STUDY OF GEOMETRICAL AND ELECTRONIC PROPERTIES OF ZnS WURTZOIDS VIA DFT

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In the present research, ZnS bare and hydrogen passivated nanotubes structures are building from molecular change sizes of ZnS wurtize to become ZnS wurtzoids at the nanoscale structure. The geometrical and electronic features of ZnS wurtzoids are investigated, include energy gap, the density of state, bond length, and geometrical optimizations. The theoretical results found that energy gaps increase with a change of sizes structures of ZnS at the nanoscale and with hydrogen passivated (Hp). Study of The Gibbs free energy proved the stability phase of ZnS wurtzoids against transition to ZnS diamodiods structure.

1. Introduction

ZnS is one of the essential chalcogenides semiconductors belong to group II-VI in periodic table that has a wide energy direct optical band gap about 3.68 to 3.78eV, has three forms of crystals zincblende, wurtize, and rock salt, the cubic phase is more stable at ambition conditions ,but the wurtzite (hexagonal) of ZnS can be more stable at high temperatures 1020 °C and melting at1650°C[1]. There are many industrial applications for two ZnS forms. Recently, Zinc sulfide at the nanoscale as nanoparticles exists in different structures, and various morphologies surfaces include several shapes like nanotubes, nanosheets, and nanospheres and other nanoshapes as nanowires, nanorods and nanoflowers, various of routes have been synthesized these shapes successfully [2]. One of the applications ZnS is used in UV-detectors due to it has wide energy gaps in the UV region, also other applications such as light emitted diode(UV-LED), laser and sensors .etc.[3].Some theoretical studies focused on the electronic properties for diamondoids vai DFT for some materials [4].

In this study, geometrical and electronic characteristics of the molecular and nanostructures bare and hydrogen passivated of ZnS as nanotubes has investigated using Ab – initio approximation method dependent on density functional theory (DFT).

2. Theory

In this work, it can employ one of the theoretical approximations methods to simulate the features and nanostructures of ZnS nanotubes , the approach route is used density functional theory for all electrons using B3LYP (Becke, three-parameters, Lee-Yang-Parr) as basis set with 6-311G**, the double asterisks above basis, the first, it is representing the polarization set d – function when the adding to heavy atoms, while the second representing the polarization p-functions were added to atoms of hydrogen, in sometimes be the basis as denoting 6-311G(d,p) [5].

In this study, the molecular- nanoscale limited of ZnS as bare and passivated hydrogen is investigated. In the beginning, the ZnS of wurtzite form can be as seeds for the present molecules, the smallest of the molecule is Zinc sulfide with formula ZnS when hydrogen atoms are passivated

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with the molecule become with formula $ZnSH_6$. The second cause, the molecules most important are Zn_3S_3 cyclohexane as bare (without hydrogen) and $Zn_3S_3H_{12}$ with passivated hydrogen, these molecules will be considered as a base, after that can build blocks the wortziods or diamondoids from this molecule that has hexagonal ring-shaped.

