃ nanowire	7.9 pm/V	d = 100	PFM	[98]	
PZT nanoshell	90 pm/V	d = 700 - t = 90	PFM	[151]	
PZT nanofiber	piezoelectric voltage constant ~0.079 Vm/N	d = 10	Bending using a tungsten probe	[110]	
PZT nanowires	d~114 pm/V	H = 35–75 nm	PFM on etched nanowires	[102]	
BaTiO ₃ nanowires	45 pC/N	d ~ 280	Direct tensile test	[80]	
BaTiO₃ nanowire	16.5 pm/V	d = 120	PFM	[90]	
BaTiO ₃	e ₃₃ < 6.71 C/m ²	d = 0.4–2.4 nm	Molecular Dynamics	[113]	
GaN nanowire	generated potential = 150 mV	d ~ 25 30	Bending with AFM cantilever	[111]	
GaN nanowires	d ₁₅ ~10 pm/V	d = 64 nm	PFM	[9]	
GaN nanowires	d ₃₃ = 12.8 pm/v, d ₁₃ = 9.75 pm/V, d ₁₅ = 10.2 pm/V	d = 64–191 nm	Extended 3D PFM	[10]	

and electromechanical behavior of these nanostructures is critical prior to their successful integration into optimized reliable nanodevices.

In the context of elastic properties, it has been shown that the characterization of mechanical properties of piezoelectric nanowires has been spearheaded by works on ZnO, possibly because of its availability and ease of synthesis. Several methods have been applied, and convergence to a reliable set of identified elastic properties reached. This has been achieved by a steady improvement in the experimental and computational techniques employed in the characterization of 1D nanostructures. In particular, it is clear that ZnO nanowires grown in the [0001] orientation display larger elastic modulus at dimensions below ~100 nm, and that the measured enhancement is a result of the decrease in interatomic spacing near the nanowire surface.^[7] Furthermore, it has become evident that loading modes where surface elasticity dominates (such as bending) will display a larger enhancement in elastic modulus. A similar type of convergence to unambiguous elastic properties is within reach for GaN nanowires. These nanowires however, display a lessprominent size-effect, resulting from a lesser reduction in the interatomic spacing at the surface, as compared to ZnO.

In terms of failure properties, results reported in the literature point to the fact that ZnO nanowires exhibit significantly larger fracture strains and strengths than the material in bulk. However, unambiguous identification of size-dependence remains elusive because the role played by defects on fracture properties remains to be accurately quantified. Furthermore, direct comparison between experimental and computational results will require the development of new analysis methods capable of incorporating defects, thus allowing the simulation of more realistic nanowires. In the case of GaN, further experimentation is needed, but the data available suggests likelihood that fracture strengths are significantly higher than those measured in bulk. In both cases, further research should lead to a continuous reduction of the data scatter and a better understanding of the underlying physics.

It has also been shown that the mechanical characterization of other piezoelectric nanostructures is in its infancy. However, the experience acquired in the characterization of ZnO and GaN nanowires should lead to more accurate measurements in the short term. Specifically, for the characterization of these nanowires it should be expected that any method used for characterization should reliably measure bulk properties for nanostructures above a characteristic dimension. Techniques that do not yield such results should be revised, as they probably lack well-defined boundary conditions, accurate metrology, or exhibit other artifacts. The technique of choice is in situ TEM because the method provides a level of detail that allows exclusion of several uncertainties, such as nanowire diameter, local strain measurement and identification of atomic defects. In situ SEM or AFM lack this feature. On the computational side, comparison of the empirical MD potentials with first-principles calculations should be carried out whenever possible in order to validate force fields. Clearly, these conclusions are not only valid for the mechanical characterization of piezoelectric nanowires, but for other nanomaterials as well.

With respect to piezoelectric properties, several important physical effects have been reported in nanowires, including nonvolatile electric polarization, stable and one-dimensional mono-domain polarization, piezoelectric hysteresis and ferroelectric switching, and strong piezoelectricity. Initial results point to an enhancement of piezoelectric properties below 100 nm in diameter but significant scatter in the data is still



present, which can be attributed to the lack of experimental techniques allowing in situ atomic characterization, as well as current challenges in bridging experimental and computational studies. This is primarily due to the challenging nature of the former and the size limitation of the latter. Even first principle calculations are subject to variations depending on the functionals used^[8] and therefore comparing with experiments, similar to what has been done for mechanical properties, is a critical need.

