Uniaxial stress influence on lattice, band gap and optical properties of n-type ZnO: first-principles calculations*

Yang Ping(杨 平)†, Li Pei(李 培), Zhang Li-Qiang(张立强), Wang Xiao-Liang(王晓亮), Wang Huan(王 欢), Song Xi-Fu(宋喜福), and Xie Fang-Wei(谢方伟)

Laboratory of Advanced Manufacturing & Reliability for MEMS/NEMS/OEDS, School of Mechanical Engineering, Jiangsu University, Zhenjiang 212013, *China*

(Received 16 May 2011; revised manuscript received 22 August 2011)

The lattice, the band gap and the optical properties of n-type ZnO under uniaxial stress are investigated by first-principles calculations. The results show that the lattice constants change linearly with stress. Band gaps are broadened linearly as the uniaxial compressive stress increases. The change of band gap for n-type ZnO comes mainly from the contribution of stress in the *c*-axis direction, and the reason for band gap of n-type ZnO changing with stress is also explained. The calculated results of optical properties reveal that the imaginary part of the dielectric function decreases with the increase of uniaxial compressive stress at low energy. However, when the energy is higher than 4.0 eV, the imaginary part of the dielectric function increases with the increase of stress and a blueshift appears. There are two peaks in the absorption spectrum in an energy range of 4.0–13.0 eV. The stress coefficient of the band gap of n-type ZnO is larger than that of pure ZnO, which supplies the theoretical reference value for the modulation of the band gap of doped ZnO.

Keywords: uniaxial stress, first-principles, optical properties, n-type ZnO

PACS: 68.60.Bs, 71.15.Mb, 78.20.Ci, 71.20.Nr **DOI:** 10.1088/1674-1056/21/1/016803

1. Introduction

In recent years, as a new II-VI semiconductor compound, ZnO has been used in lasers, solar cells, detectors, sensors, flat panel displays and other fields[1−5] due to its non-toxic, low cost, wide band, high temperature resistance and other advantages. In addition, n-type ZnO has attracted wide attention for its better photovoltaic performance by doping with Al, Ga, In and other elements.[6−8] Many coating technologies such as vacuum evaporation deposition, magnetron sputtering and chemical vapour deposition have been used to prepare ZnO thin film. In the preparation process, the stress-strain induced by lattice mismatch between the film and substrate as well as the thermal mismatch caused by different thermal expansion coefficients inevitably exist in the thin film.[9−11] It affects the crystal quality and optical performance of ZnO film. Therefore, it is very significant to study the changes of lattice, band gap and optical properties of ZnO film under stress for the preparation of and the research on epitaxial layers and heterojunctions.

Currently, studies on the physical properties of ZnO under uniaxial or biaxial stress-strain have attracted the wide interest of researchers. X-ray diffraction (XRD),[12,13] Raman spectroscopy[14] and other techniques are used to measure the residual stress. Meanwhile, first-principles calculations have been used to analyse the physical mechanism of ZnO under stress-strain.[15] Although it has made some progress in the studies of ZnO[16] and p-type ZnO[17] under stress-strain, the performance of n-type ZnO is still rarely reported. In this article, the lattice constants, the band gap and the optical properties of In-doped n-type ZnO under uniaxial stress are calculated by the first-principles[18,19] based on the density functional theory (DFT). The results show that the stress coefficient of the band gap of n-type ZnO is large as compared with that of undoped ZnO, which offers a theoretical reference value for the modulation of band gap of doped ZnO.

*Project supported by the National Natural Science Foundation of China (Grant No. 61076098) and the Innovative Foundation for Doctoral Candidate of Jiangsu Province, China (Grant No. CX10B_252Z).

†Corresponding author. E-mail: yangpingdm@ujs.edu.cn

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2. Computational details

The stable phase of ZnO crystal has a hexagonal structure with a $P6_3mc$ space group. The primitive cell structure of wurtzite ZnO is shown in Fig. 1. The computational model was an $InZn_{15}O_{16}$ (2×2×2) supercell with a Zn atom substituted by an In atom. The calculation was performed using first-principles based on the DFT combined with the plane-wave pseudo-potential method.[20] The ionic potential was described by a Vanderbilt-type ultra-soft pseudo-potential to reduce the computation. Valence electron configurations for Zn, O and In were considered as $3d^{10}4s^2$, $2s^22p^4$ and $4d^{10}5s^25p^1$, respectively. The exchange-correlation function was handled by the generalized gradient approximation (GGA). A non-spin polarized calculation was adopted. To ensure the convergence of our calculation, we carefully tested the total energy depending on the cutoff energy and k-point sampling. The final set of cutoff energy was chosen to be 340 eV and the k-point set mesh parameter was 3×3×2. According to the result obtained by Ghosh *et al.*[12] that the strain was along the direction of c-axis, the uniaxial stress σ_c was set along the c-axis, and the stresses along the a-axis and the b-axis were not restricted, which were $\sigma_a = \sigma_b = 0$. Here, $\sigma_c > 0$ represents compressive stress; $\sigma_c < 0$ represents tensile stress.