In the last years, the researchers were working to form the wurtziods molecules at nano-scale limited that be in an origin wurtzite phase structures($a=b\neq c$) of material and have same its properties and using simulation by programs Gaussian 09 ,inverse the diamondoids that came from the cubic structure($a=b=c$) of material in bulk of solid materials [6], a result of there is the symmetry in these structures can be formed as bare and passivated of H-atom ,therefore it can be shaped by the bundles of ZnS nanotubes (3,0) . Where the structures wurtziods as a bare involve the Zn_7S_7 ,$Zn_{13}S_{13}$, and $Zn_{21}S_{21}$ while these structures with passivated of H-atom on their surface include $Zn_7S_7H_{14}$, $Zn_{13}S_{13}H_{26}$ and $Zn_{21}S_{21}H_{30}$, as shown in the figures (1,2and3), illustrates the bare and passivated of H-atom of ZnS wurtziods for some molecules (wurtziod (one nanotube), wurtziod 2c (two nanotubes along c–lattice constant) and triwurtziod (three nanotubes) at nanoscale size.
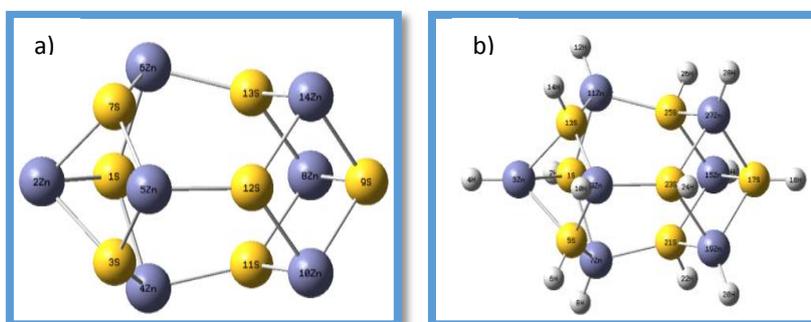
Fig. 1. Represent the molecules of wurtzoid of ZnS (a)- bare of Zn_7S_7, and (b)-H-passivated of $Zn_7S_7H_{14}$ after geometrical optimization
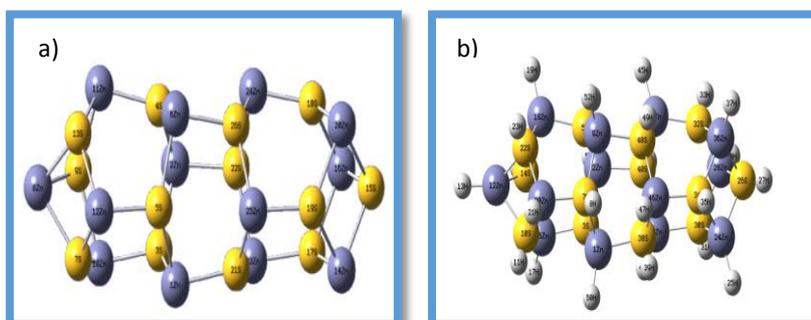
Fig. 2. The wurtzoid of ZnS nanotubes structure a) bare and b) H-passivated after optimization.
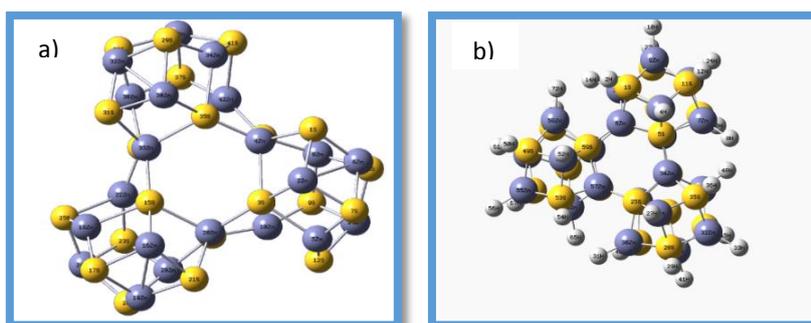
Fig. 3. The triwurtzoid of ZnS nanotubes structure (a) bare and b) H-passivated after optimization.

3. Results and discussion

In the present work , study the bare and passivated hedgron of ZnS where found that energy gaps increasing with exist the hydrogen passivation on the surface ZnS molecules as shown in Fig. 4 , denote that energy gaps of bare and H-passivated of ZnS molecules as function to the total number of atoms Zn and S also LUMO and HOMO that expresses with unoccupied and occupied levels of ZnS molecules of bare and passivated as function to same atom above, the energy gaps at nanoscale increasing due to quantization confinement therefore values energy gaps are calculated theoretical with H-passivated of ZnS molecules were high if compared with experimental values of ZnS wurtizet [1] , the values of gaps with exist H-atom on their surface for each molecules that represent with the stoichiometry $ZnSH_6$, $Zn_3S_3H_{12}$, $Zn_7S_7H_{14}$, $Zn_{13}S_{13}H_{26}$ and $Zn_{21}S_{21}H_{30}$ give (2,6.88,6.06,5.8 and 5.3) eV respectively, while bare of ZnS clusters, ZnS, Zn_3S_3, Zn_7S_7, $Zn_{13}S_{13}$ and $Zn_{21}S_{21}$ illustrate that the theoretical results of energy gaps approached to experimental value of ZnS wurtize can see under the dashed line as in Fig(4) , the bare clusters of ZnS have values less than H-paasivated of these clusters due to there are dangling bonds that insert levels of energy into the forbidden gap, and the other hand , the LUMO levels are more sensitive than HOMO levels for surface effects ,through appearance small difference between two levels for both cases (bare and HP) especially when the clusters be large[7] as seen in the two curves, whereas the LUMO levels be large difference between them due to adding the electrons [8] the values of energy gapes in this work of bare clusters of ZnS be approximated to the experimental bulk value wherefore it can be considered a good results.
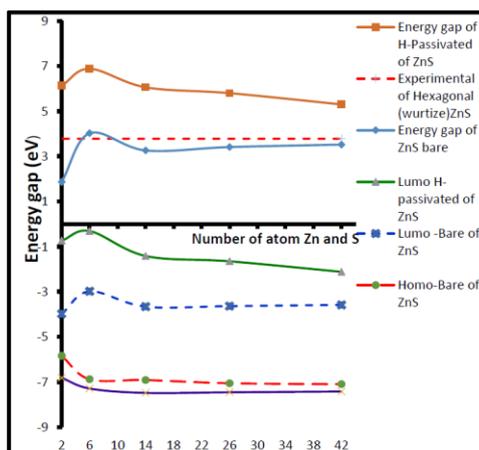
Fig. 4. the energy gaps of bare and hydrogen passivated of ZnS as function of total number of atoms Zn and S and compare with the experimental bulk of ZnS wurtize.

