Theoretical determination of the necessary conditions for the formation of ZnO nanorings and nanohelices

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The formation of ZnO nanorings and nanohelices with large polar surfaces observed in experiments [Nano Lett. 3, 1625 (2003); J. Am. Chem. Soc. 126, 6703 (2004)] is shown to be a result of the competition between elastic energy, spontaneous polarization-induced surface energy, volume energy, and defect-induced energy. It is found that nanorings and nanohelices observed in experiments are stable and energetically favorable structures.

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I. INTRODUCTION

Piezoelectric material produces electrical charges when subjected to pressure, and stretches or contracts when an electrical field is applied,1 which has been widely used as acoustic transducers in telephones, musical instruments, and so on. Piezoelectric crystals have no center of symmetry, which induces spontaneous polarization.2 ZnO is a typical piezoelectric material with wurtzite structure.3 Zn2+ and O2− planes arranging alternately along its c axis results in spontaneous polarization along this direction that induces divergent surface energy of Zn-(0001) and O-(0001) surfaces. To keep them stable, some researchers propose that the surfaces are not reconstructed; instead about one-fourth of the charges transfer between them.4−8 However, theoretical calculations and experiments reveal that the reconstruction is preferable to charge transfer7,8 in reducing the surface energy.

After the discovery of ZnO nanobelts,9 Kong and Wang synthesized ZnO nanobelts, in particular, nanorings and nanohelices whose surfaces were dominated by polarized Zn-(0001) and O-(0001) facets.10 They attributed the observed phenomena as a result of surface polar charges and explained that the formation of these nanostructures as a consequence of minimizing the total energy contributed by spontaneous polarization and elasticity.10 This model requires the ratio of the thickness t to the radius R of the nanorings to be smaller than a constant, and later more experimental data located in the green domain of Fig. 5(a) in Ref. 11 supported this model. However, the optimal relation between the thickness and the radius of nanorings [black line of Fig. 5(a) in Ref. 11] in their concise model cannot fit well the experimental data. To improve this relation, an elaborate theory considering more factors than their model but keeping its main spirit is needed.

Additionally, because of the symmetry of wurtzite structure, we know that there are five independent elastic constants for bulk ZnO that have been measured as c11 =190 GPa, c12 =110 GPa, c13 =90 GPa, c33 =196 GPa, and c44 =39 GPa.12 From these experimental values, we see c11 = c33, c12 = c13, and c44 = (c11 − c12)/2. That is, bulk ZnO can be roughly regarded as an isotropic material, and thus its Young’s modulus can be calculated as ~120 GPa from these experimental data. It is very surprising that Young’s modulus of ZnO nanobelt is measured experimentally only ~50 GPa,13,14 which is much smaller than that of bulk ZnO. One needs to understand what makes this large difference in Young’s modulus between bulk ZnO and the nanobelt.

In the present paper we try to address these issues. The rest of this paper is organized as follows. In Sec. II, we construct the shape formation energy of ZnO nanobelts that consists of elastic energy, spontaneous polarization-induced surface energy, volume energy, and defect-induced energy. We then put forward necessary conditions of structure existence. In Sec. III, we use necessary conditions of structure existence to explain nanorings and nanohelices observed in experiments. We find that they are stable and energetically favorable structures. In Sec. IV, we give a brief summary and discussion. Some detailed derivations are supplied in the Appendix.

II. CONSTRUCTION OF SHAPE FORMATION ENERGY

In order to quantitatively understand morphological problems of nanostructures in the theoretical point view, such as helices of multiwalled carbon nanotubes15,16 and cholesterol filaments,17,18 Ou-Yang and his co-authors proposed a concept that the shape formation energy determines the morphology of structures. Their concept can be summarized and generalized as follows: a structure can exist if its shape formation energy is minimum and less than zero, provided that the thermal fluctuation can be neglected. We will define and construct the shape formation energy of ZnO nanobelts in this section, and then express explicitly the necessary conditions of structure existence.

