The Investigation of the Cadmium Effect on Properties of ZnCdO Alloys Using $Zn_{36-x}Cd_xO_{36}$ Clusters

L. Ovsiannikova[a,*]

Frantsevich Institute for Problems of Material Science, NASU, Kiev, Ukraine

The structural, cohesive, and electronic properties of a fullerene-like $Zn_{n-x}Cd_xO_n$ ($n = 36$) clusters have been investigated within the framework of the electron density hybride functional method (B3LYP) with a set of 3-21G(d) split valence basis functions. These clusters are used as a model in an investigation of the change in the band-gap width in the case of the substitution of Zn atoms by Cd atoms in the ZnO matrix in ZnCdO ternary structures. The presented investigations showed that a substitution of Zn atom to Cd (5.5, 11, 16.7, 22 and 33 at.% Cd) leads to reduction of cluster stability and monotonous decrease of energy gap (0.145, 0.259, 0.354, 0.436, 0.586 eV, accordingly).

1. Introduction

In recent years, investigations of the structure, electric properties, and optical properties of semiconducting nanostructures based on ZnO are being intensively performed. There is a large number of papers on ZnO nanoclusters. Some of them, e.g. [1] has above 800 citations. Low-dimensional materials have aroused great scientific interest due to their promising applications in photocatalysis and nanoscale optoelectronic devices. In particular, ZnCdO ternary alloys have been attracting growing attention due to their tunable band-gap. Despite much progress in the synthesis technology of thin films and nanostructures based on ZnO, the controlled change in the energy-band structure, the problem of the controlled change in the energy-band structure and implantation of defects into these materials remains incompletely solved [2–4]. Using the models of fullerene-like atomic clusters based on ZnO for the solution of problem of band-gap engineering of nanomaterials based on ZnO was proposed [5, 6]. Previously the dependences of electronic structure of Zn_nO_n fullerene-like and wurtzitic-like clusters on the amount of atoms in cluster and their geometry were investigated. To determine the size dependence of the stability of the fullerene-like based on ZnO cluster, a relative evaluation of the stability of the fullerene-like cluster $(ZnO)_n$ ($n = 12, 36, 48, 60$) was performed. The model of fullerene-like $Zn_{60}O_{60}$ cluster with the shell of diamond-like structure and sp^2/sp^3 type of bonds has been constructed.

Model of the fullerene-like $Zn_{24}Cd_{12}O_{36}$ cluster (33 at.% Cd) with sp^2 bonds and fullerene-like $Zn_{48}Cd_{12}O_{60}$ (20 at.% Cd) cluster with the shell of diamond-like structure and sp^2/sp^3 type of bonds was proposed for investigations of the influence of the cad-

mium impurity in the ZnO matrix on the geometric structure, cohesive properties, electronic structure and band-gap width of ZnCdO ternary alloys [5, 6]. Ab initio calculations showed that cadmium incorporation (33%) into ZnO matrix of the fullerene-like $(ZnO)_{36}$ cluster with sp^2 bonds and (20 at.% Cd) into ZnO matrix of the fullerene-like $(ZnO)_{60}$ cluster with sp^2/sp^3 type of bonds leads to a decrease in the energy gap by 0.58 eV and 0.2 eV accordingly.

The aim of the present work is investigation of the influence of the cadmium impurity in the ZnO matrix on the geometric structure, cohesive properties, electronic structure and band-gap width of ZnCdO ternary alloys using $Zn_{36-x}Cd_xO_{36}$ clusters with sp^2 bonds.

2. Construction of the model and computational technique

The structural, cohesive, and electronic properties of fullerene-like clusters Zn_nO_n ($n = 12, 36, 48, 60$) proposed in [5, 6] were investigated for determine of the base model for investigation of the influence of the cadmium impurity in the ZnO matrix on the electronic structure and band-gap width of ZnCdO ternary alloys.

Calculations were performed within the framework of the B3LYP electron density hybrid functional method with 6-31G(d) basis set. The cohesive energy per ZnO unit (ZnO atomic pair) was computed as a difference between the total energy of the cluster and the total energy of non-interacting constituent atoms without regard for the energy of zero vibrations divided by the number of ZnO atomic pair in the cluster.

