First-principles study on physical properties of a single ZnO monolayer with graphene-like structure

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The elastic, piezoelectric, electronic, and optical properties of a single ZnO monolayer (SZOML) with graphene-like structure are investigated from the first-principles calculations. The phonon dispersion curves contain three acoustic and three optical branches. At Γ point, the out-of-plane acoustic mode has an asymptotic behavior \( \omega(q) = Bq^2 \) with \( B = 1.385 \times 10^{-7} \text{ m}^2/\text{s} \), while two in-plane acoustic modes have sound velocities 2.801 km/s and 8.095 km/s; the other three optical modes have frequencies 250 cm\(^{-1}\), 566 cm\(^{-1}\), and 631 cm\(^{-1}\). The elastic and piezoelectric constants are obtained from the relaxed ion model. It is found that the SZOML is much softer than graphene, while it is a piezoelectric material. The electronic band gap is 3.576 eV, which implies that the SZOML is a wide band gap semiconductor. Many peaks exist in the linear optical spectra, where the first peak at 3.58 eV corresponds to the band gap of SZOML.

I. INTRODUCTION

Many ZnO nanostructures such as nanowires, nanobelts, nanorings and nanohelices have been synthesized in recent years, which are expected to be used to make novel electronic devices such as field-effect transistors, nanogenerators and so on. Viewed from the small scales, these nanostructures are locally wurtzite type. In 2005, Claeyssens et al. found that the graphite-like structure would transit to the bulk wurtzite structure through the DFT calculation and GW approximation. They obtained the critical number of ZnO nanobelts, nanorings and nanohelixes by first-principles calculations (the ABINIT package). In 2007, Tusche et al. observed graphite-like ZnO monolayers in the thin film to be 18, beyond which the interlayer interactions because the widely used DFT packages cannot accurately describe the non-covalent bonds. The critical number was estimated to be 3 or 4.

We expect that this new material might have good physical properties. However, there is very few investigation on this topic except our previous work\(^7\) on elastic constants and the work\(^6,7,13,14\) on metallic edges and magnetic behavior in ZnO nanoribbons. Here, we will address the elastic, piezoelectric, electronic, and optical properties of an SZOML with graphene-like structure by first-principles calculations (the ABINIT package). In 2007, Tusche et al. observed graphite-like ZnO monolayers in the experiment and found that critical number to be 3 or 4.

II. STRUCTURE

The DFT calculations\(^6,7,13,14\) and the experiment\(^7\) reveal that an SZOML with graphene-like structure is chemically stable. Its structure is schematically depicted in Fig. 1 where \( a_1 \) and \( a_2 \) are the two lattice vectors. Each unit cell contains one Zn atom and one O atom. We optimize the structure by taking Troullier-Martins pseudopotentials, plane-wave energy cutoff 50 Hartree, and \( 8 \times 8 \times 1 \) Monkhorst-Pack k-point. The exchange-correlation energy is treated within the local-density approximation in the Ceperley-Alder form with the Perdew-Wang parametrization. We keep the lattice constant in \( z \)-direction 40 bohr such that our result is available for the SZOML. We obtain the two lattice constants in \( xy \)-plane \( |a_1| = |a_2| = 6.062 \text{ bohr} (=3.208 \text{ Å}) \), and correspondingly, the bond length 1.853 Å, which is close to the previous value obtained by the present author and Hu with different cut and k-points.

III. PHONON DISPERSION RELATION

The phonon dispersion relation \( \omega = \omega(q) \) entirely reflects the lattice dynamic behavior of SZOML, where \( \omega \) and \( q \) are the phonon frequency and wave number, respectively. Here, we obtain the phonon dispersion relation through the first-principles calculations following the work\(^19,20\) by Gonze and others and show the results in Fig. 2.

Three phonon dispersion branches originating from Γ point of the Brillouin zone correspond to the acoustic modes: an out-of-plane mode (the lower branch), an in-plane tangential mode (the middle branch) and an in-plane radial mode (the upper branch). Among them, the phonon dispersion curve of the out-of-plane mode near

\( \omega(q) = Bq^2 \) with \( B = 1.385 \times 10^{-7} \text{ m}^2/\text{s} \).
\[ k_c = \sigma B^2, \quad (1) \]

where \( \sigma = 1.516 \times 10^{-6} \text{ kg/m}^2 \) is the density (i.e., mass per area) of SZOML. Then we obtain \( k_c = 0.182 \text{ eV} \), which is much smaller than the bending rigidity \( (1.62 \text{ eV})^2 \) of graphene.

The remaining three branches are optical modes: one out-of-plane mode and two in-plane modes. At \( \Gamma \) point, their frequencies are non-vanishing, and the corresponding values are 250 cm\(^{-1}\), 566 cm\(^{-1}\), 631 cm\(^{-1}\), respectively.