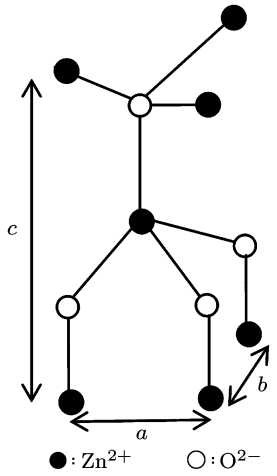


Fig. 1. Primitive cell structure of wurtzite ZnO.

3. Results and discussion

3.1. Lattice constants

The calculated lattice constants a and c under different uniaxial stresses are presented in Fig. 2. The lattice constants a and c are, respectively, 0.33 nm and 0.53 nm without the effect of stress, which are slightly larger than the lattice constants of ZnO ($a = 0.32$ nm, $c = 0.52$ nm).[21] This is mainly because the In ionic radius (0.080 nm) is larger than that of Zn ion (0.074 nm). As shown in Fig. 2, the lattice constants a and c increase almost linearly. Lattice constant c increases with the increase of uniaxial tensile stress, and decreases with the increase of uniaxial compressive stress, due mainly to the change of cell volume V_0 caused by the change of uniaxial stress, which is shown in Table 1. Because of no restriction along the a-axis, the lattice constant a has the opposite variation.

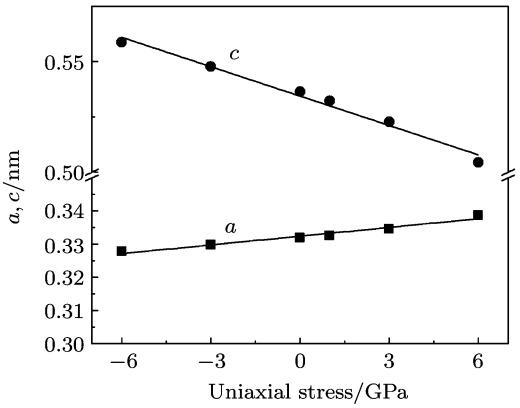


Fig. 2. Lattice constants a and c versus uniaxial stress of n-type ZnO under different stresses.

Table 1. Cell volume V_0 varying with uniaxial stress.

Stress/GPa	–6	–3	0	1	3	6
$V_0/10^{-3}$ nm^3	51.98	51.57	51.16	50.99	50.71	50.43

3.2. Band gap

The band gap of n-type ZnO varying with stress is observed in Fig. 3. The band gap of In-doped ZnO is 0.43 eV under stress-free conditions, similar to the result calculated by Liu *et al.*[22] but significantly smaller than the experimental value. This is mainly because the GGA functional calculations often underestimate the band gap.[23] Band gaps are broadened linearly with the increase of uniaxial stress. According to the data from Fig. 2, it can be found that the lattice constant c decreases by 2.55% compared with the lattice constant under stress-free conditions when the uniaxial compressive stress is 3 GPa, but a increases by 0.81% because of the structural relaxation. Thus, the change of band gap for n-type ZnO comes mainly from the contribution of stress in the c-axis direction, and this is consistent with the relationship between

band gaps and lattice constants of ZnO.[16] The relationship between band gap and stress for n-type ZnO can be described as

$$E_{\rm g} = 0.43 + 0.019\sigma_c, \tag{1}$$

where $E_{\rm g}$ represents band gap, 0.43 eV is the band gap of In-doped ZnO without the effect of stress.

Since current theoretical and experimental studies on n-type ZnO under stress are rare, the band gap of ZnO under biaxial stress σ_{11} (stress along a-axis and b-axis) calculated by Li *et al.*[24] is used for comparison. The relationship between stress and band gap for ZnO is expressed as

$$E_{\rm g} = 0.984 + 0.003\sigma_{11}, \tag{2}$$

where 0.984 eV is the calculated value of ZnO under stress-free conditions.

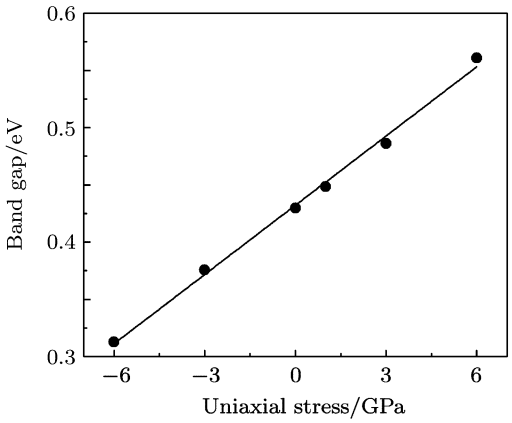


Fig. 3. Band gap of n-type ZnO versus uniaxial stress.