The calculations showed that in the set of investigated clusters there exists growing to stability (cohesive energy per ZnO atomic pair) and reduction of band-gap width with increase of a size of a cluster (Fig. 1). The apparent non-monotonicity of the energy gap of the investigated clusters exists, too. Although no clear trend to reduce of the band-gap with increasing cluster size is observed, the value of the band-gap energy for all clusters does

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*e-mail: avilon57@ukr.net

not only depend on the size of the cluster; it can be influenced by other factors such as cluster's geometry [7]. Data of the analysis for $Zn_{36}O_{36}$ and $Zn_{48}O_{48}$ clusters showed that these clusters both can be equivalently used as models for studies of the influence of Cd insert into $Zn_{n-x}Cd_xO_n$ cluster shell on its electronic features.
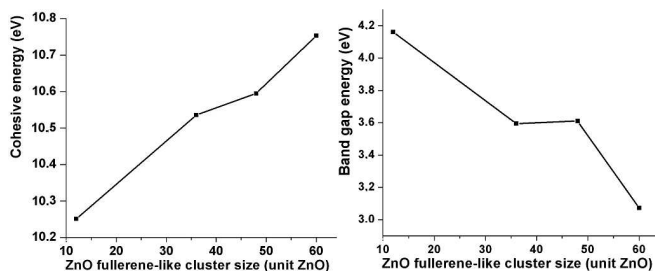

Fig. 1. The dependence of cohesive energy and band gap energy of the $(ZnO)_n$ clusters ($n = 12, 36, 48, 60$) from cluster size (number n of ZnO structural units — ZnO atomic pair in cluster).

The fullerene-like $Zn_{36}O_{36}$ cluster was determine for investigation of the influence of the cadmium impurity in the ZnO matrix on electronic structure and band-gap width of ZnCdO ternary alloys for spare computing resource.

The models of fullerene-like $Zn_{36}O_{36}$, $Zn_{34}Cd_2O_{36}$, $Zn_{32}Cd_4O_{36}$, $Zn_{30}Cd_6O_{36}$, $Zn_{28}Cd_8O_{36}$, $Zn_{24}Cd_{12}O_{36}$ clusters with contents of the cadmium impurity 0; 5.5, 11, 16.7, 22, 33 at.% with sp^2 type of bonds has been constructed (Fig. 2).
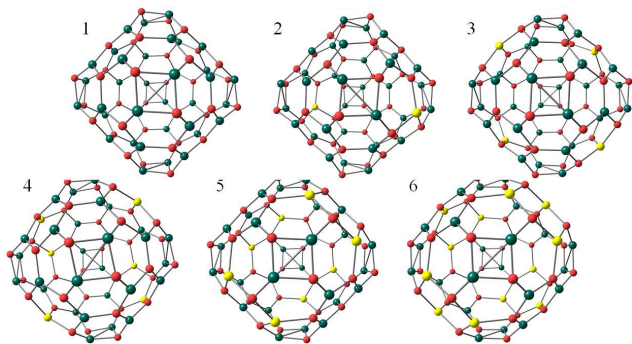

Fig. 2. Optimized geometries of clusters: (1) $Zn_{36}O_{36}$, (2) $Zn_{34}Cd_2O_{36}$, (3) $Zn_{32}Cd_4O_{36}$, (4) $Zn_{30}Cd_6O_{36}$, (5) $Zn_{28}Cd_8O_{36}$, (6) $Zn_{24}Cd_{12}O_{36}$, yellow ball — Cd, green ball — Zn, red ball — O.

The optimized geometry, total energy and band-gap width of the clusters were determined within the framework of the B3LYP electron density hybrid functional method (in which the exchange energy is calculated by using a result obtained by the Hartree–Fock method) with 3-21G(d) basis sets. The geometry was optimized by the method of gradient descent (also known as "steepest descent"). The cohesive energy was computed as a

difference between the total energy of the cluster and the total energy of noninteracting constituent atoms without regard for the energy of zero vibrations. In calculations, we used a complex of GAMESS'09 programs [8], ChemCraft and Molekel 5.4 programs for visualization of computed results [9].

3. Results and analysis

The results of the computing experiment are the optimized geometries (Fig. 2) and electronic structures of the investigated clusters. The energy characteristics (cohesive energy, energy band gap) of the $Zn_{36-x}Cd_xO_{36}$ clusters with growing Cd content are presented in Table and Fig. 3. Molecular orbitals diagrams of the investigated clusters within the range of energy $-14 \div 0$ eV are presented in Fig. 4.

TABLE I

Energy characteristics of $Zn_{36-x}Cd_xO_{36}$ clusters: at.% Cd – contents atomic percent of Cd, E_c - cohesive energy, E_g - energy band gap, Δ - difference to band gap energy between ZnO and Zn(Cd)O clusters.

