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Lattice and internal relaxation of ZnO thin film under in-plane strain

Qin Guoqiang [a,b], Zhang Guanglei [b], Li Dongchun [a], Liu Shimin [a,*]

[a] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, 066004 Qinhuangdao, China
[b] Department of Materials Science and Engineering, Shijiazhuang Tiedao University, 050043 Shijiazhuang, China

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ABSTRACT

Detailed *ab initio* density-functional calculations were carried out on the effect of lattice and internal relaxation of ZnO thin film under in-plane strain. It was found that the classical elastic deformation behaves under a restricted joint mechanism including lattice relaxation and internal relaxation. The internal relaxation works to enhance the effect of the in-plane strain on the perpendicular direction and, reduce the residual stress and the strain energy and, thus finally elevate the energetic stability of the resulting structure. By contrast, the free lattice and internal relaxation could consume part of the elastic strain energy to lead to a more stable structure with a degenerated space–group symmetry and no residual stress in any direction. In addition, the free relaxation brings about some different behaviors in many respects relative to the elastic deformation, such as the smaller Poisson ratio, the decreased piezoelectric effect, a "Λ" shaped variety in bandgap at the Γ point and the reduced shift in homogeneity of charge distribution between the two kinds of Zn–O bonds.

1. Introduction

The considerable demands for faster (or more efficient), smaller, and cheaper devices have brought enormous impetus for the extensive studies of materials with restricted scales in one (thin film), two (nanotube, nanowire) or three dimensions (nanocluster, quantum dots). In these nanomaterials, *intentional* or *unintentional* stress and strain is a common phenomenon, largely due to the higher sensitivity to the environment (pressure, temperature or contact) compared to their corresponding bulk forms. The understanding of strain fields is critical to device functions, since lattice strain has a strong impact on the electronic structure and other related properties. In fact, the strain technique has been employed in some fields to improve the performance of devices, such as the strained Si where the electron mobility can be enhanced spectacularly by a factor of 1.7 to 2 [1], but it is still worthwhile to carry out comprehensively studies on the effects of strain.

As indicated by many researchers [2,3], ZnO is a "key technological material" that has three main advantages: 1) semiconductive with wide energy band gap ($Eg\sim3.4$ eV at 300 K) and large exciton binding energy (60 meV); 2) highly piezoelectronic; 3) bio-safe and bio-compatible. These superior properties along with other characteristics allow ZnO to play essential roles in numerous applications [4–8].

There have been several theoretical and experimental studies concerning the strain or stress and the relative effects in ZnO films. It shows that the ZnO film synthesized in most experiments is crystallized as the preferentially *c*-axis-orientated wurtzite (*B*4) structure. In this case the classic plane stress or strain model, i.e., the biaxial model, was widely employed to characterize the deformation behavior and the consequent effects. Since this model was based on the framework of continuum-elasticity theory, it presents a general scheme to calculate the elastic response upon biaxial deformations and associated linear changes around equilibrium. Therefore, using the elastic stiffness constants obtained experimentally or theoretically we can ascertain the value of Poisson ratio ν, which was defined as $\nu=-2C_{13}/C_{33}$ for *B*4 ZnO within the biaxial model and reported to be 1.0568 [9], 1.0165 [10], 1.0095 [11] and 0.91837 [12]. Because the Poisson ratio corresponds to the rearrangement of atoms and electrons under strain, it plays as a characteristic index for a certain material and can be used as a criterion to judge the correctness of a strain or stress model by checking the deduced strain relaxation coefficient defined as $R^B=-\varepsilon_{zz}/\varepsilon_{xx}$, just like the cases in Refs. [13] and [14].

Studies have exhibited the success of the elastic model, where the measured Poisson number (0.298) under strains <0.5% coincided well with data for unstrained *B*4 ZnO (0.302–0.336) [15,16]. However, there are more experimental examples showing big discrepancy to the elastic model with substantially small Poisson ratios, such as the cases reported by Ashrafi [17,18] and Zhao [19]. The Poisson ratios there were only 0.61 [17], 0.50, 0.38 [18], 0.28 and 0.07 [19].Compared to the linear *elastic* deformation behavior, the universality of the ZnO film with such smaller Poisson ratio actually implies the existence of a different response involving a non-equilibrium or metastable state of material under in-plane strain, but no theoretical explanation was

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* Corresponding author. Tel.: +86 3358074726; fax: +86 3358074545.
E-mail address: lsm@ysu.edu.cn (L. Shimin).

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proposed for this “unusual” phenomenon. The exploration of the non-equilibrium or metastable state of material has shown intriguing prospects in a number of applications, such as the nanogenerator created by Wang [20]. This further emphasizes the importance of a broader scope in comprehensive investigations into basic physical mechanisms such as deformation behavior. Therefore in this paper, we present *ab initio* studies on the deformation behavior of ZnO thin films under in-plane strain to clarify the origin of the small Poisson ratio and its effects on relative properties.

2. Calculation methods

The *ab initio* calculations were performed by the CASTEP code [21,22]. The exchange and correlation effects were as described by Perdew–Burke–Eruzerhof in generalized gradient approximations (GGA) [23] within the density-functional theory (DFT) [24–26]. The states O $2s^2 2p^4$ and Zn $3d^{10} 4s^2$ were treated as valence states. Ultrasoft pseudopotentials [27] were expanded within a plane-wave basis set with an energy cutoff of 800 eV and K points mesh of 12 × 12 × 7 for the Brillouin zone. This made the separation of the reciprocal space less than 0.03 $Å^{-1}$. All forces on atoms were converged to less than 5×10^{-7} eV/Å. This type of configuration is believed to be adequate to guarantee the reliability of the calculations according to Ref. [28].

