

The electronic structure of cubic boron nitride nanocrystals using ab initio method

التركيب الإلكتروني لبلورة نتريد البورون المكعبة النانوية باستعمال
طريقة المبادئ الأساسية

Dr. Hamad R. Jappor

College of Education for Pure Sciences, University of Babylon.

Abstract

The ab initio restricted Hartree-Fock method is used to simulate the electronic structure of cubic boron nitride (c-BN) nanocrystals (NCs) with sizes ranging up to about 1.5 nm in diameter. The calculations are divided into two parts, surface and core. The oxygenated (001)-(1×1) facet that expands with larger sizes of nanocrystals is investigated to determine the rule of the surface in nanocrystals electronic structure. Results show that lattice constant and ionicity of the core part show decreasing order as nanocrystals grow up in size. The smallest investigated nanocrystal is 1.35% larger in lattice constant and 14.9% larger in ionicity than the converged value of largest investigated nanocrystal. Increasing nanocrystals size also resulted in an increase of core cohesive energy (absolute value), decrease of core energy gap, and increase of core valence bandwidth. The surface states are found mostly non-degenerated because of the effect of surface discontinuity and oxygen atoms. Valence bandwidth is wider on the surface due to splitting and oxygen atoms.

The method also shows fluctuations in the converged energy gap, valence bandwidth and cohesive energy of core part of nanocrystals duo to shape variation. The present work suggests the addition of ionicity and lattice constant to the quantities that are affected by quantum confinement phenomenon. The present model has threefold results; it can be used to approach the electronic structure of crystals bulk, surface, and nanocrystals.

الخلاصة

استعملت طريقة المبادئ الأساسية المحددة لهارترتي-فوك لمحاكاة التركيب الإلكتروني لبلورة نتريد البورون المكعبة النانوية بقطر يصل إلى 1.5nm. قسمت الحسابات إلى جزئين هما السطح والقلب. وقد درس الوجه المؤكسد (001)-(1×1) والذي يتوسع بزيادة حجم البلورة النانوية لتحديد دور السطح في التركيب الإلكتروني للبلورات النانوية. أظهرت النتائج ان ثابت الشبكة والأيونية للقلب تتناقص بزيادة حجم البلورات النانوية. ان ثابت الشبكة للبلورة النانوية الأصغر قيد الدراسة اكبر بمقدار 1.35% والتأينية اكبر بمقدار 14.9% من قيمهما في البلورة النانوية الأكبر. بينت النتائج أيضا ان زيادة حجم البلورة النانوية في القلب يؤدي إلى زيادة طاقة الترابط (القيمة المطلقة)، تناقص فجوة الطاقة، و زيادة عرض حزمة التكافؤ. ولقد بينت النتائج أن حالات السطح تكون قليلة التحلل قياسا بالقلب بسبب عدم استمرارية السطح ووجود ذرات الأوكسجين.

أظهرت الطريقة تقلبات في تقارب فجوة الطاقة وعرض حزمة التكافؤ وطاقة الترابط للقلب، نتيجة لتغيرات شكل البلورة. العمل الحالي يقترح إضافة الأيونية وثابت الشبكة للكميات التي تتأثر بظاهرة الحصر (التقييد) الكمي. ان النموذج الحالي له ثلاث استعمالات؛ فهو يمكن ان يستعمل للحصول على التركيب الإلكتروني للمادة الصلبة و للسطح و للبلورات النانوية.

1 Introduction

Boron nitride is a material that has attracted continuous interest for more than three decades. Like carbon, boron nitride forms a variety of atomic structures of which the hexagonal and the cubic phase, in particular, have been the subject of extensive theoretical and experimental work [Hang-Sheng *et al.*, 2010; Khavryuchenko *et al.*, 2010; and Zhao and Wang, 2009].

Cubic boron nitride (c-BN) is an indirect, wide-gap semiconductor. The minimum of the conduction band is located at the X point of the Brillouin zone. The top of the valence band has the structure common to all zinc-blende semiconductors [Martienssen and Warlimont, 2005]. The cubic phase of boron nitride (c-BN), has a zinc-blende (zb) lattice structure with sp^3 -hybridised B-N bonds [Märliid, 2001].

In recent years, more and more attention [McCarson, 1998] has been paid to the use of c-BN based field emitters as an electron source of a highly reliable performance because c-BN has superior properties such as negative electron affinity, chemical inertness, mechanical hardness, high melting point and exhibiting a wide band gap with the possibility of bipolar doping. Moreover, field emission experiments on flat type c-BN [2] have shown that considerable emission currents are attainable. It is a material combining an excellent corrosion resistance and chemical inertness with ultrahardness. Obviously, it makes c-BN attractive for a broad field of applications like tribological and anti-corrosion coatings or as a starting material for high-temperature and high-power electronic devices.

The theoretical work of the last decade, usually performing highly sophisticated first-principal self-consistent (SCF) calculations within the Hartree-Fock and the local density functional theory was mainly limited to calculations of ground state properties of the crystalline phases and electronic band structures. Due to their high computational costs, these calculations are restricted to small periodic super cells. However, the simulation of dynamical structure formation processes requires including hundreds of atoms in the calculation. Therefore, approximate schemes such as semiempirical Hartree-Fock or tight-binding schemes became important. These methods combine high numerical efficiency with transferability and accuracy comparable to that of SCF methods.

The present work addresses large NCs that have the size range of 216 total atoms. These atoms are divided between core and surface. The present lower limit (of atoms) is chosen since it provides the first occurrence of idle core part (nearly ideal zb structure) that is far from surface reconstruction by more than three surface layers.