\section*{IV. ELASTICITY AND PIEZOELECTRICITY}

We have mentioned that the elastic constants of SZOML cannot be directly derived from the phonon dispersion relation because the coupling between elasticity and piezoelectricity. However, we can directly calculate the elastic and piezoelectric constants by using the ABINIT package. Because the SZOML has threefold rotation symmetry around \( z \)-axis and a reflection symmetry with respect to the \( y \)-axis as shown in Fig. 1, the elasticity and piezoelectricity for zero external electric field can be expressed in the matrix form\(^{22}\) as

\[
\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_6
\end{bmatrix} =
\begin{bmatrix}
c_{11} & c_{12} & 0 \\
c_{12} & c_{11} & 0 \\
0 & 0 & \frac{c_{12}^2}{c_{11}}
\end{bmatrix}
\begin{bmatrix}
s_1 \\
s_2 \\
s_6
\end{bmatrix},
\quad (2)
\]

and

\[
\begin{bmatrix}
P_1 \\
P_2 - P_2^0
\end{bmatrix} =
\begin{bmatrix}
0 & 0 & -d_1 \\
-d_1 & d_1 & 0
\end{bmatrix}
\begin{bmatrix}
s_1 \\
s_2 \\
s_6
\end{bmatrix},
\quad (3)
\]

respectively. In the above expressions, \( \sigma_1 \) and \( \sigma_2 \) are the normal stresses along \( x \) and \( y \) directions, respectively. \( s_1 \) and \( s_2 \) are the normal strains along \( x \) and \( y \) directions, respectively. \( \sigma_6 \) and \( s_6 \) are the in-plane shear stress and shear strain, respectively. \( P_2 \) is the spontaneous polarization in the \( y \)-direction. \( P_1 \) and \( P_2 \) are polarizations along \( x \) and \( y \) directions, respectively. \( c_{11} \) and \( c_{12} \) are two independent elastic constants, while \( d_1 \) is the independent piezoelectric constant. Because the thickness of SZOML is unknown, we let it be implicit in \( c_{11} \), \( c_{12} \), and \( d_1 \). Based on the relaxed ion model\(^{22}\) we obtain \( c_{11} = 56.8 \text{ eV/ZnO}, c_{12} = 40.3 \text{ eV/ZnO}, \) and \( d_1 = 3.0 \text{ pC/m}^2 \) from DFT calculations, where \( \rho_e = 8.5 \times 10^{-30} \text{ C m} \) is the atomic unit of electric dipole moment.

Using the elastic constants, we can derive the in-plane Young’s modulus \( (Y) \), shear modulus \( (G) \), and Poisson ratio \( (\nu) \) of SZOML as follows:

\[
Y = c_{11}(1 - c_{12}^2/c_{11}^2) = 28.1 \text{ eV/ZnO},
\quad (4)
\]

\[
G = (c_{11} - c_{12})/2 = 8.2 \text{ eV/ZnO},
\quad (5)
\]

\[
\nu = c_{12}/c_{11} = 0.71.
\quad (6)
\]
The Young’s modulus and shear modulus of SZOML are much smaller than those of graphene, 115.4 and 49.6 eV/CC, respectively, while the Poisson ratio of SZOML is much larger than that of graphene, 0.16.\textsuperscript{2,3,25}

V. ELECTRONIC BAND STRUCTURE

As a new material, we expect that SZOML has a good electronic property. Its band structure is calculated within the DFT framework. In Fig. 3, we plot energy dispersion curves for 9 valence and 5 conduction bands along high symmetry directions in the Brillouin zone. There are 1 low energy valence band, 5 middle energy valence bands, and 3 high energy bands among the 9 valence bands. The direct gap between the lowest conduction band and the highest valence band is \( E_{\text{gap}} = 1.762 \text{ eV} \).

![Energy dispersion curves](image)

FIG. 3: (Color online) Energy dispersion curves for 9 valence and 5 conduction bands plotted along high symmetry directions in the Brillouin zone.

The large underestimation of the band gap is a well-known problem in DFT calculations. We use the GW approximation\textsuperscript{26,27} to obtain the correct band gap \( E_{\text{gap}}^{\text{gw}} = 3.576 \text{ eV} \) which is larger than the calculated band gap (2.6 eV)\textsuperscript{28} of the bulk ZnO. Thus the SZOML can be regarded as a wide band gap semiconductor.