Here, the biaxial tensile stress (along the a-axis and the b-axis) is the same as the uniaxial compressive stress (along the c-axis). Comparing Eq. (1) with Eq. (2), it is not difficult to find that the band gaps change in direct proportion with stress before and after doping. The band gap of n-type ZnO is smaller than that of ZnO under stress-free conditions, but the stress coefficient becomes larger. That is, the band gap of n-type ZnO is more significantly affected by stress, which offers some theoretical reference for the modulation of the band gap of doped ZnO.

The band structures of ZnO and In-doped ZnO near the Γ point changed by uniaxial compressive stress are shown in Fig. 4. Both the valence-band maximum (VBM) and the conduction-band minimum (CBM) are located at the Γ point, so ZnO and doped ZnO are direct band gap semiconductor compounds. Figure 4(a) shows that the CBM and the VBM of ZnO under stress-free conditions are respectively controlled by the energy levels Γ_1 and Γ_5. The Fermi level of ZnO is located near the VBM. The band structure of In-doped ZnO near the Γ point under stress-free conditions is shown in Fig. 4(b). It is not difficult to find that the CBM is controlled by the impurity level Γ_2. The Fermi level emerges in the conduction band, indicating that the In-doped ZnO is an n-type semiconductor.

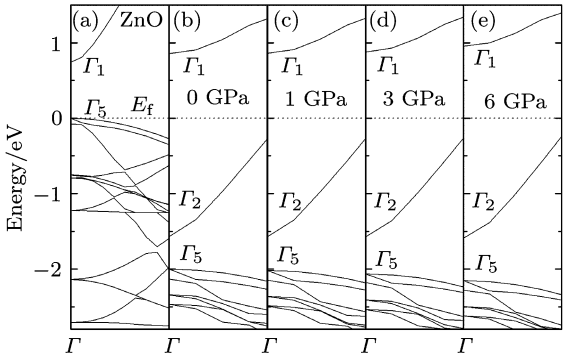


Fig. 4. VBM and CBM near the Γ point (the dotted line denotes the Fermi level $E_{\rm f}$): (a) ZnO under stress-free conditions, (b)–(e) n-type ZnO changed by stress.

To explain the reason why the band gap of n-type ZnO is changed by stress, it is necessary to analyse VBMs and CBMs under different stresses. With the increase of uniaxial compressive stress shown in Figs. 4(b)–4(e), the VBM apparently shifts toward lower energy, but the CBM slightly shifts toward lower energy. The offset of the VBM is greater than that of the CBM, which directly causes the broadening of the band gap. Moreover, the energy level Γ_1 is formed mainly by electrons on the bonding orbit of Zn 4s. The energy level Γ_2 is formed mainly by electrons on the bonding orbit of In 5s. The VBM is controlled by doublet Γ_5, formed mainly by electrons on the antibonding state O 2p. When the uniaxial compressive stress increases, the energy level Γ_1 shifts toward the higher energy while the level Γ_5 shifts in the opposite direction. This is mainly due to electron scattering caused by the strain brought by uniaxial compressive stress on the wurtzite semiconductor, generating valley deformation potential.[25] However, the effect on the impurity level Γ_2 by uniaxial stress is very small. It shifts toward lower energy in a small scale instead of shifting toward higher energy under the influence of deformation potential. This may be because the interaction energy formed by electrons introduced by an impurity is larger than the valley deformation potential generated by compressive stress, and their signs are opposite.

3.3. Optical properties

The optical properties of a medium can be described by the complex dielectric response function $\varepsilon(E) = \varepsilon_1(E) + \mathrm{i}\varepsilon_2(E)$ in a linear response range. As is well known, the imaginary part $\varepsilon_2(E)$ is the overview of optical properties for any material. The relationships between the imaginary part $\varepsilon_2(E)$ and energy under different uniaxial compressive stresses are shown in Fig. 5. There are three main peaks, respectively, at 1.3, 6.6 and 10.4 eV in $\varepsilon_2(E)$ plot of n-type ZnO under stress-free conditions.

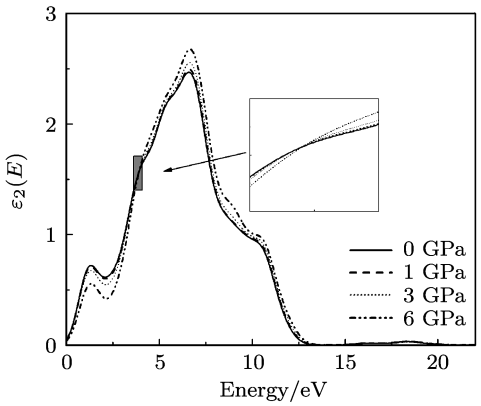


Fig. 5. Variations of the imaginary part $\varepsilon_2(E)$ with energy under different uniaxial compressive stresses.

