

Nanoporous ZnO: Structural and electronic study under biaxial strain

Alvaro D. Torrez-Baptista^a, Adalberto Fazzio^{b,c}, Jeverson T. Arantes^{a,*}

^a CECS – Center for Engineering, Modeling and Applied Social Sciences, Federal University of ABC, Santo André, SP, Brazil

^b CCNH – Center for Natural Sciences and Humanities, Federal University of ABC, Santo André, SP, Brazil

^c Brazilian Nanotechnology National Laboratory (LNNano)/CNPEM, PO Box 6192, Campinas, São Paulo 13083-970, Brazil



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ABSTRACT

We investigated a nanoporous zinc oxide, under elastic biaxial strain, through first-principles methods based on total energy ab initio calculations using spin-polarized Density Functional Theory. The system was in a high nanopore concentration regime. Using a biaxial tension above 4% of the ZnO bulk lattice parameter we observe a distortion that could result in a phase change region in the material's structure. It can be found that the values of energy band gap are tuned by the strain with an uncommon opposite trend of the bulk. The electronic modulation trend was confirmed by changes in the density of states. Our results show that the elastic strain leads to a non-uniform distribution of the charge localization in the nanoporous surface.

1. Introduction

One of the primary motivations of technological interest in semiconductor materials is the control possibility on electrical, magnetic and optical properties, among others. One way to achieve the property control is through structural modifications. A well-studied paradigm is obtaining porous materials that are an area of intense research [1–4].

In particular, nanoporous materials based on zinc oxide (ZnO) are technologically interesting. ZnO is one of the most important semiconductors due to its unique physical characteristics and the pore introduction tune their properties. The porous structures provide greater surface area and the possibility of controlling the bandwidth wide band gap, E_{gap} . Both are fundamental for emerging applications such as in optoelectronics [5,6], sensors [7–9] and biosensor [10], catalysis [7,10,11], solar cells [12] and gas separation [13].

In addition, strain engineering is one of the most successful ways to modulate the electronic properties, due to its tractability and continuous and robust tunability. It has been reported that the band structure of bulk and ZnO nanostructures can be tuned by a hydrostatic and uniaxial strain, increasing the band gap under compression [14–19]. This tunable band structure will affect the electronic characteristic and will decide its suitability for specific applications.

In this work, based on first-principle calculations, we investigate the electronic and structural properties of nanoporous ZnO under biaxial stress. Our model simulates a high pore concentration. We show that the surfaces states in the nanoporous were responsible for an unusual change in the energy gap. Furthermore, with the biaxial tension up to 4% of lattice parameter variation, we observed a localized atomic

structure change that could lead to a phase transition. Within our knowledge, this is the first report about opposite E_{gap} trend in strained nanopores.

2. Methodology

The porous model used in our calculations is shown in Fig. 1. Our cleavage procedure is relatively simple. The starting point is a bulk supercell of ZnO with $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$ and $[0001]$ crystallographic directions extending along x , y , and z -axes, respectively. The geometry of the pores was created by the removal of ZnO pairs, leaving $[0001]$ -directed linear pores. In-plane, the nanopores are geometrically elliptical-like, with a major axis identified by the letter D , and minor one by d (see Fig. 1). Also, the thick and thin space between pores is identified by the letters W (dense region) and w (neck region) respectively. We consider three different pore sizes. While the minor axis remains constant ($d = 13.33$), the three input lengths of major axis are 13.18, 16.47 and 19.76 nm. The nanopores are named np-small, np-medium, and np-large, respectively. This information is summarized in Table 1. The pores edge corresponding to $\{01\bar{1}0\}$ family surface. A supercell figure is provided in the support material.

The choice of model parameters (D, d, W, w , and pore axis) was deliberated to approximate the real systems and to void (0001) polar surface. The (0001) is the most commonly used surface for nanostructures growth [20,21]. Specifically, was reported ZnO pore arrangements with similar morphological characteristic to our model [3,4,9]. In many studies, the smallest pore diameter obtained was on the order of 1–2 nm [10,11,22]. After these, the structures were

* Corresponding author.

E-mail address: jeverson.teodoro@ufabc.edu.br (J.T. Arantes).

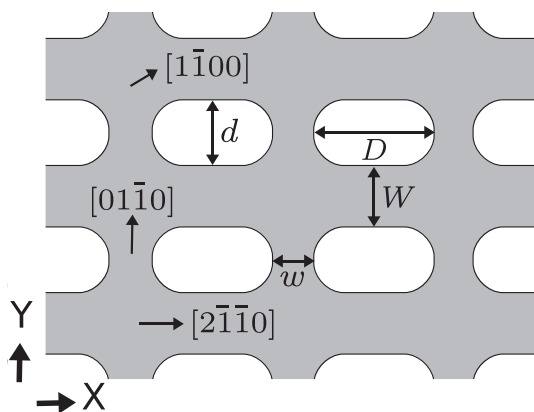


Fig. 1. Schematic representation of the nanoporous ZnO structure that illustrates a system with a high pores density. The nanopores are an elliptical-like transversal format, where D (d) represent the major (minor) axis. The thick and thin space between pores is identified with the letters W (dense region) and w (neck region) respectively. The pore axis is in $[0001]$ crystallographic direction.

Table 1

Atomic composition of supercells and major axis, D , length variation. The minor axis length, d , was constant.

Nanopore	ZnO pairs	D (Å)	d (Å)
np-large	120	19.76	13.33
np-medium	128	16.47	13.33
np-small	136	13.18	13.33

energetically relaxed. The pore surfaces are unpassivated, i.e., the nanopore incomplete surface bonds were left free.