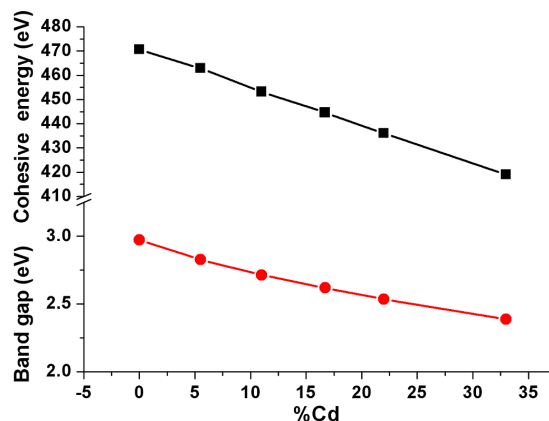| Cluster	at.% Cd	E_c [eV]	E_g [eV]	Δ [eV]
$Zn_{36}O_{36}$	0	470,615	2,972	
$Zn_{34}Cd_2O_{36}$	5,5	462,857	2,827	0,145
$Zn_{32}Cd_4O_{36}$	11	453,180	2,713	0,259
$Zn_{30}Cd_6O_{36}$	16,7	444,593	2,618	0,354
$Zn_{28}Cd_8O_{36}$	22	436,017	2,536	0,436
$Zn_{24}Cd_{12}O_{36}$	33	419,036	2,386	0,586

Fig. 3. The dependence of cohesive energy and band-gap width on Cd content in the cluster.

The results of calculations for clusters with 5.5, 11, 16.7, 22, and 33 at.% Cd content showed that a substitution of Zn atoms by Cd ones leads to changing of bond lengths, valence angles, redistribution of ions charges and, consequently, gives rise to the reduction of the cluster stability (cohesive energy) with an increase of Cd content.
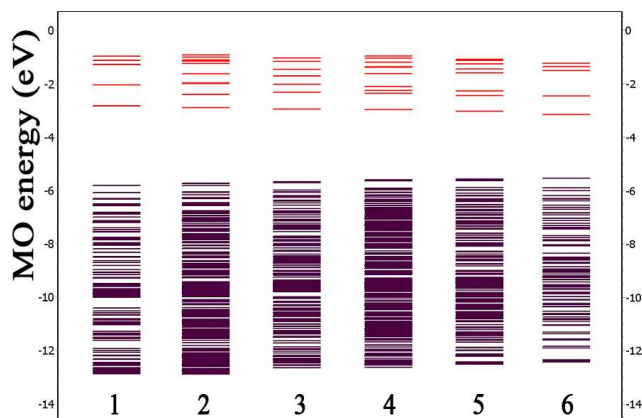
Fig. 4. Molecular orbital diagrams (within the range of energy $-14 \div 0$ eV) of the clusters: (1) $Zn_{36}O_{36}$, (2) $Zn_{34}Cd_2O_{36}$, (3) $Zn_{32}Cd_4O_{36}$, (4) $Zn_{30}Cd_6O_{36}$, (5) $Zn_{28}Cd_8O_{36}$, (6) $Zn_{24}Cd_{12}O_{36}$.

It was also revealed the monotonically decrease of the energy gap with enhancement of the Cd content on 0.145, 0.259, 0.354, 0.436, 0.586 eV, accordingly. In work [10] authors have investigated the electrical and optical properties of the n-$Zn_{0.94}Cd_{0.06}O/p$-SiC heterostructures. It was revealed that the calculated band-gap energy (2.827 eV) for $Zn_{34}Cd_2O_{36}$ cluster (≈ 6 at.% Cd) is very close to the experimental value of the band-gap (2.87 eV) for $Zn_{0.94}Cd_{0.06}O$ films grown by rf magnetron sputtering technique.

Analysis of the molecular orbital diagram shows that the Cd related levels emerge in the bandgap. Additionally, the electronic spectrum is smearing in consequence of lowering cluster's symmetry. The electronic spectrum is the set of discrete levels for the most symmetric $Zn_{36}O_{36}$ and $Zn_{24}Cd_{12}O_{36}$ clusters (symmetry T_d) in consequence of degeneracy of the molecular orbital. The substitution of Zn atom to Cd leads to lowering of symmetry in clusters: $Zn_{34}Cd_2O_{36}$ (symmetry C_2), $Zn_{32}Cd_4O_{36}$ (symmetry D_{2d}), $Zn_{30}Cd_6O_{36}$ (symmetry C_2), $Zn_{28}Cd_8O_{36}$ (symmetry D_{2d}) and lowering of degree of degeneracy and levels splitting.

4. Conclusions

Model of the fullerene-like $Zn_{36-x}Cd_xO_{36}$ cluster with sp^2 bonds was proposed for investigations of the influence of the cadmium impurity into the ZnO matrix on the electronic structure and band-gap width of ZnCdO ternary alloys.

The results of the size effect investigation for Zn_nO_n clusters showed that $Zn_{36}O_{36}$ and $Zn_{48}O_{48}$ clusters can be equivalently used as models for studies of the influence of the Cd inserted in cluster shell on their electronic features.

The presented investigations showed that a substitution of Zn atom to Cd leads to reduction of cluster stability and monotonous decrease of energy gap with growing Cd content.

The presented investigation and its development can be used for the directed synthesis of new promising ZnO-based materials with a required band gap width.

Acknowledgments

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