In Fig. 5 (a) indicate that densities of states of wurtziod(Zn_7S_7), wurtzoid 2c $Zn_{13}S_{13}$ and triwurtziod $Zn_{21}S_{21}$ of ZnS (bare and HP) respectively, as functions to energies levels of them after optimization geometric, also the densities of states increase with wurtzoids size ,it found that the band gaps(between HOMO (V.B)and LUMO(C.B)) of wurtzoids with exist H-atoms passivated increasing about the experimental value of molecule ZnS in range of (6.06,5.8, 5.3 eV)respectively while the bare of these structure are 3.26,3.41,3.52 eV respectively closed to experimental value of ZnS wurtizet (3.78)[1] this means the wurtzoids structures with H-passivated near to nano-scale lead to increase values of these gaps, then their other explanations explain that increase of energy gaps effect with additional states besides the splitting of states 9] . Also, the density of states have degenerated of states are high due to the high symmetry according to [10]

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(a)   *(b)*
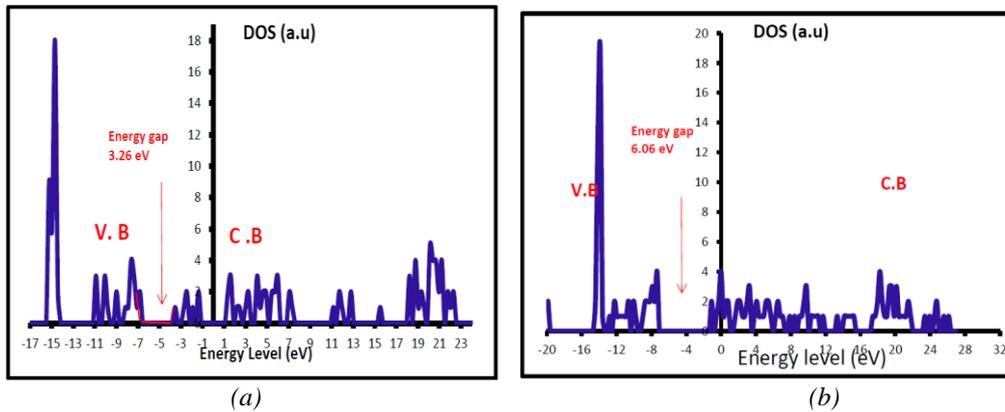
Fig. 5. (a) Density of state(DOS) of Zn_7S_7 bare wurtzoid as a function of energy levels;
(b) Density of state of $Zn_7S_7H_{14}$ HP wurtzoid as a function of energy levels.

Fig. 6 illustrates that distribution of density of bonds length of ZnS wurtziod (bare and HP) together and compare with experimental values of bonds, denote that the density bond length of Zn-S in the bare wurtzoid is the highest from HP about bond length 2.38 A° and coincide with experimental value is 2.38 A° , while the other bonds of structure S-H is 1.34 and Zn-H is 1.53 exists in HP but disappear in Bare, the experimental values of the above bonds is 1.34 and 1.56 respectively[5] . Also, the experimental value of bond Zn-S mediate the bare and H-passivated of molecules; the reason belongs to type the bonds of sp^2 as well known be short and strong on inverse sp^3 bonds.
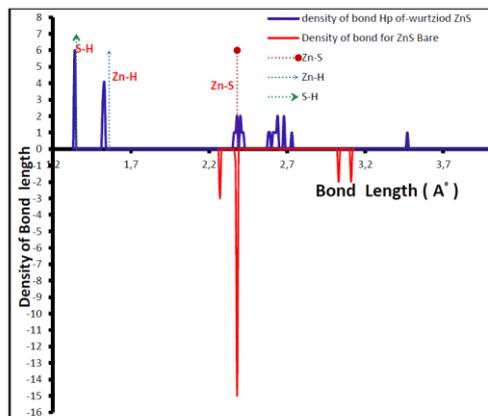
Fig. 6. Density of bond length for wurtzoid bare and HP as function of Bond length compare with experimental value Zn-H, S-H, and Zn-S.

