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# Buckling effects on electronic and optical properties of BeO monolayer: First principles study

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ABSTRACT

Using *ab initio* study, we apply full potential augmented plane waves plus local orbital and generalized gradient approximation for expanding wave functions and exchange–correlation functional term to investigate the electronic and optical properties of beryllium oxide nanosheet. The different values of planar buckling are considered to study. Also the results for fluorinated BeO nanosheet is compared to corresponding non-fluorinated buckled nanosheet. A red-shift in optical spectra is observed obviously as a result of weakening of $\sigma$ bonds and increasing the number of $\pi$ electrons. Also optical transparency property for visible range of the electromagnetic spectrum and vanishing energy-band degeneracy is concluded from our data.



## 1. Introduction

Graphene, a single atomic layer composed of $sp^2$-hybridized carbon, is rapidly rising star materials, which has very broad applications, e.g. graphene-base transistor [1,2], gas sensors [3,4] and light emission diodes [5,6] thanks to its unique physical and chemical properties. Graphene was successfully isolated from graphite using a technique called mechanical exfoliation [7].

In fact, monolayer structures are not limited to graphene, similar to graphene, two-dimensional semiconductors are its two-dimensional and isostructural counterparts based on the typical layer-structured compounds, such as h-BN [8,9], transition metal dichalcogenides [10,11], III–VI semiconductors [12,13] and some promising two-dimensional structures that theoretical studies envisioned good capability for them in this field such as ZnO [14], BeO [15] and ZnS [16].

Beryllium oxide as a member of alkali earth oxides group crystallized in wurtzite phase with $sp^3$ hybridization interaction between their components [17], whereas the other members of this group with cubic crystal structures [18]. In recent years, with regards to a high potential characteristic that is predicted in nanostructures of materials, extensive studies have been done to investigate different aspects of physical and chemical properties of BeO nanostructures. Theoretical study on graphite-like BeO in comparison with wurtzite phase clarified some aspects of its stability and preferable phase [19].

The first attention on BeO nanotube has been paid to its structural and electronic properties in 2006 by Sorokin et al. [20]. They found that these nanotubes are thermodynamically stable, and its binding energy is close to the binding energy of beryllium oxide in wurtzite phase. Baumeier et al. studied elastic and electronic properties of BeO nanotubes with considering diameter variations. Their results show that the energy gap value gets an increase in low diameters, while it reaches to a steady state by increasing the tube diameter [21]. Because of favorable physical and chemical properties of this compound, some research is presented about these nanotubes recently e.g. the bundle of them can be utilized for gas sensing [22]. Furthermore, the tunable band gap is gifted by multi-wall BeO nanotubes [23]. Also, elastic constants of these nanostructures have been calculated to prove their piezoelectric features [24].

Regarding to different efforts done for synthesizing of nanostructures, Reinelt et al. research led to form BeO monolayer by oxidizing cleansed Be surface naturally in 2009 [25]. In fact, the retention of 1 keV $D^+$ ions implanted into clean and oxidized single crystalline Be at room and elevated temperatures was investigated by a combination of in situ analytical techniques including temperature programmed desorption, nuclear reaction analysis, low-energy ion spectroscopy and X-ray photoelectron spectroscopy.

In our previous work, the electronic and optical properties of BeO nanosheet, honeycomb structure, were investigated and compared to wurtzite phase results [26]. The electronic results

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represented that the BeO nanosheet has indirect energy band gap type, in contrast to wurtzite bulk phase. The first main peak in eloss spectrum occurs in 9.6 eV that is related to $\pi$ electrons plasmon. The second main peak occurs in the range 14–21 eV that is corresponding to $\pi + \sigma$ electrons plasmon. Also the static refractive index of BeO nanosheet is smaller than that of BeO wurtzite structure.

There are a lot of methods to energy gap modulation of low dimensional nanostructures. Zhang and Guo studied the energy band gap variations of BN nanoribbon by applying different electric field strength [27]. Their results showed that the effect of electric field on different edge arrangement of nanoribbon, armchair and zigzag, causes different behavior for electronic properties of BN nanoribbon. one of the other ways is hydrogenating and fluorinating surface of monolayer nanostructures. The energy gap tuning of BN nanosheet has been studied by hydrogenating process [28]. The results represented that the value of energy band gap is so sensitive to adsorbing different atoms on BN monolayer. In this work, our main goal is energy band gap tuning of BeO monolayer by exerting planar buckling and fluorination of the surface. We focus on investigating the effects of fluorination and planar buckling on electronic and optical properties of BeO honeycomb monolayer. First the electronic properties of pristine BeO nanosheet is studied by exerting different planar buckling values. Moreover the electronic and optical properties of fluorinated BeO monolayer are investigated and compared to corresponding pristine buckled BeO monolayer.