In the present work, we study the electronic structure and physical properties of c-BN NCs core and surface part with different sizes by using an ab initio restricted Hartree-Fock (RHF) method coupled with large unit cell method (LUC-RHF). LUC method was formulated and used before for several kinds of bulk materials including diamond and zb structured materials [Harker and Larkins, 1979; Abdulsattar and Al-Bayati, 2007].

2 Computational details

Ab initio self-consistent Hartree-Fock (RHF) is used to obtain c-BN NCs molecular orbitals. Correlation corrections are neglected in the present calculations relying on Koopmans theorem [Hehre *et al.*, 1986]. Simple STO-3G basis is used in the present work to reach higher number of core and surface atoms.

This method uses ($k=0$) approximation, that is one point in the wave vector space. The LUC method is one kind of supercell methods with the above $k=0$ restriction. In this method, instead of adding more k points, the single central cell is expanded to contain more atoms, which are now called core atoms in the present work. The LUC method was first suggested and applied to covalent semiconductors in the 1970s [Dobrotvorskii and Evarestov, 1974]. The method was found suitable for NCs calculations because the $k=0$ approximation retains only one central cluster of atoms surrounded by other atoms to passivate the outer dangling bonds. The method

is used to simulate parts of specific symmetry in the NCs (core and surface) in the same way it is used for bulk materials.

We used 3D PBC (Periodic Boundary Condition) method in GUSSIAN 03 code [Frisch *et al.*, 2003] to calculate ab initio restricted Hartree-Fock electronic structure of c-BN NCs internal core. The 2D PBC calculations are used to simulate oxygenated (001)-(1×1) surface.

In the present work, we divided the work into two parts, core and surface which is the traditional method used in microscopic-size solid-state calculations. In LUC core part only the lattice constant is optimized, at the surface part all bond lengths and lattice constant still need to be optimized because of surface reconstruction. The (001) chosen surfaces are terminated by oxygen atoms to passivated dangling bonds. The width of surface part is set to one conventional lattice that is deduced from BN surface bonds calculations. The oxygenated (001)-(1×1) BN surface in the oxygen double bonding configuration is investigated to obtain the total electronic structure of the BN NCs with (001)-(1×1) facets. The oxygenated (001)-(1×1) BN surface is chosen since it is one of the least reconstructed surfaces. Unlike the core part, the bond lengths and lattice constant are not unique and a variation of geometrical parameters is needed. Normally surface effects do not penetrate more than four layers (one lattice constant) from the crystal surface [Kittel, 1976]. On the other hand, short-range sp^3 bonds do not require more than fourth neighbor's interaction range to conduct electronic structure calculations successfully using molecular orbital methods. The upper two identical conditions are applied in the present calculations.

Two kinds of core LUCs are investigated, namely cubic and parallelepiped cells. The cubic cells are multiples of zb structure Bravais unit cells, while the parallelepiped cells are multiples of primitive zb structure unit cells. Cubic core cells include 8, 64, and 216 atoms. Parallelepiped cells include 16, 54, and 128 atoms.

3 Calculations and results

In this section, we present the calculated band structures of BN NCs. Figure 1 shows the total energy for BN NCs as a function of lattice constant for 8 core atoms, from which we obtained the equilibrium lattice constant. Figure 2 shows the variation of the lattice constant of BN NCs core as a function of number of core atoms. This figure is obtained after minimizing the energy lattice curve of every investigated number of core atoms. From this figure we see that the lattice constant for the core part of the crystal decrease with increasing number of atoms, the lattice constant for BN NCs shows decreasing values from 0.371 nm for 8 atoms to 0.366 nm for 64 atoms LUC, then the lattice constant tends to be constant for LUC of atoms number greater than 64. The present lattice constant of 8 atom large unit cell (0.366 nm) is approximately 1.1% larger than the experimental value (0.362 nm) reported by Mujica for bulk [Mujica *et al.*, 2003]. The optimization shows that the smallest investigated nanocrystal core (8 atoms) has a lattice constant that is nearly 1.35% larger than the converging lattice constant value for larger nanocrystals for BN NCs.

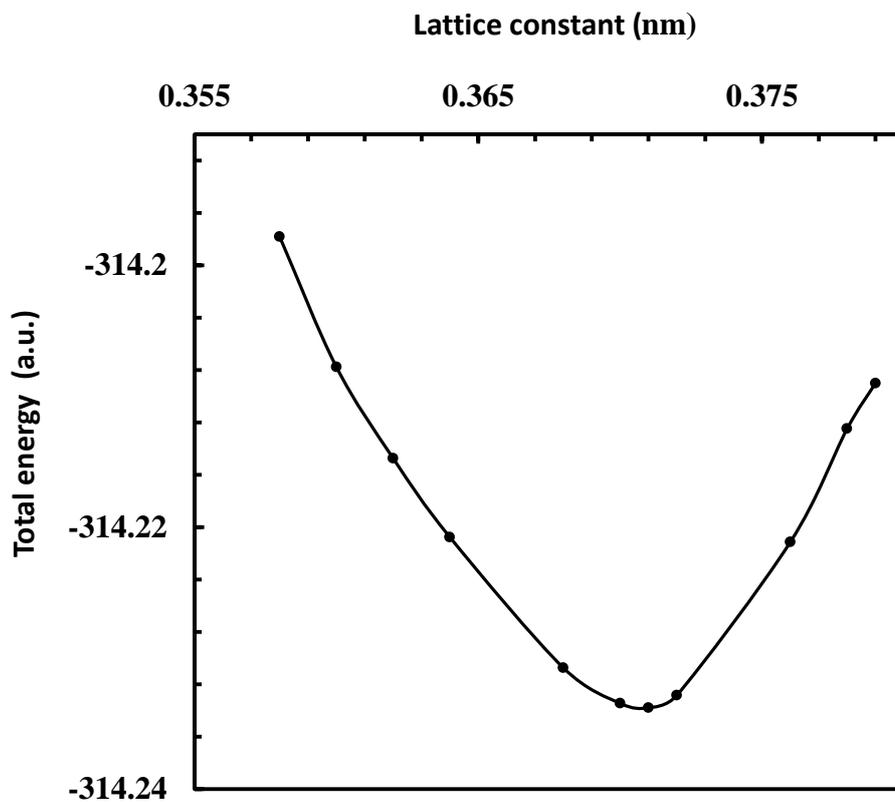


Figure (1): Total energy of 8 BN core atoms as a function of lattice constant.