As mention above that ZnS has polymorphs zinc blende structure and wurtize phase in the bulk , while at nano-scale region represented by damiondzoid or wurtziod and in order to know which of these more stable can use the Gibbs free energy(GFE) to study the stability ,equilibrium and phase transformation for these structures from nanomaterials that have two cases either stable or metastable , if the molecules have the same chemical formula but different in their geometry structures as in Fig. 7, Fig. 1, where(**Zn_7S_7**) represent the chemical formula of both structures of ZnS diamante (bare)and wurtzoid(bare),also note that the number of dangling bond for both them be different as in Table(1) below, therefore both of the structure for molecules was different ,it is an important to study the Structures transition in solid state, this the transition phenomenon is different at nano-scale from the bulk because of surface effect, sometimes, at nano-scale can be observed that the stable structures that don't appear in bulk[11].
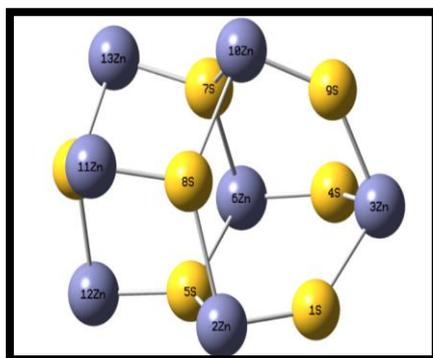
Fig. 7. ZnS Bare Diamantane after optimization.

In this work , notice that the ZnS wurtziod with (HP)and without (bare) –hydrogen atoms more stable than the ZnS diamantante (bare and HP) due to the Gibbs free energy(GFE) has high(negative) for as mention in Table (1) after take absolute value of them , The diamantante has number of bonds than wurtzoid therefore the dangling bonds be more on their surface, than the passivation of H –atom be large, this effect on values of the energy gaps and the longitudinal frequencies modes.

*Table 1. The relation among several parameters associated ZnS wurtziod (bare and H-passivated)
with ZnS diamantante.*

STRUCTURE	Formula	Energy Gap (ΔE)eV	Dangling bonds	Gibbs Free Energy GFE(eV)
Diamantane ZnS (Bare)	Zn_7S_7	3.44	20	-58.078
Wurtzoid ZnS(Bare)	Zn_7S_7	3.66	14	-59.23
Partial Diamantane(HP)	$Zn_7S_7H_{14}$	5.61	6	-60.23
Wurtzoid (Hp)	$Zn_7S_7H_{14}$	6.06	0	-60.50

Gibbs Free Energy (GFE} computes as results of subtracting the energy number of clusters from the bulk material. The negative value of GFE is spontaneous processes can represent a maximum of work possible [12] The absolute values of negative GFE give high values of wurtzoid and low of diamantane. This belongs to dangling bonds at the fourth column as in Table (1). As a result of these reasons will transform to wurtzoid from diamantane at a constant of the pressure and temperature, in all the cases the wurtzoid be will more stable either bare or Hp or bulk.

The values of energy gap for Diamantane (ZnS) are lower than that of Wurtzoid(ZnS) for both cases (bare and H-passivated) as shown in the table because of the dangling bonds of them.

4. Conclusions

ZnS nanotubes bare and hydrogen passivated were investigated theoretically. The theoretical study of these structures found that increase energy gaps with passivated hydrogen more than the structures without hydrogen (Bare) , also notice that the geometry of structures as wurtziod and wurtzoid-2c as two tubes sharing along c-constant while triwurtziod (three tubes) which form a bundle (3,0) nanotube, The calculations of the Gibbs free energy found that the transformation to the wurtzoid phase(bare and HP) were most stable than diamamtante structure .

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