The total density of states (TDOS) of In-doped ZnO and ZnO and the partial density of states (PDOS) of different atoms in In-doped ZnO are shown in Fig. 6. Figure 6(a) shows that the Fermi level E_f of ZnO is located near the VBM, which indicates that ZnO is an insulator. The Fermi level of In-doped ZnO emerges in the conduction band, showing that electrons go into the conduction band. According to the software integration of the part of the TDOS occupied by electrons,[26] the relative number of electrons in the conduction band is about 0.81, while the relative number in the conduction band of ZnO is 0. It reveals that In doping increases the conductivity of ZnO. Combined with the calculated PDOS of different atoms shown in Figs. 6(b)–6(d), it can be known that the first peak at 1.3 eV originates mainly from the electron transition between O 2p and In 5s orbitals; the transition between Zn 3d and O 2p orbitals and the transition between In 4d and O 2p orbitals may lead to the second peak at 6.6 eV; the third peak at 10.4 eV is derived mainly from the electron transition between O 2s and Zn 3d orbitals. When the photon energy is greater than 4.0 eV, there is a small blueshift with the increase of uniaxial compressive stress. When the energy is less than 4.0 eV, the imaginary part $\varepsilon_2(E)$ decreases as the stress increases, which is shown in local enlarged plot in Fig. 5. This may be due to the serious distortion caused by the increase of stress, which enhances phonon scattering and weakens the optical response, thereby making the imaginary part $\varepsilon_2(E)$ decrease. When the energy is greater than 4.0 eV, the energy loss caused by phonon scattering can be suppressed. The increase of peak energy causes a small blueshift.

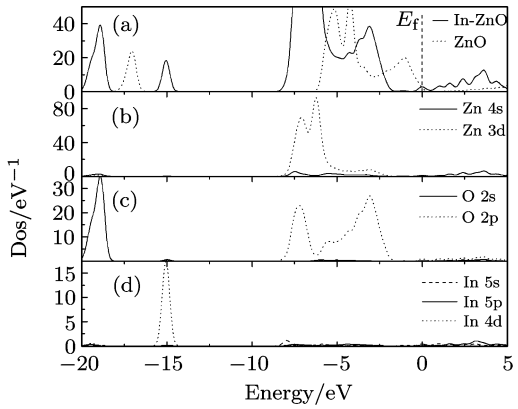


Fig. 6. Variations of (a) TDOS of In-doped ZnO and ZnO, (b)–(d) PDOS of different atoms for In-doped ZnO with energy under stress-free.

Figure 7 shows the variations of absorption coefficient $\alpha(E)$ with energy under different stresses. Two absorption peaks appear in the spectrum in an energy range of 4.0–13.0 eV. The peaks are located at 7.3 eV and 10.7 eV, respectively. The absorption increases and the blueshift emerges in the absorption spectrum with the increase of stress. However, the absorption intensity decreases as the stress increases in an energy region less than 4.0 eV. The turning energy is 4.0 eV, the same as the turning point of $\varepsilon_2(E)$ as shown in Fig. 5.

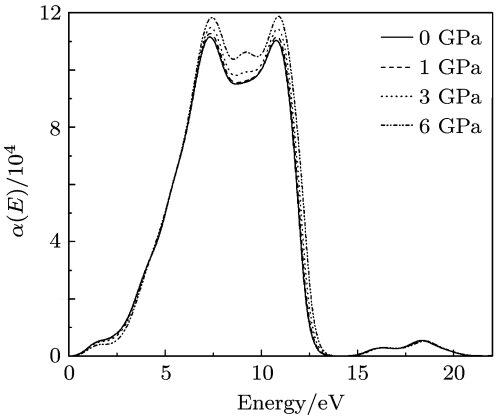


Fig. 7. Variations of absorption coefficient α (E) with energy under different stresses.

4. Conclusion

We find that the lattice constants a and c of n-type ZnO change linearly with stress. The band gap is broadened linearly as the uniaxial compressive stress increases, and comes mainly from the contribution of stress in the c-axis direction. It follows from the structural diagram that the effect on the impurity level, caused by uniaxial stress, is very small. The imaginary part of the dielectric function decreases with the increase of compressive stress at low energy. However, when the energy is higher than 4.0 eV, the imaginary part is directly proportional to the compressive stress and a blueshift emerges. Two absorption peaks appear in the absorption spectrum. The stress coefficient of the band gap of n-type ZnO is larger than that of pure ZnO, which provides a theoretical foundation for the modulation of the band gap of doped ZnO.

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