The experimental landscape of piezoelectricity is dominated by piezo-response force microscopy (PFM). In PFM, the electric field penetrates into the sample approximately on the size of the AFM probe (~50 nm). Therefore, the measured piezoelectric properties are local and may change from point to point along the sample. In direct piezoelectric measurement, the tiny amount of generated potential with a very short decay time constant makes it difficult to obtain quantitative measurements.^[34] Thus, complementary efforts are required to develop new experimental methods to probe electromechanical behavior. Recent reports of MEMS devices with capabilities of coupled in situ electrical and mechanical testing are promising in this respect.^[31,114] Furthermore, in situ TEM structural characterization and dopant characterization through complementary techniques such as atom probe tomography will prove important in achieving unambiguous results that elucidate size effects and not particular synthesis routes.

Overall, *rate-dependent* nanomechanical properties and *size-dependent piezoelectric* properties are areas in which future research has the potential to achieve the highest impact. Moreover, while results from single specimens are required and desirable, the low yield of most of the current methods prevents examining *statistical variations* across different samples. Batch fabrication and synthesis methods for nanostructures are available, however, still there is no such high-throughput measurement technology for examining samples sets.

Acknowledgements

HDE acknowledges the support of the NSF through awards DMR-0907196 and EEC-0647560 (NSF-NSEC). We thank Dr. Tobin Filleter and Dr. Allison Beese for critical review of the manuscript and helpful discussions.

Received: December 15, 2011 Published online: May 11, 2012

- [1] P. Yang, R. Yan, M. Fardy, *Nano Lett.* **2010**, *10*, 1529–1536.
- [2] J. G. Lu, P. Chang, Z. Fan, Mater. Sci. Eng. R 2006, 52, 49–91.
- [3] Y. Li, J. Xiang, F. Qian, S. Gradeclœak, Y. Wu, H. Yan, D. A. Blom, C. M Lieber, *Nano Lett.* 2006, 6, 1468–1473.
- [4] W. Wu, Y. Wei, Z. L Wang, Adv. Mater. 2010, 22, 4711-4715.
- [5] J. C. Johnson, H.-J. Choi, K. P. Knutsen, R. D. Schaller, P. Yang, R. J. Saykally, *Nat Mater* 2002, 1, 106–110.
- [6] J. Zhou, Y. Gu, P. Fei, W. Mai, Y. Gao, R. Yang, G. Bao, Z. L. Wang, *Nano Lett.* 2008, *8*, 3035–3040.
- [7] R. Agrawal, B. Peng, E. E. Gdoutos, H. D. Espinosa, Nano Lett. 2008, 8, 3668–3674.
- [8] R. Agrawal, H. D. Espinosa, Nano Lett. 2011, 11, 786-790.
- [9] M. Minary-Jolandan, R. A. Bernal, H. D. Espinosa, MRS Commun. 2011, 1, 45–48.