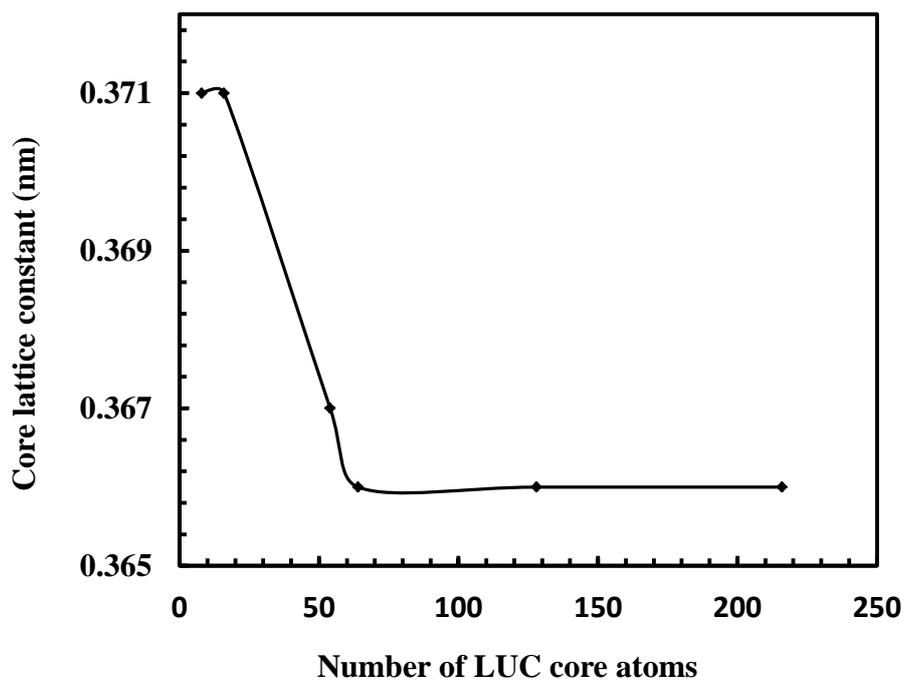


Figure (2): Energetically optimized BN core lattice constant as a function of the number of atoms in the core.

The bulk modulus (B) has been calculated from Cohen's theory [Kaxiras, 2003]:

$$B = \frac{N_C (1971 - 220\lambda)}{4 d^{3.5}} \quad (\text{GPa}) \quad (1)$$

where N_C is the coordination number ($= 4$), λ is a dimensionless number which describes the ionicity: ($= 0, 1$ and 2 for IV, III-V and II-VI groups respectively) [Zheng, 1999], d is the first-neighbor distance in Å, i.e., the interatomic distance, for the zb structure we have [Adachi, 2009]:

$$d = \frac{\sqrt{3}}{4} a \quad (2)$$

Bulk modulus of BN nanocrystal as a function of number of atoms in the core is shown in Figure (3). This Figure shows that the bulk modulus increases with the number of atoms in the core. This relation can be simply attributed to the fact that the lattice constant for the core part of the crystal decrease with increasing number of atoms, the latter equation means that the decrease in lattice constant entails a decrease in interatomic distance (d) which leads to increasing in the bulk modulus according to equation (1). We note that the bulk modulus for BN nanocrystal of 349.5GPa smaller than the experimental results of 369 GPa [Kulisch, 1999] of the bulk taking into consideration that Hartree-Fock theory always overestimates bulk modulus values [Jappor *et al*, 2012].

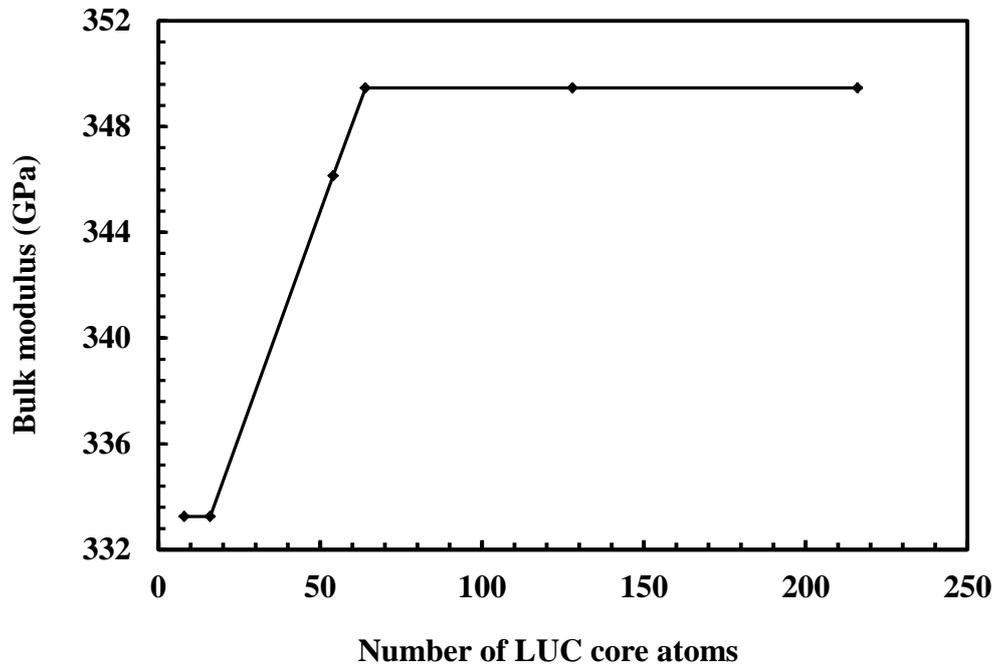


Figure (3): Bulk modulus as a function of the number of core atoms for BN NCs.

