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A multiscale bridging model for piezeoelctric ZnO nanowires using first principles calculation and continuum theory

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ABSTRACT

A multiscale analysis of piezoelectric nanostructures is necessary in order to reflect nanoscale material properties and macroscale continuum theory. In this work, a multiscale bridging model is introduced for piezoelectric ZnO nanowires based on first principles calculation for nanoscale analysis and continuum theory for macroscale investigation. Through a first principles calculation, nano-sized physical properties were calculated and atomic behaviors such as geometric changes and electronic structure were also investigated. Considering nanoscale effects of piezoelectric ZnO nanowires calculated by first principles calculation, multiscale bridging model was established so that continuum model of the ZnO nanowires can be well-explained not only macroscale material behavior, but also nano-sized effect of nanowire atomic model. On the analysis of ZnO nanowire, surface atomic distortion and electronic changes are observed because of anti-symmetric atomic forces caused by surface cleavages. These kinds of nano-sized effects have an inclination to cause macroscale behavior of nanowires to change different from that of bulk case. In situation which is hard to find this sort of multiscale analysis scheme having access to both characters of nanoscale and macroscale, the multiscale bridging model introduced in this work is expected to help various analyses of multiscale piezoelectric nanowire problem.

1. INTRODUCTION

As a nanotechnology has been developed considerably, various nanostructure models of smart materials are researched by lots of researchers. Among the smart materials piezoelectric materials have been highlighted. Piezoelectricity means that electric potential differences can be generated from changes of mechanical strains and vice versa. Zinc oxide (ZnO) has a fascinating piezoelectric material with high piezoelectricity, high electron mobility, good transparency, and semiconducting.

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Furthermore, nanostructured ZnO shows remarkable material properties compared to bulk ZnO (Wang 2006, Agrawal 2011).

Although many of experimental researchers have fabricated various ZnO piezoelectric nanostructures and revealed their remarkable characters, reliable theoretical analysis models are scarce to find yet. In fact, multiscale analysis which investigates from nanoscale to macroscale continueously is necessary to understand that how a nanoscale physical character works on macroscale realistic model. Until now, several research groups have tried to a multiscale analysis. (Dai 2011) reported the concept of surface piezoelectricity using a combination of a theoretical framework and atomistic calculations, and (Yvonnet 2011, Yvonnet 2012) suggested a finite element procedure for modeling crystalline nanostructures which is completed with computational procedure based on first principles calculations to extract elastic coefficients of general anisotropic surfaces. Fortunately, in continuum theory of view, (Park 2011) developed multi-scale continuum formulation for the electromechanical behavior developed by the total potential energy that combines both mechanical and electrostatic terms. Therefore, the multi-scale bridging model elaborately to describe both nano-sized effect of piezoelectric nanostructures on macroscale model is truly required.

In this work, we have focused on ZnO piezoelectric nanowire so as to establish a multiscale bridging model which can describe nano-sized effect of the nanowire through atomic investigation and continuum theory. At first, we investigated surface morphology of ZnO nanowire to determine atomic simulation model. On the basis of the before atomic model, we studied the changes caused by nano-sized effect such as electronic charge, geometry, and bond length compared to bulk model. These kinds of atomic investigation can give useful information when a multiscale bridging model is established. From the results of atomic investigation, we established multiscale bridging model based on continuum theory.

2. MULTISCALE BRIDGING MODEL

In this chapter, atomic investigation conducted by first principles calculation and continuum theories for establishing multiscale bridging model are introduced. Not only computational details such as calculation conditions and methods are explained, but also analysis results are discussed

2.1 Atomic investigation

As a first step of atomic calculation, atomic model have to be determined. Many of experimental papers showed that ZnO nanowire have an inclination to growth in the [0001] direction (Ngo-Duc 2012, Yang 2012). For this reason, the most probable surface of ZnO nanowire are (21-10) and (01-10) surface as described in Fig. 1(a). In order to figure out which surface is more favorable to form on ZnO nanowire, surface energy of each surface should be calculated and it is calculated by first principles calculation in Table 1. According to Table 1, surface energy of (21-10) is 0.189eV and that of (01-10) surface is 0.173eV, so more favorable surface of ZnO nanowire is likely to be (01-10) surface. Therefore, ZnO nanowire is likely to be formed like Fig. 1(b),

which is composed of six facets with (01-10) surface.