- [10] M. Minary-Jolandan, R. A. Bernal, I. Kuljanishvili, V. Parpoil, H. D. Espinosa, *Nano Lett.* **2012**, *12*, 970–976.
- [11] F. Boxberg, N. Søndergaard, H. Q. Xu, Nano Lett. 2010, 10, 1108-1112.
- [12] Z. L. Wang, J. Song, Science 2006, 312, 242-246.
- [13] Y. Hu, Y. Zhang, C. Xu, G. Zhu, Z. L. Wang, Nano Lett. 2010, 10, 5025–5031.
- [14] S. Xu, Y. Qin, C. Xu, Y. Wei, R. Yang, Z. L. Wang, Nat. Nanotechnol. 2010, 5, 366–373.
- [15] Y. Qi, N. T. Jafferis, K. Lyons, C. M. Lee, H. Ahmad, M. C. McAlpine, *Nano Lett.* **2010**, *10*, 524–528.
- [16] C. Chang, V. H. Tran, J. Wang, Y.-K. Fuh, L. Lin, Nano Lett. 2010, 10, 726–731.
- [17] R. Agrawal, O. Loh, H. Espinosa, Exp. Mech. 2011, 51, 1-9.
- [18] D. E. Perea, J. E Allen, S. J. May, B. W. Wessels, D. N. Seidman, L. J. Lauhon, *Nano Lett.* **2006**, *6*, 181–185.
- [19] I. Levin, A. Davydov, B. Nikoobakht, N. Sanford, P. Mogilevsky, *Appl. Phys. Lett.* 2005, 87, 103110-3.
- [20] D. Tham, C. Y. Nam, J. E. Fischer, Adv. Funct. Mater. 2006, 16, 1197–1202.
- [21] K. H. Lee, J. Y. Lee, Y. H. Kwon, T. w. Kang, J. H. You, D. U. Lee, T. Kim, J. Mater. Res. 2009, 24, 3032–3037.
- [22] Y. Ding, Z. L. Wang, Micron 2009, 40, 335-342.
- [23] B. W. Jacobs, M. A. Crimp, K. McElroy, V. M. Ayres, Nano Lett. 2008, 8, 4353–4358.
- [24] R. Agrawal, B. Peng, H. D. Espinosa, *Nano Lett.* **2009**, *9*, 4177–4183.
- [25] K. A. Bertness, N. A. Sanford, J. M. Barker, J. B. Schlager, A. Roshko, A. V. Davydov, I. Levin, *J. Electron. Mater.* **2006**, *35*, 576–580.
- [26] B. Sieber, A. Addad, S. Szunerits, R. Boukherroub, *The J. Phys. Chem. Lett.* 2010, 1, 3033–3038.
- [27] W.-H. Chu, H.-W. Chiang, C.-P. Liu, Y.-F. Lai, K.-Y. Hsu, H.-C. Chung, Appl. Phys. Lett. 2009, 94, 182101-3.
- [28] H. Morkoç, Handbook of Nitride Semiconductors and Devices Vol. 1, 2008.
- [29] C. Shi, P. M. Asbeck, E. T. Yu, Appl. Phys. Lett. 1999, 74, 573-575.
- [30] M. Legros, D. S. gianola, C. Motz, MRS Bull. 2010, 35, 354-360.
- [31] M. A. Haque, H. D. Espinosa, H. J. Lee, MRS Bull. 2010, 35, 375.
- [32] H. S. Park, W. Cai, H. D. Espinosa, H. C. Huang, MRS Bull. 2009, 34, 178–183.
- [33] B. Peng, M. Locascio, P. Zapol, S Li, S. L. Mielke, G. C. Schatz, H. D. Espinosa, *Nat. Nanotechnol.* 2008, *3*, 626–631.
- [34] M. Alexe, S. Senz, M. A Schubert, D. Hesse, U. Gosele, Adv. Mater. 2008, 20, 4021–4026.
- [35] D. A. Scrymgeour, J. W. P. Hsu, Nano Lett. 2008, 8, 2204–2209.
- [36] Y. Gao, Z. L. Wang, Nano Lett. 2009, 9, 1103-1110.
- [37] G. Mantini, Y. Gao, A. D'Amico, C. Falconi, Z. Wang, Nano Res. 2009, 2, 624–629.
- [38] A. R. Hutson, Phys. Rev. Lett. 1960, 4, 505.
- [39] J. E Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer, L. J. Lauhon, *Nat. Nanotechnol.* **2008**, *3*, 168–173.
- [40] L. J. Lauhon, P. Adusumilli, P. Ronsheim, P. L. Flaitz, D. Lawrence, MRS Bull. 2009, 34, 738–743.
- [41] R. Agrawal, R. A. Bernal, D. Isheim, H. D. Espinosa, J. Phys. Chem. C 2011, 115, 17688–17694.
- [42] R. A. Bernal, R. Agrawal, B. Peng, K. A. Bertness, N. A. Sanford, A. V. Davydov, H. D. Espinosa, *Nano Lett.* 2011, *11*, 548–555.
- [43] X. Wang, J. Song, F. Zhang, C. He, Z. Hu, Z. Wang, Adv. Mater. 2010, 22, 2155–2158.
- [44] C. T. Huang, J. H. Song, C. M. Tsai, W. F. Lee, D. H. Lien, Z. Y. Gao, Y. Hao, L. J. Chen, Z. L. Wang, *Adv. Mater.* **2010**, *22*, 4008–4013.
- [45] M. Y. Lu, J. H. Song, M. P. Lu, C. Y. Lee, L. J. Chen, Z. L. Wang, ACS Nano 2009, 3, 357–362.