BN has an indirect minimum gap with the conduction band minimum at X point of the Brillouin zone. Figure (4) shows the energy gap of the core part of the investigated nanocrystals against the number of core atoms. In nanostructures, normally, the dimensions are commensurate with the de Broglie wavelength of the charge carriers; so that quantum confinement effects become important and the

properties of the semiconductors are significantly modified. Due to the quantum confinement effect, the energy band gap of nanocrystals decreases with increasing the size of the quantum structure [Bruno *et al.*, 2005]. Figure (4) shows the band gap of nanocrystalline c-BN NCs changing with the change in the number of core atoms, it can be seen that the change in the bandgap is distinct as the number of core atoms is larger than 64 atoms. This changing is associated with fluctuations depending on the geometry of the nanocrystal core. Figure (4) shows that the size of the cell has pronounced effect on the electronic structure of the core of nanocrystals in the large number of atoms, whereas the effect of size is less pronounced in the case of small LUC size (8, 16, and 54 atoms) this is also found in [Chelikowsky and Saad, 2004]. The energy gap of 8 atoms large unit cell 6.77eV is in good agreement with the experimentally reported energy gap (6.1-6.6 eV) for bulk c-BN [Kulisch 1999] and within the trends of nanocrystals blue shift [Shimazaki and Asai, 2010]. At the SCF level, Koopmans' theorem holds, and the task of determining the band energies and energy gap can be reduced to finding the one-electron energies of the respective Bloch states. It is well known that SCF (HF) calculations tend to overestimate the energy gap, giving too low an energy for the top of the upper valence band and too high an energy of the conduction band bottom. The reason for this is that HF theory optimizes a wavefunction. SO, to determine the same property using a wavefunction, we need to know the correct quantum mechanical operator. HF orbitals, experience varying potentials, and, in particular, HF virtual orbitals experience the potential that would be felt by an extra electron being added to the molecule. As a result, HF virtual orbitals tend to be too high in energy and anomalously diffuse. This fact is especially important for crystalline solids and explains why HF band gaps are overestimated compared to those in experiment and other ab initio methods .This convergence is associated with fluctuations depending on the geometry of the nanocrystal core.

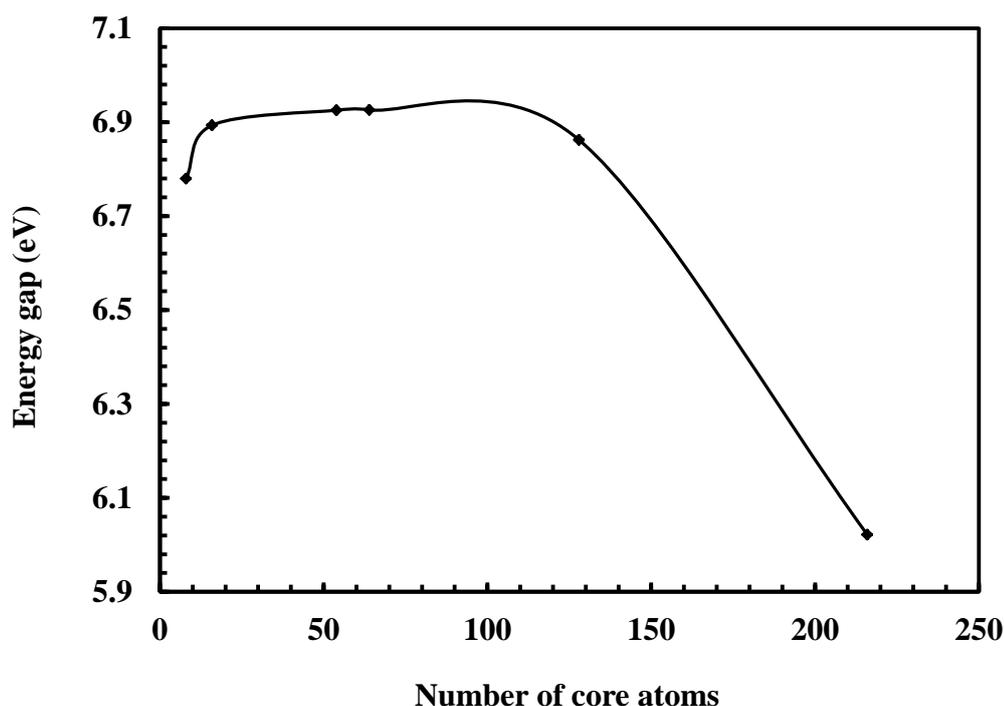


Figure (4): Energy gap of the core part of BN nanocrystals as a function of the number of core atoms.

The cohesive energies (Figure (5)) of BN NCs have a high value in comparison with the experimental value of (13.2 eV) [Wentzcovitch *et al.*, 1986].

These values of cohesive energy belong not to the nanocrystals as a whole but to the core only since the surface consists of two kinds of atoms and when the researcher add the surface effect we expect that the cohesive energy will be reduced to the experimental value and this is not done in the present work since it takes very long time and a lot of memory out of the disk space.