A. Definition of shape formation energy

The synthesis process of ZnO nanobelts is briefly described as follows.10,11 When ZnO powders are heated to 1350 °C at a heating rate of 20 °C/min, they decompose into Zn2+ and O2− at low pressure 10−3 Torr. After a few minutes of evaporation and decomposition, the Ar carrier gas...
Since the bending energy is determined uniquely by its central line than the length of the nanobelt, the geometry of the nanobelt and angle between should depend merely on geometric quantities of the final form of the shape formation energy of the nanobelt because of the cross section of the nanobelt.

B. Elastic energy, surface energy, and volume energy

The elastic energy per unit arc length can be written in an invariant quadratic form including infinitesimal displacements of the frame \( \{e_1, e_2, e_3\} \):

\[
E_c = \frac{k_{12}}{2} \left( \frac{de_1}{ds} \cdot e_2 \right)^2 + \frac{k_{13}}{2} \left[ \left( \frac{de_1}{ds} \cdot e_3 \right)^2 + \beta \left( \frac{de_2}{ds} \cdot e_3 \right)^2 \right],
\]

where \( ds \) is the arc length element, \( (de_1/\!ds) \cdot e_2 \) and \( (de_1/\!ds) \cdot e_3 \) represent, respectively, the bending deformations around \( e_2 \) and \( e_3 \), while \( (de_2/\!ds) \cdot e_3 \) represents the torsion deformation around \( e_3 \). \( k_{12} = Y_0 tw^3/12 \) and \( k_{13} = Y_0 wt^3/12 \), \( \beta k_{13} \) with \( \beta = 2/(1 + \nu) \) are the bending and torsion rigidities, where \( Y_0 \) and \( \nu \) are Young's modulus and the Poisson ratio of ZnO, respectively. For normal materials \( 0 \leq \nu \leq 1/2 \), \( \beta \) is in the range between 4/3 and 2.

Consider the geometric relations \( e_2 = N \cos \theta - B \sin \theta, e_3 = N \sin \theta + B \cos \theta \), and the Frenet formula:

\[
\begin{align*}
\frac{dN}{ds} &= -\kappa N + \tau B, \\
\frac{dB}{ds} &= -\tau N + \kappa B.
\end{align*}
\]

Equation (1) is simplified as

\[
E_c = \frac{k_{13}}{2} \left[ (\alpha \cos^2 \theta + \sin^2 \theta) \kappa^2 + \beta (\kappa - d\theta/\!ds)^2 \right],
\]

where \( \alpha = k_{12}/k_{13} \). Especially, for \( \theta = \pm \pi/2 \), the elastic energy per unit arc length can be written as

\[
E_c = \frac{k_c}{2} (\kappa^2 + \beta \tau^2),
\]

where \( k_c = k_{13} = Y_0 wt^3/12 \).

Because the nanobelt has two large polar surfaces, we must take into account their surface energy. The surface energy per unit arc length is phenomenologically expressed as

\[
E_s = 2\gamma w,
\]

where \( \gamma \) is a constant quantity with the dimension of energy per unit area.

The volume energy comes from two sources. One is the Gibbs free energy difference between the solid phase and the mesophase (condensation products); another is the electric energy induced by the spontaneous polarization. The volume energy per unit arc length is phenomenologically expressed as

\[
E_v = g_0 w t,
\]

where \( g_0 \) is a constant quantity with the dimension of energy per unit volume.

C. Defect-induced energy

As mentioned in Sec. I, the value of experimental Young's modulus of nanobelts (\( \sim 50 \) GPa) is less than half of bulk
ZnO’s value (~120 GPa). In order to compare the elastic constants of perfect ZnO thin films with bulk ZnO, we adopt a slab model and density functional theory (DFT) method to calculate them. To reduce the computational task, we take the frozen-ion approximation and concentrate on the elastic constant $c_{11}$. The computed ratio $c_{11}^{\text{slab}}/c_{11}^{\text{bulk}}$ as a function of the slab thickness is shown in Fig. 3. It is clear that the values of $c_{11}^{\text{slab}}/c_{11}^{\text{bulk}}$ are close to 1, which implies that the mechanical properties of perfect ZnO nanobelts have little difference from bulk ZnO. Thus the nanobelts observed in experiments must contain defects that reduce Young’s modulus of nanobelts significantly.