The most stable phase of ZnO under ambient conditions among its four or five polymorphs is the *B*4 phase which consists of two formula ZnO molecules embodied in a unit cell, as demonstrated in Fig. 1. In the present study, both the lattice parameters and the atomic coordinates were optimized within the classic Broyden–Fletcher–Goldfarb–Shanno geometry[29–32]. For the unstrained ZnO, the optimized lattice parameters for a, c and u were 3.256 Å, 5.255 Å and 0.379, respectively, which are in accordance with previous experimental and theoretical results [33,34]. By adopting the method described in Ref. [35], the calculated cohesive energy of *B*4 ZnO was 4.62 eV/ atom, identical to that reported elsewhere [36].

To apply the in-plane strain to a ZnO thin film, strain tensors take a diagonal form as follows:

$$\varepsilon_{xx} = \varepsilon_{yy} = (a - a_0) / a_0 \tag{1a}$$

$$\varepsilon_{zz} = (c - c_0) / c_0. \tag{1b}$$

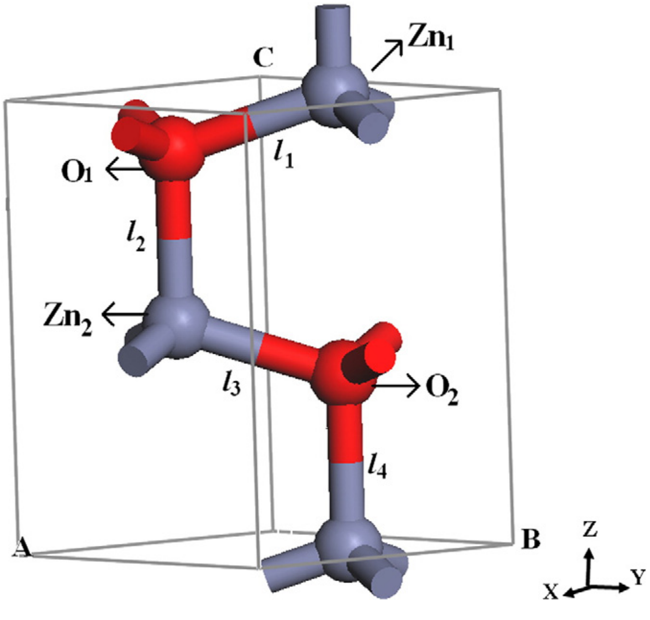

Fig. 1. Schematic illustration of *B*4 ZnO.

where a_0 (a) and c_0 (c) denote the lattice constants of the unstrained (strained) crystal, and by convention, $\varepsilon_{xx} < 0$ ($\varepsilon_{xx} > 0$) for layers under compressive (tensile) strain. The lattice parameters a and b were varied synchronously close to the equilibrium parameter, then they were constrained to enforce the in-plane strain on the *B*4 ZnO.

In the biaxial strain model, the C_{6v}^4 the space–group symmetry was conserved. In addition, the lattice parameter c was not free to relax but set artificially under the imposed in-plane strain. The final structure with a certain ε_{zz} (hence a certain Poisson) could be achieved by optimize and minimize the total energy via two approaches: varying the value of c and (or) the positions of atoms relative to the lattice cell. The former could be called as lattice relaxation, the latter as internal relaxation [37]. Thereby, we can get two distinct combinations: lattice relaxation without internal relaxation and lattice relaxation with internal relaxation, which is expected to lead to two different deformation responses.

Because of the huge gap in the Poisson ratios between experiments and the elastic biaxial model, one can assume the presence of a third relaxation mechanism. Referring to the elastic model with set c and conserved space–group symmetry, we can assume that in the third manner the above restrictions will be cancelled, giving a much wider space for the lattice and atoms to relax. According to this assumption we built a relaxation model, where the above restrictions in c and symmetry for the ZnO thin film after applying the in-plane strain are eliminated, leaving the lattice and atoms totally free to relax until reaching the energetically favored structure. This relaxation manner is called “free lattice and internal relaxation” or “free relaxation” in short in order to distinguish with the restricted relaxation above.

3. Structural properties

3.1. Effects of internal relaxation

Fig. 2 displays the variations of the out-of-plane strain ε_{zz} and the calculated stress along the a axis. All residual components of the Hellmann–Feynman stress tensor orthogonal to the applied strain are less than 0.1 GPa. An evident linear relationship can be seen in Fig. 2a, in agreement with previous reports [13]. The negative slope reveals that materials resist a change in volume more than a change in shape. In addition, the participation of internal relaxation in the deforming process causes very different strain relaxation coefficient. The value of L2 is 0.94, about twice as L1 but inconsistent with other studies employing the classic biaxial model [14]. It indicates that the elastic relaxation follows a joint mechanism including lattice relaxation and internal relaxation. On the other hand, if no internal relaxation happens, the value of R^B is only 0.46. This reveals that the internal relaxation could transfer and enhance the effect of the in-plane strain at the perpendicular direction through relative atomic rearrangement in the lattice cell.

The application of strain commonly induces stress along the strain field. A certain material under strain will relax the stress via a number of approaches, such as elastic deformation through the Poisson effect. We can see a clear linear dependence between the in-plane and the calculated residual stress in Fig. 2b. As pointed out by Karch [38], the in-plane stress is related to the in-plane strain by the biaxial modulus through $\sigma_{xx} = Y\varepsilon_{xx}$. The biaxial modulus is given in terms of the elastic stiffness constants as:

$$Y = C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}}. \tag{2}$$

The deduced Y is 228.38 ± 19.49 GPa, in accordance with the slope of L2 with its value of 216 GPa. This further confirms the elastic nature of the biaxial strain model. By comparison, the slope of L1 is 322 GPa, about 50% larger than L2 and is unreasonable for *B*4 ZnO and less probable to happen practically. The internal relaxation could reduce