In present work, we calculated valence bandwidth which is the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The valence bandwidth as a function of number of atoms for BN nanocrystal core part is shown in Figure (6). One can see from the figure that this band generally increases with increasing number of atoms and become nearly stable at the 64 core atoms. The valence bandwidths of 8 atoms are calculated to be 20.13 eV for BN NCs. The valence bandwidths are in good agreement with that of the bulk (20.6 eV) [Jayawardane, 2001].

At the HF level, Koopmans' theorem suggests that the energy of the HOMO is a good approximation to the negative experimental ionization potential. Similarly, it suggests that the electron affinity for a N_e -electron system is equal to the negative of the LUMO energy [Sque *et al.*, 2006], assuming that the orbitals do not relax. Figure (7) shows the variation of HOMO and LUMO as the core of nanocrystals grows up in size and changes its shape. This curve fluctuates strongly because of the change in size and shape that produces different surfaces with different properties. Not all quantities have definite convergence behaviour similar to the upper investigated quantities.

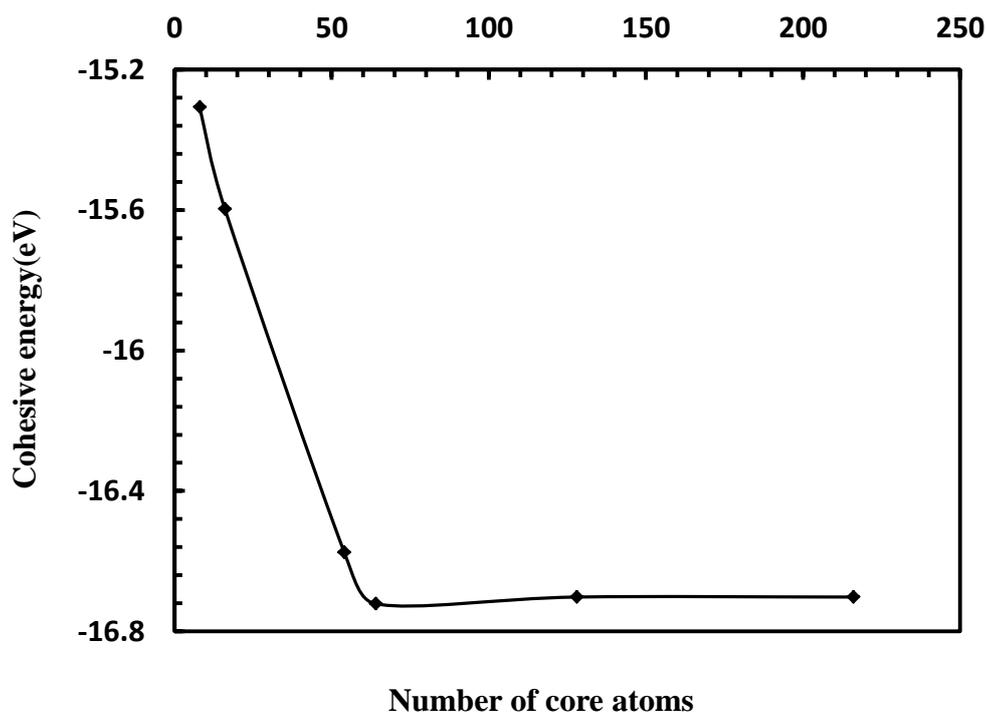


Figure (5): Cohesive energy of the core part of BN NCS as a function of the number of core atoms.

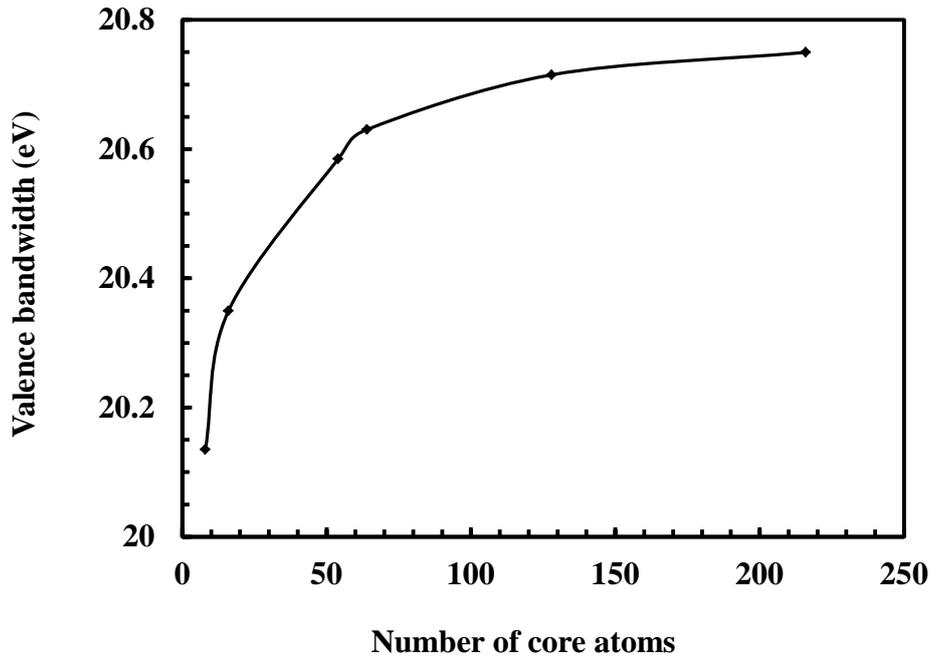


Figure (6): Valence bandwidth of the core part of BN nanocrystals as a function of core atoms.