VI. OPTICAL DIELECTRIC FUNCTIONS

The frequency dependent optical dielectric functions of semiconductor can be computed from the first principles.\textsuperscript{29,30} In terms of the symmetry of SZOML, the non-vanishing dielectric functions are \( \epsilon_{xx}, \epsilon_{yy}, \epsilon_{zz}, \epsilon_{xy} = \epsilon_{yx} \), which can be calculated by taking 81 bands, \( 19 \times 19 \times 1 \) Monkhorst-Pack k-points, and an “scissor shift” 1.813 eV (i.e., the correction of band gap obtained from GW approximation).

![Dielectric functions](image)

FIG. 4: Dielectric functions. ‘Im’ and ‘Re’ represent the imaginary part and real part, respectively. \( h \) is the unknown thickness of SZOML.

In Fig. 4, we show the frequency dependent real parts and imaginary parts of dielectric functions \( \epsilon_{yy}(\omega) \) and \( \epsilon_{zz}(\omega) \), where \( h \) is the unknown thickness of SZOML. \( \epsilon_{xx} \) and \( \epsilon_{xy} \) are not shown because their shapes are similar to \( \epsilon_{yy} \). The peaks in the linear optical spectra \( \text{Im}(h\epsilon_{yy}) - \omega \) exist at 3.58 eV, 3.80 eV, 3.93 eV, 4.20 eV, 4.38 eV, 4.52 eV, 4.87 eV, and so on, which can be identified from the band structure. In particular, the first peak at 3.58 eV marked with an arrow in \( \text{Im}(h\epsilon_{yy}) - \omega \) curve corresponds to the band gap, 3.576 eV, obtained from GW approximation.

VII. CONCLUSION AND DISCUSSION

We have obtained the phonon dispersion relation, the elastic and piezoelectric constants, the electronic band structure, and the optical response functions from the first-principles calculations. The main results are listed as follows.

(i) The phonon dispersion curves contain three acoustic and three optical branches as in Fig 2. At \( \Gamma \) point, the out-of-plane acoustic mode has an asymptotic behavior \( \omega(q) = Bq^2 \) with \( B = 1.385 \times 10^{-7} \text{ m}^2/\text{s} \), while two in-plane acoustic modes have sound velocities 2.801 km/s and 8.095 km/s; the other three optical modes have frequencies 250 cm\(^{-1}\), 566 cm\(^{-1}\), and 631 cm\(^{-1}\).

(ii) The elastic and piezoelectric constants are \( c_{11} = 56.8 \text{ eV/ZnO}, \); \( c_{12} = 40.3 \text{ eV/ZnO}, \) and \( d_1 = 3.0 \text{ pC/ZnO}. \) The SZOML is a piezoelectric material. The in-plane Young’s modulus, shear modulus, and Poisson ratio are calculated as 28.1 eV/ZnO, 8.2 eV/ZnO, and 0.71, respectively. The out-of-plane rigidity is estimate to be 0.182 eV. These values reveal that the SZOML is much softer than graphene.
(iii) The SZOML is a wide band gap semiconductor with electronic band gap 3.576 eV. This value corresponds to the first peak in the linear optical spectra \( \text{Im}\{\varepsilon_{yy}\} - \omega \).

We hope these results can be verified by experiments in the future. These main results also help us to infer the possible physical properties of single-walled ZnO nanotubes (SWZONTs). Interestingly, there are a lot of first-principles investigations on the elastic, electronic, and optical properties of SWZONTs\(^{7,31-32}\) although they have not been synthesized yet. The geometrical construction of SWZONTs from SZOML was discussed in the previous work\(^{7,32}\). Here we make some predictions on the physical properties of SWZONTs as follows.

(i) In terms of our experience on the elasticity of graphene and carbon nanotubes\(^{23-24}\), the in-plane Young’s modulus, Poisson ratio and out-of-plane bending rigidity of SWZONTs should be similar to those of SZOML, which is weakly dependent on the chirality of the SWZONTs.

(ii) The piezoelectricity depends on the chirality of SWZONTs viewed from the symmetry. Zigzag nanotubes possess the largest piezoelectricity while armchair nanotubes have no piezoelectricity.

(iii) Through zone folding method\(^ {24}\) we can obtain most of phonon dispersion curves of SWZONTs from the phonon dispersion relation of SZOML. In particular, the sound velocity of twisting mode of SWZONTs is about 2.801 km/s because this mode corresponds to the in-plane tangential acoustic mode of SZOML.

(iv) Through zone folding method\(^ {33,34}\) we can obtain the electronic band structure of SWZONTs from the band structure of SZOML. Because the SZOML is a wide band gap semiconductor, SWZONTs should also be wide band gap semiconductors although the band gap depends on their chirality. This point supports the result obtained by Elizondo and Mintmire\(^ {35}\) but not by Erkoç and Kökten\(^ {36}\). Thus electronic property of SWZONTs is quite different from that of single-walled carbon nanotubes\(^ {37}\), which can be metallic or semiconducting.

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