ADVANCED MATERIALS

www.advmat.de



www.MaterialsViews.com

- [46] Y.-F. Lin, J. Song, Y. Ding, S.-Y. Lu, Z. L. Wang, Appl. Phys. Lett. 2008, 92, 022105–3.
- [47] R. Agrawal, H. D. Espinosa, J. Eng. Mater. Technol. 2009, 131.
- [48] Y. Zhu, C. Ke, H Espinosa, Experimental Techniques for the Mechanical Characterization of One-Dimensional Nanostructures, *Exp. Mech.* 2007, 47, 7–24.
- [49] G. Stan, R. F. Cook, Mechanical Properties of One-Dimensional Nanostructures, in Scanning Probe Microscopy in Nanoscience and Nanotechnology. 2010, Springer-Verlag: Berlin Heidelberg.
- [50] B. Varghese, C.-H. Sow, C. T. Lim, Nanosci. Nanotechnol. Lett. 2010, 2, 268–281.
- [51] Y. Zhu, H. D. Espinosa, Proc. Natl. Acad. Sci. USA 2005, 102, 14503–14508.
- [52] J. J. Brown, A. I. Baca, K. A. Bertness, D. A. Dikin, R. S. Ruoff, V. M. Bright, Sens. Actuators A 2011, 166, 177–186.
- [53] M. He, J. Appl. Phys. 2011, 109, 123504.
- [54] M.-R. He, J. Zhu, Phys. Rev. B 2011, 83, 161302.
- [55] F. Xu, Q. Qin, A. Mishra, Y. Gu, Y. Zhu, Nano Research 2010, 3, 271–280.
- [56] M. He, Appl. Phys. Lett. 2009, 95, 091912.
- [57] J. Y. Huang, H. Zheng, S. X. Mao, Q. Li, G. T. Wang, Nano Lett. 2011, 11, 1618–1622.
- [58] B. Wen, J. E. Sader, J. J. Boland, Phys. Rev. Lett. 2008, 101, 175502.
- [59] N. Hai, L. Xiaodong, *Nanotechnology* **2006**, *17*, 3591.
- [60] C. Q. Chen, Y. Shi, Y. S. Zhang, J. Zhu, Y. J. Yan, Phys. Rev. Lett. 2006, 96, 075505.
- [61] H. Yunhua, B. Xuedong, Z. Yue, J. Phys.: Condensed Matter 2006, 18, L179.
- [62] X. Bai, Appl. Phys. Lett. 2003, 82, 4806.
- [63] H. Morkoç, Ü. Özgür, Zinc Oxide: Fundamentals, Materials and Device Technology, Wiley-VCH, Weinheim, Germany 2009.
- [64] Y. Chen, I. Stevenson, R. Pouy, L. Wang, D. N. McIlroy, T. Pounds, M. G. Norton, D. E. Aston, *Nanotechnology* 2007, 18, 135708.
- [65] P. Zhou, C. Wu, X. Li, Measurement Sci. Technol. 2008, 19, 115703.
- [66] A. V. Desai, M. A. Haque, Sens. Actuators A: 2007, 134, 169-176.
- [67] A. Asthana, K. Momeni, A. Prasad, Y. K. Yap, R. S. Yassar, Nanotechnology 2011, 22, 265712.
- [68] J. He, C. M. Lilley, Nano Lett. 2008, 8, 1798-1802.
- [69] X.-P. Zheng, Y.-P. Cao, B. Li, X.-Q. Feng, G.-F. Wang, Nanotechnology 2010, 21, 205702.
- [70] N. M. Pugno, R. S. Ruoff, Phil. Mag. 2004, 84, 2829-2845.
- [71] N. M. Pugno, R. S. Ruoff, J. Appl. Phys. 2006, 99, 024301-4.
- [72] J. Wang, J. Appl. Phys. 2010, 107, 023512.
- [73] J. Wang, A. J. Kulkarni, F. J. Ke, Y. L. Bai, M. Zhou, Comput. Methods Appl. Mech. Eng. 2008, 197, 3182–3189.
- [74] A. J. Kulkarni, M. Zhou, K. Sarasamak, S. Limpijumnong, Phys. Rev. Lett. 2006, 97, 105502.
- [75] R. Agrawal, J. T. Paci, H. D. Espinosa, Nano Lett. 2010, 10, 3432–3438.
- [76] N. A. Sanford, L. H. Robins, M. H. Gray, Y. S. Kang, J. E. V. Nostrand, C. Stutz, R. Cortez, A. V. Davydov, A. Shapiro, I. Levin, A. Roshko, *Phys. Status Solidi (c)* **2005**, *2*, 2357–2360.
- [77] H. Chen, D. Shi, J. Qi, B. Wang, Physica E 2009, 42, 32-37.
- [78] A. Mitrushchenkov, G. Chambaud, J. Yvonnet, Q. C. He, Nanotechnology 2010, 21, 255702.
- [79] R. E. Newnham, Properties of Materials, First ed, Oxford University Press, New York 2005.
- [80] Z. Wang, J. Hu, A. P. Suryavanshi, K. Yum, M.-F. Yu, Nano Lett. 2007, 7, 2966–2969.
- [81] R. Resta, D. Vanderbilt, Physics of Ferroelectrics: A Modern Perspective 2007, 105, 31–68.
- [82] S. X. Dai, M. L. Dunn, H. S. Park, Nanotechnology 2010, 21.
- [83] P. Güthner, K. Dransfeld, Appl. Phys. Lett. 1992, 61, 1137.
- [84] O. Kolosov, A. Gruverman, J. Hatano, K. Takahashi, H. Tokumoto, *Phys. Rev. Lett.* **1995**, *74*, 4309–4312.