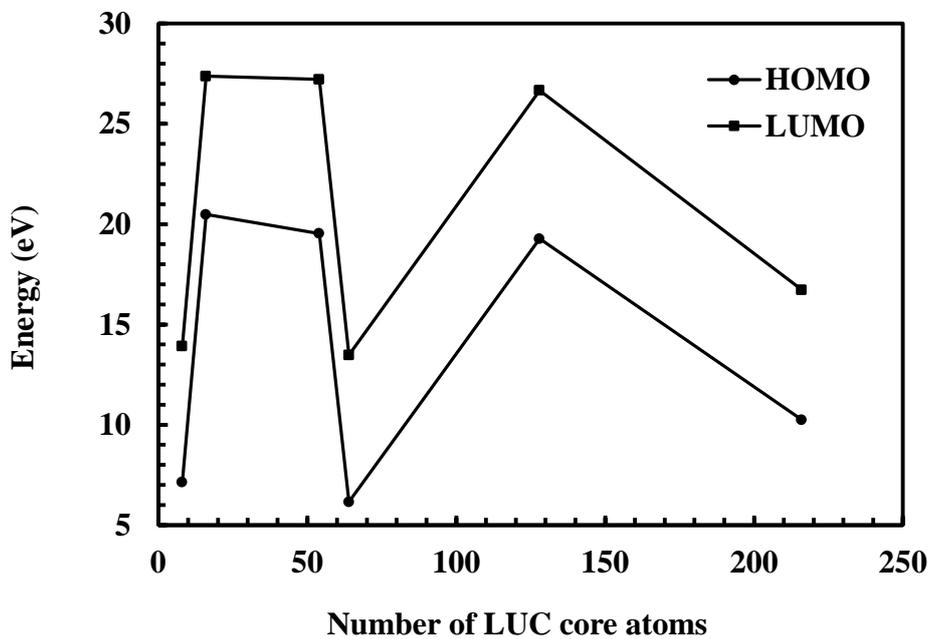


Figure (7): HOMO and LUMO energies that correspond to different core sizes of BN nanocrystals.

HOMO and LUMO energy levels plotted in Figure (7) show fluctuating behaviour that continues indefinitely. As nanocrystals grow up in size they develop different shapes and surfaces. Each of the developed surfaces has different properties such as the upper mentioned ionization potential and affinity or HOMO and LUMO energy levels. Therefore, these fluctuations start at the nano-scale, continue to the micro, and bulk scale. A similar behaviour is observed for SiGe nanocrystals [Abduljalil *et al.*, 2011].

The ionicity charge is calculated as a function of number of atoms using Gaussian program as shown in Figure (8), which shows that the ionicity charge decrease with increasing number of atoms for core part; smaller nanocrystals are more ionic than larger ones ionicity nearly converges after 64 core atoms to nearly 0.4. This behaviour is encountered not only for the ionicity but also for the energy gap and lattice constant. However, the ionic charge of boron atoms equal ionic charge of nitrogen atoms and the net charge equals to zero.

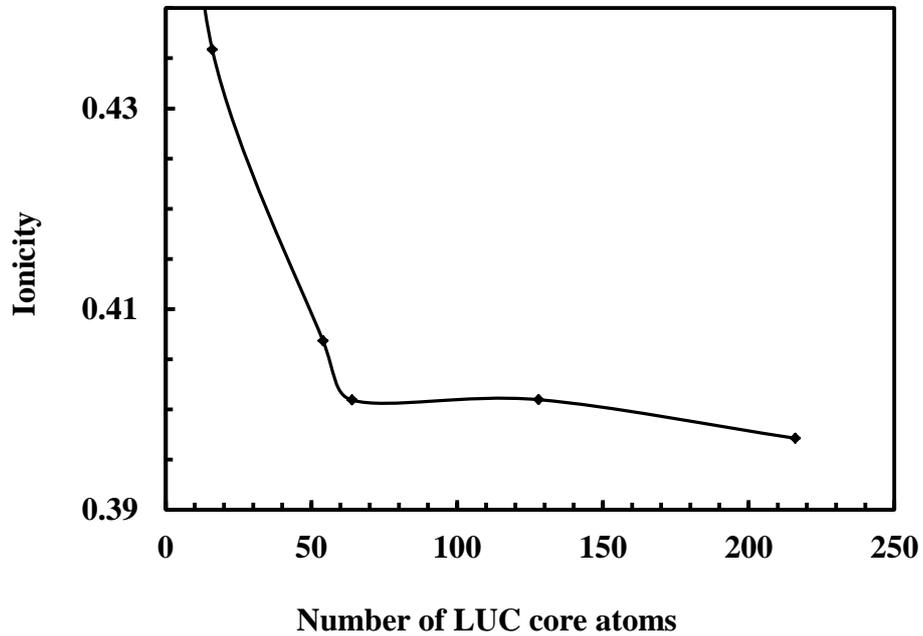


Figure (8): Ionicity of the core part of BN nanocrystals as a function of the number of core atoms.