To examine the dependence of the elastic strain stiffness on the structural variables and electronic properties, we changed in-plane lattice constant, a . In other words, the x and y -axis were changed simultaneously. The z -axis was kept fixed in the supercell lattice parameter converged without the pore. By convention, a/a_0 represent the biaxial strain relation with a simultaneous x and y -axis variation.

All calculations were done based on the Density Theory Functional (DFT) [23,24]. We have used Projector Augmented Waves (PAW) [25], Generalized Gradient Approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) exchange–correlation functional [26]. The VASP code was used [27,28] with an energy cut-off of 400 eV. The structures were allowed to relax until the forces were less than 0.025 eV, and the k -points mesh was $3 \times 3 \times 5$, within Monkhorst–Pack scheme [29].

3. Results and discussion

3.1. Structural properties

We first calculated the equilibrium state for the three nanopores. From relaxed structures, the biaxial strain was simulated changing the x and y lattice vectors simultaneously (see Fig. 1) from $a/a_0 = 1.06$ to $a/a_0 = 0.94$, where a_0 is the equilibrium lattice constant of the structures without stress, and a is the lattice constant of the strained structure. If $a/a_0 < 1$ the strain is compressive, on the other hand, in the case of $a/a_0 > 1$ is tensile. To estimate the feasibility, the total energy differences were computed for strained and unstrained pores. In Fig. 2 we show the total energy differences of the nanopores and bulk per ZnO pair, where the wurtzite energy is the reference. At zero stress ($a/a_0 = 1$), as expected, the total energy increases directly with the pore major axis, D . The energy differences related to the small, medium and large pores is 0.08, 0.10 and 0.12 eV per ZnO pair, respectively. Within the studied range of stress, we observed a monotonic increase in the energy differences with strain. The maximum energy difference reached

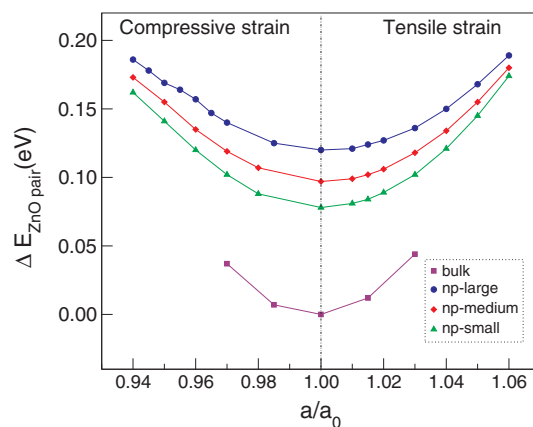


Fig. 2. Nanoporous structures and bulk total energy differences, per ZnO pair, under biaxial strain.

was 0.19 eV. Our results are in concordance with previous studies. The energy differences are within the upper bound proposed in Ref. [30], related with experimentally synthesized of ZnO rock-salt [31]. Thus, the nanopores under stress are experimentally viable.

In Fig. 3 we show the relaxed np-large under compressive (a) and tensile strain (b). The compressive biaxial strain is related to $a/a_0 = 0.95$ and the tensile one represents $a/a_0 = 1.04$. The structural changes are more pronounced with the biaxial compression increasing, particularly in the thinnest region of the structure (neck region, identified by the letter w in Fig. 1). Around this compression, approximately 5%, we observed a drastic transformation in the neck region, indicating one localized crystallographic phase change, from wurtzite to rock-salt-like because new bonds arose in xy plane, as seen in Fig. 3(a). For tensile biaxial strain, the neck region is also the most modified (Fig. 3(b)). Bond lengths in this region increase and the ZnO bilayers in the xy plane are flattened. However, does not become a graphitic-like structure because of the periodic bonds in the $[0001]$ direction.

To obtain detailed insight about the stressed nanopores, the structural differences of the np-large are present in Fig. 4. We investigate these modifications by computing the bond length differences related to bulk. The color maps of the two columns represent the bond length differences in xy plane and along $[0001]$ direction, z -axis, related to the bulk. We can observe that the nanopore without strain ($a/a_0 = 1.00$) has two important characteristics: the pore surface layer was compressed, and the adjacent one was under tension. The largest decrease in surface bonding distances was along $[0001]$ direction. This difference is about -0.14 Å, while in the xy plane this difference is about -0.7 Å. On the other hand, the largest increase in the adjacent surface layer was in the xy plane and correspond to 0.9 Å. The bond length increase in $[0001]$ direction was about 0.2 Å. Our results are in agreement with the previous results referring to $(01\bar{1}0)$ infinite surface [32–36]. The dangling bonds in the surface are the principal responsible for these structural changes, as will be discussed later. These characteristics define an initial structural configuration of the pores and will be the reference for comparing with the strain effects.

We will first analyze the effect of the compressive strain on nanopores ($a/a_0 = 0.97, 0.95, 0.93$) in Fig. 4. The pore surface layer bonds increase with the biaxial compression, both in-plane and in $[0001]$ direction, compared to without stress pore. The adjacent bonds to surface layer have the same behavior. We can observe that the neck region (see the w region in Fig. 1) received most of the mechanical load, since the bonds of this region present larger modifications. The bond lengths in the bulk-like region show a small decrease. However, the surface structural changes are the most pronounced.

In the case of the tensile strain ($a/a_0 = 1.02, 1.04, 1.06$), the trending of the bonds in the surface and the adjacent layer is very similar to what happens with the compression (Fig. 4). The surface layer change from

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