There are several clues for the existence of defects in real nanobelts. A direct one is high-resolution images of nanobelts. For example, the nanoring shown in Fig. 4(d) of Ref. 10 is not a perfect, uniform structure. High-resolution transmission electron microscopy also reveals that planar defects exist in the nanobelts.

It is hard to write an exact expression of defect-induced energy. However if we only consider structures with $|\kappa\tau| \ll 1$ and $|\pi| \ll 1$, the defect-induced energy can be locally expanded up to the second-order terms of $\kappa\tau$ and $\pi\tau$. It is expressed formally as

$$E_d = -[A_1(\kappa\tau)^2 + A_2(\pi\tau)^2 + \mu(\kappa\tau) + A_3] wt,$$  

where $A_1$, $A_2$, $A_3$, and $\mu$ are constant quantities with dimension energy per unit volume. To avoid the symmetry breaking of chirality, the linear term of $\pi\tau$ is not included in the above expression. Comparing Eq. (7) with Eqs. (4) and (6), we find that $A_1$ and $A_2$ play similar roles with respect to the Young’s modulus, while $A_3$ influences the value of volume energy density $g_0$. The rest term can induce a local spontaneous curvature of nanobelts randomly. Recently, the idea that defects induce a local spontaneous curvature has also been proposed to explain the cyclization phenomenon of short DNA.

**D. Necessary conditions of structure existence**

The final form of the shape formation energy is thus written as

$$F = \int (E_c + E_s + E_g + E_d) ds = \int \left[ \frac{Yt^3}{24} (\kappa^2 + \beta \tau^2) + (2\gamma + gt - \mu t^2 \kappa) \right] wds,$$  

where $Y$ and $g$ are the effective Young’s modulus and the volume energy density of ZnO nanobelts, respectively. For example, the value of $Y$ can be taken as the experimental value 50 GPa.

Now we estimate the effect of thermal fluctuation on the shapes of nanobelts. Considering the typical growth temperature $T \sim 10^3$ K, the Young’s modulus $Y = 50$ GPa, the typical thickness $t \sim 10$ nm, and the width $w > 50$ nm in the experiments, we estimate the persistence length of nanobelts $\xi = \gamma wt^3/12T \sim 1$ cm, which is much larger than the typical length of nanobelts of several micrometers. Thus, the effect of thermal fluctuation can be neglected and the necessary conditions of structure existence can be expressed as

$$\delta F = 0,$$  

$$\delta^2 F \gg 0,$$  

$$F \leq 0,$$  

where $\delta F$ and $\delta^2 F$ represent the first- and second-order variations of the shape formation energy, respectively. If a structure satisfies the above three conditions, we call it a stable and energetically favorable structure.

From Eq. (9), we arrive at the following shape equations of nanobelts

$$\kappa_{ss} + \frac{\kappa^3}{2} - \kappa \tau^2 + \frac{\beta}{2} \left[ 4 \pi \kappa_s + \frac{2 \tau^2}{\kappa} + 3 \kappa \tau^2 \right]$$  

$$+ \frac{\tau^2}{t} - \frac{(\eta + \xi t) \kappa}{2 t^2} = 0,$$  

$$2 \kappa_s \tau + \kappa \tau_s + \beta \left[ \tau_s (\tau \kappa_s - \frac{\tau_s}{\kappa}) \right] - \frac{\chi \tau_s}{t} = 0,$$  

where $\chi = 12 \mu/Y$, $\eta = 48\gamma/Y$, and $\xi = 24g/Y$. $(\cdot)_s$ represents the derivative respect to $s$. The detailed derivations of above two equations are shown in the Appendix. The necessary conditions of structure existence are transformed into Eqs. (10)–(13).