## 2. Computational details

Electronic and optical properties of BeO monolayer are investigated within first principle full potential augmented plane-waves plus local orbital (FP-APW+lo) via the density functional theory as implemented in WIEN2k code [29].The exchange and correlation term is approximated by generalized gradient approximation in Perdew–Burke–Ernzerhof method (GGA-PBE) [30]. The number of $k$-points is considered 500 ($12 \times 12 \times 2$) and 5000 ($30 \times 30 \times 5$) in the whole Brillouin zone for electronic and optical calculations, respectively. The basis function expands up to $R_{MT}K_{max} = 8$ ($R_{MT}$ is the least Muffin-Tin sphere radius, and $K_{max}$ is the maximum modulus for the reciprocal vectors). The Fourier expansion of charge density is truncated by $G_{max} = 14$ Ry$^{1/2}$. Also 20 Å vacuum space in the non-periodic directions ($z$ direction) has been used to avoid two neighboring image interactions.

## 3. Electronic properties

### 3.1. Planar buckling

In this section, electronic properties of BeO monolayer are studied by considering different values of planar buckling. Once there is a planar buckling in the nanosheet, beryllium atoms are situated in the same plane and all oxygen atoms are arranged in another plane. Planar bucking is defined as the vertical distance, $\Delta$ parameter in Fig. 1a, between beryllium and oxygen planes that has been considered $\Delta = 0$, 0.16, 0.32 and 0.48 Å. In the first step, formation energy of all systems has been calculated to investigate the structural stability of buckled systems in comparison with flat BeO nanosheet. Our results show that all buckled systems have a good mechanical stability, but increasing planar buckling cause decreasing in mechanical stability of systems.

A model for $px + py$ and $pz$ orbitals is schematically demonstrated in the presence of planar buckling (Fig. 1b). Here we investigate atomic hybridization variations and the effect of that on electronic properties. Once all atoms are situated in the same

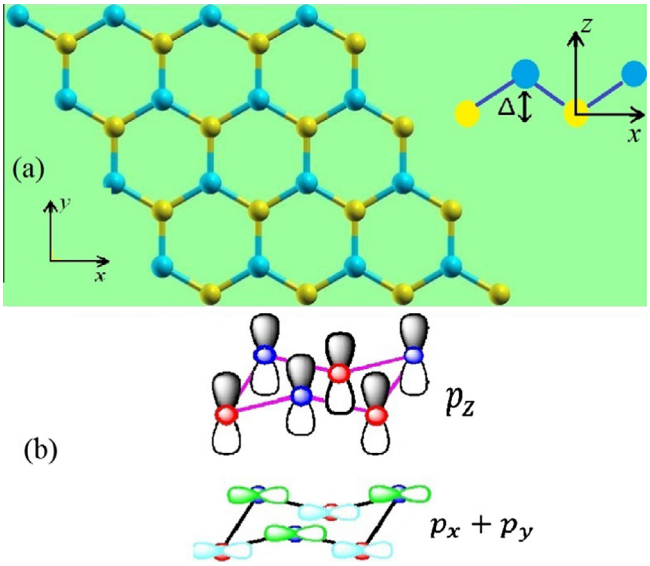


**Fig. 1.** (a) Top view of BeO nanosheet and (b) $p_z$ and $p_x + p_y$ orbitals represented schematically.

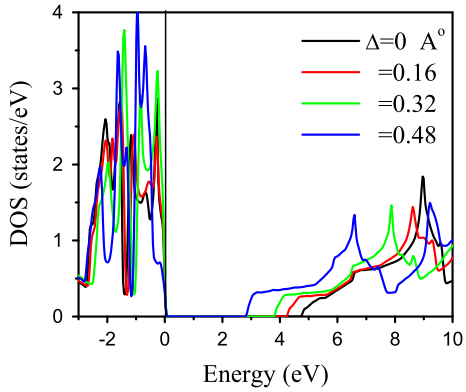


**Fig. 2.** Total density of states for all buckling values.

**Table 1**
Calculated results for energy gap ($E_g$ (eV)), Fermi energy (eV), binding energy (eV) and fractional ionic character (FIC) for all different values of planar buckling $\Delta$ (Å).

| $\Delta$ (Å) | $E_g$ (eV) | $E_F$ (eV) | $E_b$ (eV) | FIC (%) |
|---|---|---|---|---|
| 0 | 4.77 | −3.58292 | −7.90 | 46 |
| 0.16 | 4.28 | −3.58482 | −7.88 | 46.4 |
| 0.32 | 3.86 | −3.58972 | −7.80 | 46.7 |
| 0.48 | 2.87 | −3.19069 | −7.67 | 47 |
| 0.68 (without $F$) | 0.54 | – | −7.12 | 70 |
| 0.68 (with $F$) | 0.86 | – | −7.6 | 30 |

planes ($\Delta = 0$), strong sigma bonds are formed through $sp^2$ orbital overlapping whereas the planar buckling reduce $sp^2$ overlapping and bond symmetry is broken simultaneously. The total density of states (DOS) for all cases is shown in Fig. 2. It can be seen obviously that increasing planar buckling decline the energy gap through shifting the conduction band minimum (CBM) toward the Fermi level as the vertical axis is plotted based on "$E - E_{Fermi}$". So Fermi energy set on zero energy, but the real values of Fermi energy are presented in Table 1 for all considered systems. It is obvious that the valence band shape do not change by exerting