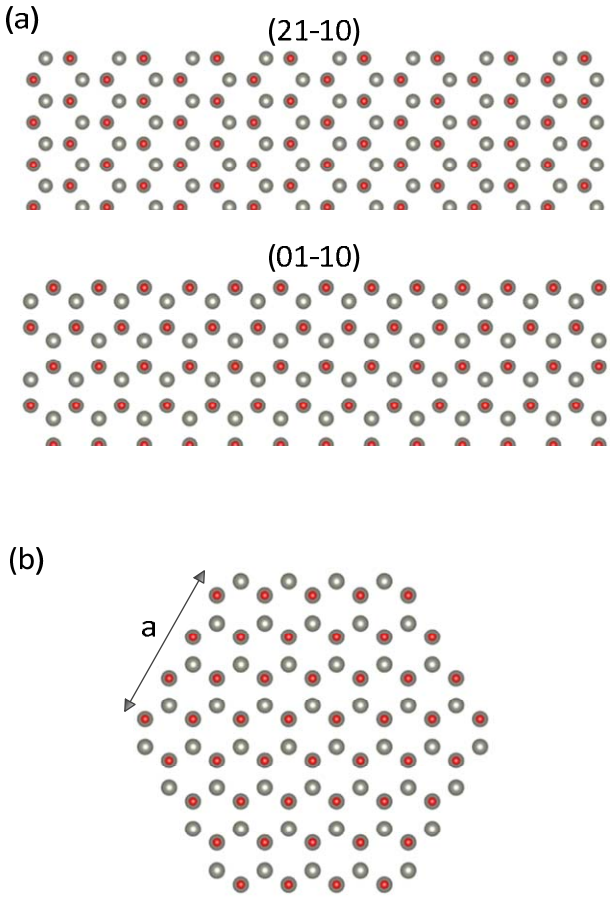

Fig 1. (a) Two most probable facets of ZnO nanowire, (b) Cross section of ZnO nanowire with facets of (01-10) surface

Table 1. Surface energy of (21-10) and (01-10) surfaces

	(21-10) Surface	*(01-10) Surface*
Surface energy (eV)	0.189	0.173

Based on the model in Fig 1(b), we need to figure out the physical character of ZnO nanowire so as to develop multiscale bridging model. We modeled two ZnO nanowire model (a=0.53nm, 0.85nm) due to large computational cost. The electronic charge distribution and bond length changes investigated by first principles calculation are shown in Fig 2.

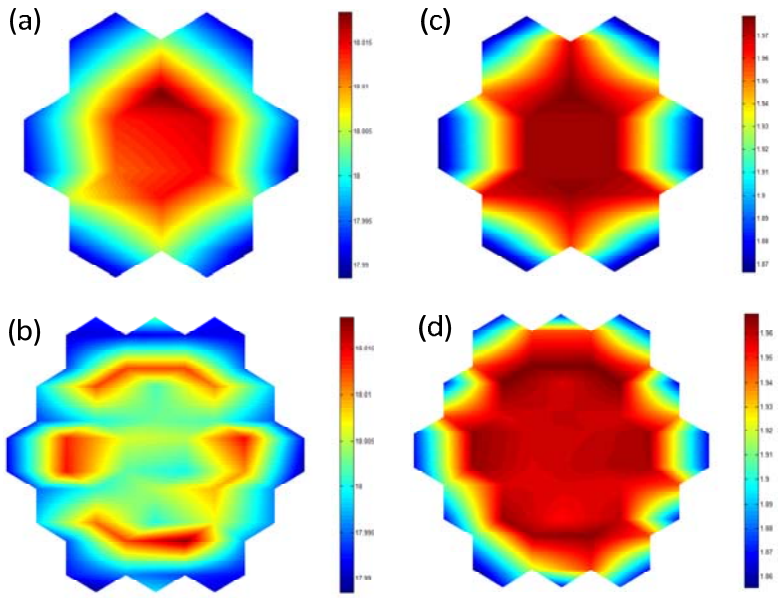

Fig 2. Electronic charge distribution of ZnO nanowires with (a) a=0.53nm and (b) a=0.85nm. Average bond length configuration of ZnO nanowires with (c) a=0.53nm and (d) a=0.85nm