- [85] A. Gruverman, O. Auciello, H. Tokumoto, Ann. Rev. Mater. Res. 1998, 28, 101–123.
- [86] M. Alex, A. Gruverman, Nanoscale characterisation of ferroelectric materials: scanning probe microscopy approach, Springer, New York 2004.
- [87] T. Hidaka, T. Maruyama, M. Saitoh, N. Mikoshiba, M. Shimizu, T. Shiosaki, L. A. Wills, R. Hiskes, S. A. Dicarolis, J. Amano, *Appl. Phys. Lett.* **1996**, *68*, 2358–2359.
- [88] H. Birk, J. Glatz-Reichenbach, L. Jie, E. Schreck, K. Dransfeld, J. Vaccum Sci. Technol. B 1991, 9, 1162–1165.
- [89] Z. Wang, J. Hu, M.-F. Yu, Appl. Phys. Lett. 2006, 89, 263119-3.
- [90] Z. Wang, A. P. Suryavanshi, M.-F. Yu, Appl. Phys. Lett. 2006, 89, 082903-3.
- [91] S. V. Kalinin, A. N. Morozovska, L. Q. Chen, B. J. Rodriguez, *Rep. Progr. Phys.* 2010, 73.
- [92] S. V. Kalinin, B. J. Rodriguez, S. Jesse, E. Karapetian, B. Mirman, E. A. Eliseev, A. N. Morozovska, Ann. Rev. Mater. Res. 2007, 37, 189–238.
- [93] S. V. Kalinin, A. Rar, S. Jesse, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 2006, 53, 2226–2252.
- [94] M.-H. Zhao, Z.-L. Wang, S. X. Mao, Nano Lett. 2004, 4, 587-590.
- [95] J. Wang, C. S. Sandu, E. Colla, Y. Wang, W. Ma, R. Gysel, H. J. Trodahl, N. Setterb, M. Kuball, *Appl. Phys. Lett.* **2007**, *90*, 133107.
- [96] W. S. Yun, J. J. Urban, Q. Gu, H. Park, *Nano Lett.* 2002, 2, 447–450.
 [97] T.-Y. Ke, H.-A. Chen, H.-S. Sheu, J.-W. Yeh, H.-N. Lin, C.-Y. Lee,
- H.-T. Chiu, J. Phys. Chem. C 2008, 112, 8827–8831.
- [98] J. Wang, C. Stampfer, C. Roman, W. H. Ma, N. Setter, C. Hierold, *Appl. Phys. Lett.* 2008, *93*, 223101.
- [99] X. Feng, B. D. Yang, Y. Liu, Y. Wang, C. Dagdeviren, Z. Liu, A. Carlson, J. Li, Y. Huang, J. A. Rogers, ACS Nano 2011, 5, 3326-3332.
- [100] Y. Qi, J. Kim, T. D. Nguyen, B. Lisko, P. K. Purohit, M. C. McAlpine, *Nano Lett.* 2011, 1331–1336, 1331–1336.
- [101] X. Y. Zhang, X. Zhao, C. W. Lai, J. Wang, X. G. Tang, J. Y. Dai, Appl. Phys. Lett. 2004, 85, 4190–41992.
- [102] T. D. Nguyen, J. M. Nagarah, Y. Qi, S. S. Nonnenmann, A. V. Morozov, S. Li, C. B. Arnold, M. C. McAlpine, *Nano Lett.* 2010, 10, 4595–4599.
- [103] H. J. Fan, W. Lee, R. Hauschild, M. Alexe, G. Le Rhun, R. Scholz, A. Dadgar, K. Nielsch, H. Kalt, A. Krost, M. Zacharias, U. Gosele, *Small* 2006, 2, 561–568.
- [104] Y. F. Hu, Y. F. Gao, S. Singamaneni, V. V. Tsukruk, Z. L. Wang, Nano Lett. 2009, 9, 2661–2665.
- [105] M. Minary-Jolandan, M.-F. Yu, ACS Nano 2009, 3, 1859-1863.
- [106] F. Bernardini, V. Fiorentini, Appl. Phys. Lett. 2002, 804145–4147.
- [107] M. Minary-Jolandan, M.-F. Yu, Nanotechnology 2009, 20, 085706.
- [108] Y. Gao, Z. L. Wang, Nano Lett. 2007, 7, 2499-2505.
- [109] W. S. Su, Y. F. Chen, C. L. Hsiao, L. W. Tu, Appl. Phys. Lett. 200790, 063110–3.
- [110] X. Chen, S. Xu, N. Yao, W. Xu, Y. Shi, Appl. Phys. Lett. 2009, 94, 253113-3.
- [111] X. Xu, A. Potie, R. Songmuang, J. Lee, B. Bercu, T. Baron, B. Salem, L. Montes, *Nanotechnology* **2011**, *22*, 105704.
- [112] H. J. Xiang, J. L. Yang, J. G. Hou, Q. S. Zhu, Appl. Phys. Lett. 2006, 89.
- [113] Y. H. Zhang, J. W. Hong, B. Liu, D. N. Fang, Nanotechnology 2010, 21.
- [114] Y. Zhang, X. Y. Liu, C. H. Ru, Y. L. Zhang, L. X. Dong, Y. Sun, J. Microelectromech. Syst. 2011, 20, 959–967.
- [115] C. Li, W. Guo, Y. Kong, H. Gao, Appl. Phys. Lett. 2007, 90, 033108–3.
- [116] L.-z. Kou, W.-I. Guo, C. Li, Symposium on Piezoelectricity of ZnO and its nanostructures. in Piezoelectricity, Acoustic Waves, and Device Applications, SPAWDA 2008, 2008.
- [117] A. Mitrushchenkov, R. Linguerri, G. Chambaud, J. Phys. Chem. C 2009, 113, 6883–6886.