**III. EXPLANATION OF THE EXPERIMENTS**

Now let us use Eqs. (10)–(13) to explain nanorings and nanohelices observed in experiments.

**A. Nanorings**

For nanorings with radius $R$, one has $\kappa = 1/R$ and $\tau = 0$. Equation (12) is transformed into
These values are close to the typical value 10 nm observed in experiments by using the data in Ref. 10 are summarized in Table I. Among the thickness, the pitch angle, and the radius of nanohelices, while Eq. (10) sets relations among the thickness, the pitch angle, and the radius of nanohelices, with which we can estimate the thickness. The results by using the data in Ref. 10 are summarized in Table I. These values are close to the typical value 10 nm observed in experiments. Additionally, the shape formation energy can be calculated as

\[
\varphi = \cos^4 \varphi + \frac{2\beta - 1}{4} \sin^2 \phi - \frac{\chi r_0}{t} \cos 2\phi,
\]

while Eq. (13) is trivial. By fitting this equation to the experimental data, \( a^2 \) as shown in Fig. 4, we obtain \( \xi = -0.001 \pm 0.0007 \) and \( \eta = 0.03 \pm 0.01 \) nm.

Now we test condition (10). In polar coordinate system \((r, \phi)\), any perturbation in the vicinity of a cycle with radius \( R \) can be expressed as \( r = R(1 + \sum_{n=0}^{\infty} a_n \phi^n) \), where \( a_n \) \( a_n(n=0,1,2, \ldots, \infty) \) are small constants. The second-order variation is evaluated explicitly as

\[
\delta^2 F = \sum_n (n^2 - 1)^2 |a_n|^2Y_{\omega^2} L/12R \geq 0
\]

under the validity of Eq. (14).

Next, nanorings observed in experiments must satisfy condition (11). This requires \( F = \pi Y_{\omega^2} L (1/R - \chi)/6 \leq 0 \) to be valid for all experimental data. Thus, we can take the supremum of \( 1/R \) in Fig. 4 as the value of \( \chi \); i.e., \( \chi = 0.08 \).

### B. Nanohelices

For a nanohelix with radius \( r_0 \) and pitch \( p \), the pitch angle is \( \varphi = \arctan(p/2\pi r_0) \). The curvature and the torsion are \( \kappa = \cos^2 \varphi/r_0 \) and \( \tau = -\sin \varphi \cos \varphi/r_0 \), respectively. Equation (12) is transformed into

\[
\cos^4 \varphi + (3\beta - 2) \sin^2 \varphi \cos^2 \varphi + \frac{2\chi r_0}{t} \sin^2 \phi = \frac{r_0^2 (\eta + \xi)}{t^2}.
\]

while Eq. (13) is trivial again. Equation (16) sets relations among the thickness, the pitch angle, and the radius of nanohelices, from which we can estimate the thickness. The results by using the data in Ref. 10 are summarized in Table I. These values are close to the typical value 10 nm observed in experiments. Additionally, the shape formation energy can be calculated as

\[
F = \frac{Y_{\omega^2} L}{12r_0^2} \left[ \cos^4 \varphi + \frac{2\beta - 1}{4} \sin^2 \phi - \frac{\chi r_0}{t} \cos 2\phi \right],
\]

where \( L \) is the total length of the nanohelices. Its value is listed in Table I for three nanohelices observed in the experiments using \( \chi = 0.08 \). Moreover, we also found the matrix

\[
\begin{pmatrix}
\delta^2 F/\delta \theta_0^2 & \delta^2 F/\delta \theta_0 \delta \phi & \delta^2 F/\delta \phi^2
\end{pmatrix}
\]

is positive definite for these nanohelices. Therefore, these nanohelices are stable and energetically favorable structures.