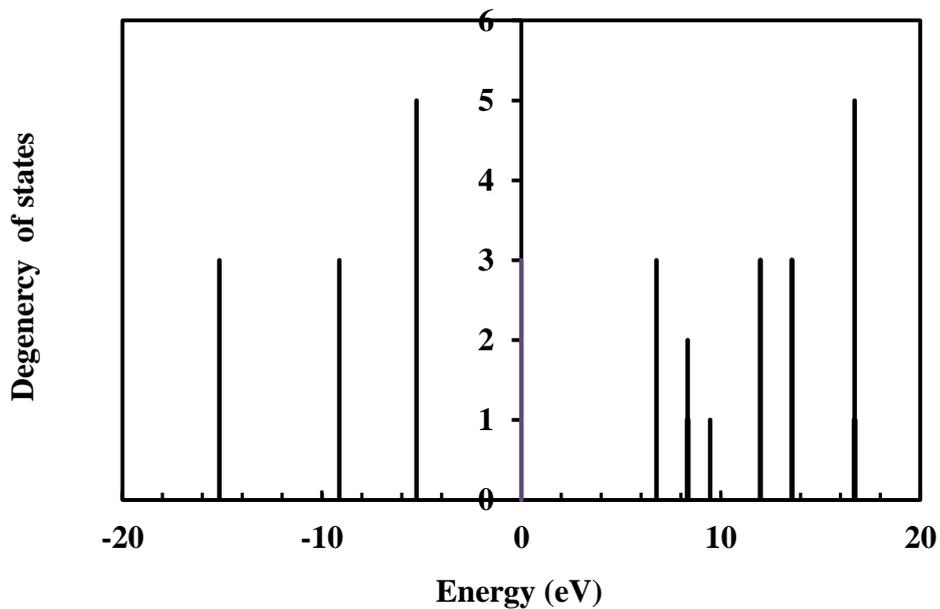


Figure (9): Degeneracy of states of 8 atoms core part of BN nanocrystal as a function of energy levels.

The degeneracy of energy level states for BN nanocrystal as a function of levels energy for the lowest energy lattice constant is calculated for core and surface parts. Figure 9 shows the degeneracy of states is 5 for 8 atoms of core part. Due to high symmetry, the number of degenerate states is high in the core part. The highest number of degenerate states in the valence band is 5 for the 8 atom core

To investigate nanocrystals surface electronic structure, it is natural to assume that larger nanocrystals to have larger surfaces. Two oxygenated oxygen terminated (001)-(1×1) BN surface stoichiometry slabs are investigated, namely, $B_8O_4N_8$, and $B_{32}O_{16}N_{32}$ with two surface areas of a^2 , and $4a^2$, respectively.

The average lattice constants of the two investigated stoichiometries are less than the corresponding core parts, but they follow the same decreasing order. The oxygenated (001)-(1×1) surface slab calculations of the nanocrystal converge to approximately the same lattice constant value of the core (0.368 nm). This good matching between surface and core lattice constants shows that good adhesion is expected between the two parts.

The energy gap of (001)-(1×1) oxidized surface show much smaller gap than that of the core part. Oxidized surface gap of BN calculated using slab geometry of the stoichiometry $B_8O_4N_8$ is 0.12 eV. This value is very near to the oxidized germanium surface gap 0.19 eV calculated using the same geometry [Aysa *et al.*, 2011], the same surface for silicon has 1.4 eV [Nama *et al.*, 2010]. From these values we can conclude that the core BN part of nanocrystals is the governor of the energy gap value and that the oxidized surface gap does not alter final gap value. Figures 10 represent the degeneracy of states for oxygenated (001)-(1×1) surface part of $B_8O_4N_8$ stoichiometry slab nanocrystal surface. This surface has lower number of degenerate states compared with core part of Figure 9. This low degeneracy is due to broken symmetry at the surface discontinuity. The existence of oxygen atoms leads to varying the bond lengths and lattice constant.

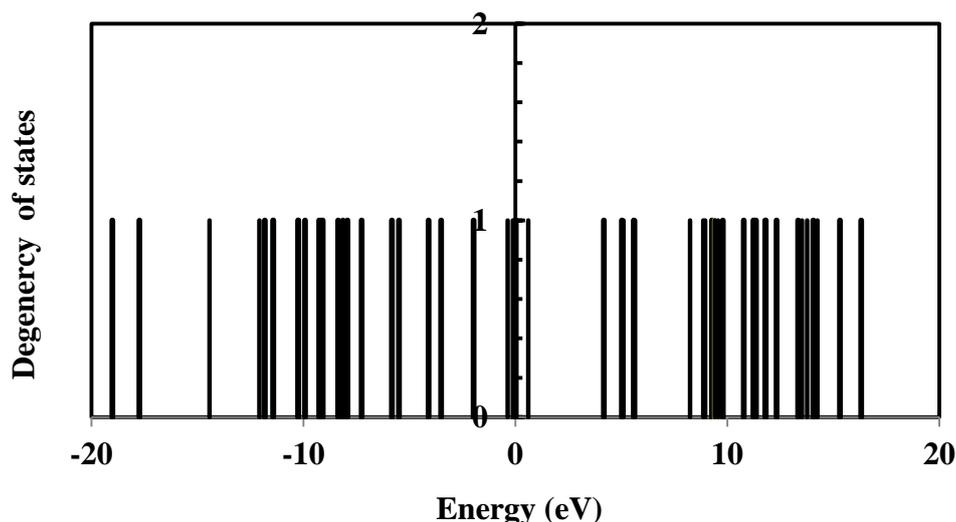


Figure (10): Degeneracy of states of surface part of $B_8O_4N_8$ stoichiometry slab as a function of energy levels.

In the surface part, discontinuity of surface imposes level splitting on the degenerate energy levels. The splitting of energy levels dose not only affects the number of degenerate states, but also the valence bandwidth which is wider in surface part (23.12 eV). On the other hand, the splitting of states and additional oxygen surface states strongly affect the energy gap and considerably reduce its value.

Conclusions

In this paper, we studied some properties of c-BN nanocrystals. The total energy, lattice constant, bulk modulus, cohesive energy, energy gap, valence bandwidth, ionicity, and degeneracy of energy levels have been calculated by the self-consistent restricted Hartree–Fock method coupled with the large unit cell method (RHF-LUC). The lattice constant and ionicity decreases with increasing size of large unit cell for core and surface parts. Core and surface energy gap decreases with increasing size of LUC. Cohesive energy of BN nanocrystals increases (absolute value) with the increase of number of atoms. Valence bandwidth increases with increasing size of LUC for core and surface part. HOMO and LUMO energy levels show fluctuating behaviour. As nanocrystals grow up in size they develop different shapes and surfaces. Each of the developed surfaces has different properties such as the upper mentioned ionization potential and affinity. The valence bandwidth in surface part is larger than for core part caused by the existence of oxygen atoms and surface states splitting. The degeneracy of states of core part for all sizes of LUC is larger than the degeneracy of surface part. On the other hand, (001)-(1×1) oxidized surface and core parts have approximately the same lattice constant that reflects the good adherence of the oxide layer at the surface. The present work, in addition to previous LUC results, suggests the inclusion of lattice constant, ionicity and other properties to the quantum confinement affected properties that already include energy gap of nanocrystals. Some properties, such as ionization potential and affinity, continue to fluctuates from nano-scale to micro-scale because they are the kernels of different shapes and surfaces of ordinary size crystals.