- [118] C. Q. Chen, Appl. Phys. Lett. 2007, 90, 043105.
- [119] J. Song, X. Wang, E. Riedo, Z. L. Wang, Nano Lett. 2005, 5, 1954–1958.
- [120] C.-C. Röhlig, M. Niebelschütz, K. Brueckner, K. Tonisch, O. Ambacher,
 V. Cimalla, *Physica Status Solidi (b)* 2011, 247, 2557–2570.
- [121] H. Ni, X. Li, G. Cheng, R. Klie, J. Mater. Res. 2006, 21, 2882– 2887.
- [122] Q. Xiong, N. Duarte, S. Tadigadapa, P. C. Eklund, Nano Lett. 2006, 6, 1904–1909.
- [123] G. Stan, C. V. Ciobanu, P. M. Parthangal, R. F. Cook, Nano Lett. 2007, 7, 3691–3697.
- [124] M. Lucas, W. Mai, R. Yang, Z. L. Wang, E. Riedo, Nano Lett. 2007, 7, 1314–1317.
- [125] Z. Cai, Ph. D. Thesis: Synthesis, Properties and Applications of Indium Nitride Nanowires and Nanonetworks. 2008, University of South Carolina.
- [126] G. Feng, W. D. Nix, Y. Yoon, C. J. Lee, J. Appl. Phys. 2006, 99, 074304–10.
- [127] X. J. Zheng, G. C. Yu, Y. Q. Chen, S. X. Mao, T. Zhang, J. Appl. Phys. 2010, 108, 094305.
- [128] Y. Fuqian, C. B. Jiang, D. Wenwen, Z. Q. Zhang, L. Suoxing, X. M. Scott, *Nanotechnology* **2005**, *16*, 1073.
- [129] X. Li, X. Wang, Q. Xiong, P. C. Eklund, Nano Lett. 2005, 5, 1982–1986.
- [130] C.-Y. Nam, P. Jaroenapibal, D. Tham, D. E. Luzzi, S. Evoy, J. E. Fischer, *Nano Lett.* 2006, 6, 153–158.
- [131] T. Henry, K. Kim, Z. Ren, C. Yerino, J. Han, H. X. Tang, Nano Lett. 2007, 7, 3315–3319.
- [132] P. Gao, K. Liu, L. Liu, Z. Wang, Z. Liao, Z. Xu, W. Wang, X. Bai, E. Wang, Y. Li, J. Electron Microsc. 2010, 59, 285–289.