### IV. CONCLUSION

In the present work, we construct the shape formation energy of ZnO nanobelts that consists of elastic energy, spontaneous polarization-induced surface energy, volume energy, and defect-induced energy. We put forward the necessary conditions of structure existence and find that nanorings and nanohelices of ZnO observed in experiments are stable and energetically favorable structures. We obtain an important result that nanorings and nanohelices must satisfy Eqs. (14) and (16), respectively. We notice that it is easy to measure experimentally the values of the radius of nanorings or the pitch and radius of nanohelices, while it is difficult to measure their thickness of about 10 nm with high precision because the error of the InLens detector is \( \pm 2 \) nm.\(^{10,11}\) Equations (14) and (16) provide a way to overcome this difficulty. The present theory may also be developed to explain the recently synthesized superlattice-structured nanohelices.\(^{20}\)

Because of the influence of defects, Young’s modulus \( Y \) and volume energy density \( g \) are quite different from the value of perfect and uniform nanobelts. For example, \( Y = 50 \) GPa is just half of the value of perfect nanobelts. \( g \) is estimated as \( \sim 10^9 \) J/m\(^3\) by \( \xi = -0.001 \). This value departs largely from the cohesive energy \( \sim 10^{10} \) J/m\(^3\) of ZnO.\(^{27}\) The surface energy density \( \gamma \) is estimated as 0.03 J/m\(^2\), which cannot compare with the cleavage energy \( \sim 4 \) J/m\(^2\) for perfect Zn-(0001) and O-(0001) surfaces obtained by \( \text{ab initio} \) calculations.\(^6\) There is no theory on the parameter \( \mu \) at present, which is expected to depend on the defect density and experimental conditions. We estimate its value \( \mu \approx 10^5 \) J/m\(^3\) from the experiment published in Ref. 11.
In the above discussion, we do not include flexoelectric effect\textsuperscript{28,29} of piezoelectric materials in the nanoscale. This effect is too small for crystals\textsuperscript{29} to influence the above results in statics. However, it may play a role in the kinetic growth of ZnO nanobelt so that nanorings with Zn-terminated and O-terminated inner surfaces have different weights in the end products. Through analyzing the weights, one may reveal the flexoelectric effect of ZnO in experiments.

Note added in proof. We only keep the second order terms of bending energy and adopt the conventional definitions of surface energy and volume energy in this paper. A more complicated theory including the higher order terms of bending energy and the modified definitions of surface energy and volume energy with the effect of the curvature and torsion might be developed.

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APPENDIX: DERIVATION OF EQS. (12) AND (13)

We present the derivation of Eqs. (12) and (13) from the first-order variation of functional (8) under the periodic boundary or fixed boundary. The basic idea is similar to Ref. 30. When we perform the variational calculation, the volume and density of a ZnO nanobelt are allowed to vary, while the total mass is conserved. However, the variation is performed for an infinitely small perturbation, which has very small effect on the elastic coefficients in Eq. (8). The final Euler-Lagrange equations obtained from the variational process including this effect are the same as those derived from the variation with elastic coefficients fixed to constant.

Let $E_1=\mathbf{e}_1$, $E_2=\mathbf{N}$, $E_3=\mathbf{B}$, and $dE_i=w_iE_i$, where Einstein’s summation convention is used and “d” is an exterior differential operator. Thus, we have $d\mathbf{r}=\Omega ds$, $w_{12}=\kappa ds$, $w_{13}=0$, and $w_{23}=\tau ds$ by considering the Frenet formula.

First, we consider $d\mathbf{r}=\Omega_2E_2$ and $dE_i=\Omega_iE_i$. Using the formulas $d\mathbf{r}=\delta d\mathbf{r}$ and $dE_i=\delta dE_i$,\textsuperscript{30} we have

\begin{align}
\delta ds &= \Omega_2 w_{21} = - \kappa ds \Omega_2, \\
\Omega_{12} ds &= d \Omega_2, \\
\Omega_{13} &= \tau \Omega_2, \\
\delta w_{ij} &= d \Omega_{ij} + \Omega_{ik} w_{kj} - w_{ik} \Omega_{kj}.
\end{align}