Fig 2 describes electronic charge and bond length in two different sizes of ZnO nanowires. Both two material characters represent that parts of surface are different appearance from parts of bulk, and parts of vertexes are also different appearance from parts of surface and bulk. In other words, Fig 2 shows that the way to reflect nano-sized effect to the nanowire. Both electronic charge and bond length graph shows a similar appearance, which represent that nano-sized effect go into parallel to a side in the middle of two near vertexes, and larger nano-sized effect go into in the direction of vertex to center. That means we need to consider nanowire different from nanofilm owing to the existence of 6 vertexes. Therefore, the multiscale model to consider a nano-sized effect from a side and a vertex is necessary to establish for reasonable analysis of ZnO nanowire.

2.2 Multiscale bridging model

As mentioned before research results, we should consider not only effects from sides, but also effects caused by vertexes to reasonably analyze nanowires. Based on Fig 2, we are able to regard a middle part of vertexes as surfaces in nanofilms, and a vertex parts can be approximated by the influences of surfaces and their angle θ as shown in Fig 3.

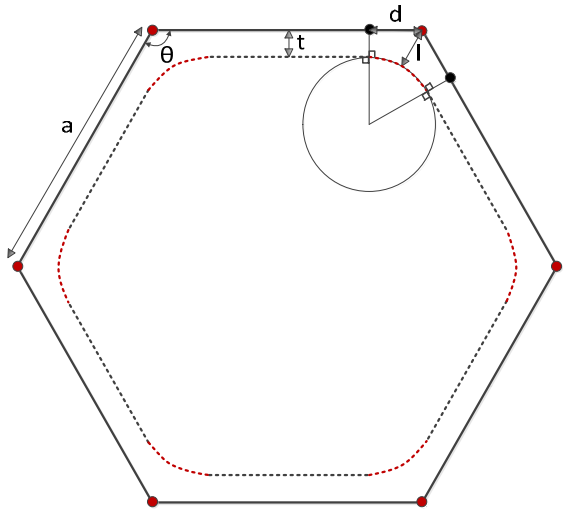

Fig 3. ZnO nanowire hexagon shape and description of surface effect range. Black solid line is hexagon shape, Dot line is surface effect range. Red filled circle is atom located in vertex and black filled circle is a nearest atom from vertex atom. Distance t is range of surface effect at the middle part of vertexes and distance l is range of surface effect near the vertexes.

In existing surface continuum theory if we consider nanofilm thicker than several nanofilm, surface effect with thickness h can be described as

$$E_{total} = E_b + \frac{E_s}{h}, \tag{1}$$

where, E_b is bulk quantity and E_s is surface quantity. However, we should treat nanowire differently considering vertex parts and six surfaces. If we take modified surface quantity $\bar{E}_s$ and characteristic thickness $\tilde{h}$, total quantity in nanowire can be rewritten as

$$E_{total} = E_b + \frac{\bar{E}_s}{\tilde{h}}, \tag{2}$$

where, geometrically

$$\bar{E}_s \cong \left(a + \frac{2d^2}{t \cdot \cos\frac{\theta}{2}} \left(1 - \sin\frac{\theta}{2} \right) \right) \frac{E_s}{a}, \tag{3}$$

and from energy density function equilibrium

$$\tilde{h} = \frac{3\sqrt{3}}{2} a. \tag{4}$$

Therefore, by developing existing surface continuum theory for nanofilm to nanowire based on specific atomic investigation, we can investigate nanowire successfully through multiscale analysis involving both nanoscale and macoscale characteristics.

3. CONCLUSIONS

Multiscale bridging model for ZnO nanowire is introduced in this paper. Firstly, by investigating ZnO nanowire using atomic quantum simulation, we can deduce various nano-sized effects and their range from surfaces. Furthermore, this work studied region near vertexes in order to analysis considering not only surface part, but also vertex part beyond existing surface continuum theory. That is why, we suggested modified surface quantity and characteristic thickness for nanowire compared to nanofilm. Based on established multiscale bridging model in this work, we anticipate that more favorable nanowire analysis can be performed.

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