References

- Abdulsattar, M. A., and Al-Bayati, K., 2007, "Corrections and parameterization of semiempirical large unit cell method for covalent semiconductors", *Phys. Rev. B* Vol. **75**, p. 245201-1.
- Adachi, S., 2009, "Properties of semiconductor alloys: group-IV, III–V and II–VI semiconductors", John Wiley & Sons Ltd, Chichester.
- Aysa, N. H., Abdulsattar, M. A., and Abdul-Lettif, A.M., 2011, "Electronic structure of germanium nanocrystals core and (001)-(1×1) oxidised surface", *Micro&Nano Lett.* Vol. **6**, p.137.
- Bruno, M., Palumbo, M., Marini, A., Del Sole, R., Olevano V., Kholod, A. N., and Ossicini, S., 2005, "Excitons in Germanium Nanowires: Quantum Confinement, Orientation, and Anisotropy Effects within a First-Principles Approach", *Phys. Rev. B* Vol. **72**, p.153310.
- Chelikowsky, J.R., and Saad, Y., 2004, "Electronic Structure of Clusters and Nanocrystals", University of Minnesota.
- Dobrotvorskii, A.M. and Evarestov, R.A., 1974, "The Quasi-Molecular Large Unit Cell Model in the Theory of Deep Levels in Imperfect Crystals: Point Defects in Graphitic Boron Nitride" *Phy. Sta. Sol. (b)* Vol. **66**, p. 83.
- Frisch, M. J., Trucks, G. W., Schlegel H. B. *et al.*, 2003, GAUSSIAN 03, Revision B.01, Gaussian, Inc., Pittsburgh, PA, 2003.
- Hang-Sheng, Y., Fa-Min, Q. and An-Min, N., 2010, *Journal of Inorganic Materials*, Vol. **25**, p.748.

- Harker, A. H., and Larkins, F. P., 1979, "A large unit cell semiempirical molecular orbital approach to the properties of solids. I. General theory", *J. Phy.C: Solid State Phys.* Vol. **12**, p. 2487.
- Hehre, W., Radom, L., Schleyer, P., and Pople, J., 1986, "Ab Initio Molecular Orbital Theory", John Wiley & Sons, New York.
- Jappor, H. R., Saleh, Z. A., and Abdulsattar, M.A., 2012, "Simulation of Electronic Structure of Aluminum Phosphide Nanocrystals Using Ab Initio Large Unit Cell Method nanocrystals", *Adv Mater Sci Eng*, Vol. **2012**, Article ID 180679, 6 pages.
- Jayawardane, D.N., Pickard, C.J., Brown, L.M. and Payne, M.C., 2001, *Physical Review B* Vol. **64**, p.11517/1-4.
- Kaxiras, E., 2003, "Atomic and Electronic Structure of Solids", Cambridge University Press, New York.
- Khavryuchenko, O., Alekseev, S.A., Beobide, A., Kandilioti, G., Voyiatzis, G.A., and Lisnyak, V., 2010, *The Journal of Physical Chemistry C*, Vol.**114**, p.1102.
- Kittel, C., 1976, "Introduction to Solid State Physics", John Wiley & Sons, New York, USA, 5th edn.
- Kulisch, W., 1999, "Deposition of superhard diamond-like materials", Springer, Heidelberg Berlin.
- Märliid, B., 2001, Theoretical modeling of thin film growth in the B-N system. *Acta Universitatis*.
- Martienssen, W., and Warlimont, H. (eds.), 2005, "Springer Handbook of Condensed Matter and Materials Data", Springer Berlin Heidelberg.
- McCarson, B.L., Schlessler, R., Sitar, Z., 1998, *J. Appl. Phys.* Vol. **84** (6), p.3382.
- Mujica, A., Rubio, A., Muñoz, A., and Needs, R. J., 2003, "High – pressure phases of group–IV, III-V, and II-VI compounds", *Rev. Mod. Phys.* Vol. **75**, p. 863.
- Nama, N.A., Abdulsattar, M.A., and Abdul-Lettif, A.M., 2010, "Surface and core electronic structure of oxidized silicon nanocrystals", *J. Nanomater.*, Vol. **2010**, article ID. 952172, 6 pages.
- Shimazaki, T., and Asai, Y., 2010 "Energy band structure calculations based on screened Hartree–Fock exchange method: Si, AlP, InP, GaP, and GaAs", *J. Chem. Phys.* Vol. **132**, p. 224105.
- Sque, S.J. Jones, R., and Briddon, P.R., 2006, "Structure, electronics, and interaction of hydrogen and oxygen on diamond surfaces", *Phys. Rev. B* Vol.**73**, p.085313.
- Wentzovitch, R.M., Chang, K. J. and Cohen, M. L., 1986, *Phys.Rev. B* Vol **34**, p.1071 .
- Zhao, Y., and Wang, M., 2009, *Journal of Materials Processing Technology*, Vol. **209**, p.355.
- Zheng, J. C., Huan, C.H., Wee, A. T ., Wang, R.Z., and Zheng, Y.M., 1999, *J Phys: Condens Matter* Vol. **11**, p.927.