Because $\delta w_{13}=0$, we obtain

\begin{align}
\Omega_{23} ds &= [d \Omega_{13} - \tau \Omega_{3} ds] / \kappa.
\end{align}

Using the above five equations, we can prove

\begin{align}
\delta k ds &= d \Omega_{12} + (\kappa^2 - \tau^2) \Omega_2 ds, \\
\delta \tau ds &= d \Omega_{23} + 2 \kappa \tau ds \Omega_2.
\end{align}

Considering Stokes’ theorem and above seven equations, we arrive at

\begin{align}
\delta \int \kappa^2 ds &= \int (4 \kappa \tau + 2 \kappa \tau) \Omega_3 ds, \\
\delta \int \tau^2 ds &= \int \left[ 4 \tau \left( \frac{\tau}{\kappa} \right) + \frac{2 \tau^2}{\kappa} + 3 \kappa \tau^2 \right] \Omega_2 ds.
\end{align}

Because $\Omega_2$ is an arbitrary function, $\delta F=0$ gives Eq. (12).

Secondly, we consider $d\mathbf{r}=\Omega_3E_3$. Using the formula $d\mathbf{r}=\delta d\mathbf{r}$ and $dE_i=\delta dE_i$, we have

\begin{align}
\delta ds &= \Omega_3 w_{31} = 0, \\
\Omega_{12} &= - \tau \Omega_3, \\
\Omega_{13} &= \kappa \Omega_3, \\
\delta w_{ij} &= d \Omega_{ij} + \Omega_{ik} w_{kj} - w_{ik} \Omega_{kj}.
\end{align}

Because $\delta w_{13}=0$, we obtain

\begin{align}
\Omega_{23} ds &= [d \Omega_{13} - \tau \Omega_{3} ds] / \kappa.
\end{align}

Using above five equations, we can prove

\begin{align}
\delta k ds &= - 2 d (\tau \Omega_3) + \Omega_3 d \tau, \\
\delta \tau ds &= d \Omega_{23} + \kappa d \Omega_3.
\end{align}

Considering Stokes’ theorem and above seven equations, we arrive at

\begin{align}
\delta \int \kappa^2 ds &= \int (4 \kappa \tau + 2 \kappa \tau) \Omega_3 ds, \\
\delta \int \tau^2 ds &= \int \left[ 4 \tau \left( \frac{\tau}{\kappa} \right) + \frac{2 \tau^2}{\kappa} + 3 \kappa \tau^2 \right] \Omega_2 ds.
\end{align}
Consequently, we obtain

$$\delta \int \tau ds = 2 \int \left[ \tau \kappa - \frac{\tau}{\kappa} \right] \Omega_3 ds, \quad (A20)$$

$$\delta \int \kappa ds = \int \tau \Omega_3 ds. \quad (A21)$$

Because $\Omega_3$ is an arbitrary function, $\delta F = 0$ gives Eq. (13).

23. The calculations with DMOL3 package [B. Delley, J. Chem. Phys. 92, 508 (1990)] use the generalized gradient approximation with the Perdew-Burke-Ernzerhof for exchange-correlation potential. The basis set consists of the double numerical atomic orbitals augmented by polarization functions. The different thickness of thin film is modeled by periodically repeated slabs containing 2, 4, 6, and 10 Zn-O double layers separated by 10 Å vacuum gaps, respectively. A Monkhorst-Pack grid of $(9 \times 9 \times 9)$ and $(9 \times 9 \times 2)$ $k$-points is used for the bulk unit cell and slab supercell, respectively. The optimized structure parameters of ZnO with wurtzite structure are $a=3.305$ Å, $c=5.309$ Å, and internal parameter $\mu=0.380$. Test calculations give the elastic constants of bulk ZnO as $c_{11}^{\text{bulk}}=236.8$ GPa, $c_{33}^{\text{bulk}}=250.6$ GPa, and $c_{44}^{\text{bulk}}=49.9$ GPa, in agreement with the previous theoretical values and experimental results.