- [133] M. E. Gaevski, W. Sun, J. Yang, V. Adivarahan, A. Sattu, I. Mokina, M. Shatalov, G. Simin, M. Asif Khan, *Physica Status Solidi (a)* **2006**, 203, 1696–1699.
- [134] Y. D. Kim, K. Heo, M. R. Cho, S. Cho, D. Yoon, H. Cheong, J. Jian, S. Hong, Y. D. Park, *Applied Physics Express* 2011, 4, 065004.
- [135] G. R. Yazdi, P. O. Ã. Persson, D. Gogova, R. Fornari, L. Hultman, M. Syväjärvi, R. Yakimova, *Nanotechnology* **2009**, *20*, 495304.
- [136] J. Hu, X. W. Liu, B. C. Pan, Nanotechnology 2008, 19, 285710.
- [137] A. J. Kulkarni, K. Sarasamak, S. Limpijumnong, M. Zhou, Phil. Mag. 2007, 87, 2117–2134.
- [138] A. J. Kulkarni, M. Zhou, F. J. Ke, Nanotechnology **2005**, 16, 2749.
- [139] Z. Wang, X. Zu, L. Yang, F. Gao, W. J. Weber, Phys. Rev. B 2007, 76, 045310.
- [140] Z. Wang, X. Zu, L. Yang, F. Gao, W. J. Weber, *Physica E* 2008, 40, 561–566.
- [141] B. Wang, Appl. Phys. Lett. 2008, 93, 021918.
- [142] G. Wang, J. Appl. Phys. 2008, 104, 113517.
- [143] A. Gulans, I. Tale, Phys. Status Solidi (c) 2007, 4, 1197-1200.
- [144] X. J. Liu, Appl. Phys. Lett. 2009, 94, 131902.
- [145] G. Wang, Appl. Phys. Lett. 2007, 91, 231912.
- [146] F. Song, G. L. Huang, H. S. Park, X. N. Liu, Int. J. Solids Struct. 2011, 48, 2154–2163.
- [147] E. Chang, G. R. Barsch, J. Phys. Chem. Solids 1973, 34, 1543-1563.
- [148] I. B. Kobiakov, Solid State Commun. **1980**, 35, 305–310.
- [149] I. Vurgaftman, J. R. Meyer, J. Appl. Phys. 2003, 94, 3675.
- [150] D. A. Scrymgeour, T. L. Sounart, N. C. Simmons, J. W. P. Hsu, J. Appl. Phys. 2007, 101, 014316–6.
- [151] Yun Luo, I. Szafraniak, N. D. Zakharov, V. Nagarajan, M. Steinhart, R. B. Wehrspohn, J. H. Wendorff, R. Ramesh, M. Alexe, *Appl. Phys. Lett.* **2003**, *83*, 440–442.