Properties of ZnO and Zn(Cd)O Fullerene-Like Clusters with a Shell of Diamond-Like Structure with sp^2/sp^3 Bonds

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The structural, cohesive, and electronic properties of a fullerene-like $(ZnO)_{60}$ cluster with a shell of diamond-like structure with sp^2/sp^3 bonds have been investigated in comparison with those of clusters differing in geometry and composed of the equal number of ZnO structural units (clusters of fullerene, onion, and coordination tetrahedron) within the framework of the electron density hybride functional method (B3LYP) with a set of 6-31G(d) split valence basis functions. The fullerene-like $(ZnO)_{60}$ cluster is used as a model in an investigation of the change in the band-gap width (the decrease in the band-gap width is ≈ 0.2 eV) in the case of the substitution of Zn atoms by Cd atoms (20% of substitution) in the ZnO matrix in ZnCdO ternary structures.

1. Introduction

In recent years, investigations of the structure, electric properties, and optical properties of semiconducting nanostructures based on A^2B^6 oxides are being intensively performed owing to the fact that these nanostructures offer many possibilities of developing new nanosized electronic and optoelectronic devices. The abundance in nature, low cost, and combination of high optical and piezoelectric properties of zinc oxide ZnO, which is a representative of A^2B^6 oxides, determine its prospects for the development of new nanoelectronic and nanooptoelectronic devices. ZnO is a direct gap semiconductor with a wurtzite structure with a band-gap width of ≈ 3.37 eV at room temperature. The large bond energy of a ZnO exciton (63 meV), low threshold power during optical pumping, and the possibility of changing the band-gap width in alloying enable us to think that ZnO is a promising material for the development of new light-emitting and laser structures of the ultraviolet region.

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 remain incompletely solved [1–3]. Difficulties also arise in the stage of diagnostics of synthesized specimens, especially in the case where nanoclusters form inside an investigated specimen. Experimental methods supplemented by theoretical modeling and by the application of methods of computational physics make it possible to find the unambiguous correspondence between experimentally observed optical, electronic, magnetic properties of the substance and its nanosized structure, which will enable one to reduce substantially the cost of the development of semiconductor materials with new operating properties and the cost

of all the stages preceding the commercialization of their manufacturing technology.

To study the above-listed effects by quantum-chemical methods, proposed to use models of fullerene-like clusters based on ZnO. Earlier, there was shown that $A^{IV}B^{IV}$, $A^{III}B^V$, and $A^{II}B^{VI}$ semiconductor compounds, including ZnO, are susceptible to formation of fullerene-like clusters [4]. For these structures, the cohesive energy is smaller than that for the main structure of ZnO and rises as the number of atoms in the cluster increases. The band-gap width also depends on the cluster size and can be controlled by other factors, in particular, by the geometry of the cluster [5, 6]. For $Zn_{n-x}Cd_xO_n$ ternary alloys, on a model of the $(ZnO)_{36}$ fullerene-like cluster with sp^2-bonds, within the framework of the B3LYP/3-21G(d) method, it was shown earlier that the substitution of 12 Zn atoms by 12 Cd atoms in the ZnO matrix (33% substitution) led to a decrease in the band-gap width by 0.58 eV [7]. For the investigation of substitution processes in structures with sp^3-bonds, a model of a $(ZnO)_{60}$ cluster with a mixed sp^2/sp^3 type of bonds was developed [7].

The aim of the present work is to study the structural, cohesive, and electronic properties of the $(ZnO)_{60}$ atomic cluster with a mixed sp^2/sp^3 type of bonds in comparison with those of clusters composed of the equal number of ZnO structural units, but differing in geometry and investigate changes in the electronic structure in the case where Zn atoms in sp^3-positions in the shell of the cluster are substituted by Cd atoms in order to extend the results of the investigation to $Zn_{n-x}Cd_xO_n$ solid-state structures.

2. Construction of the model and computational technique

To determine the dependence of the electronic structure of fullerene-like ZnO clusters on their geometry, a comparative evaluation of the stability of fullerene-

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-like $Zn_{60}O_{60}$ clusters with configurations of fullerene, onion, a diamond-like particle with a mixed sp^2/sp^3 type of bonds, and coordination tetrahedron was performed (Fig. 1).
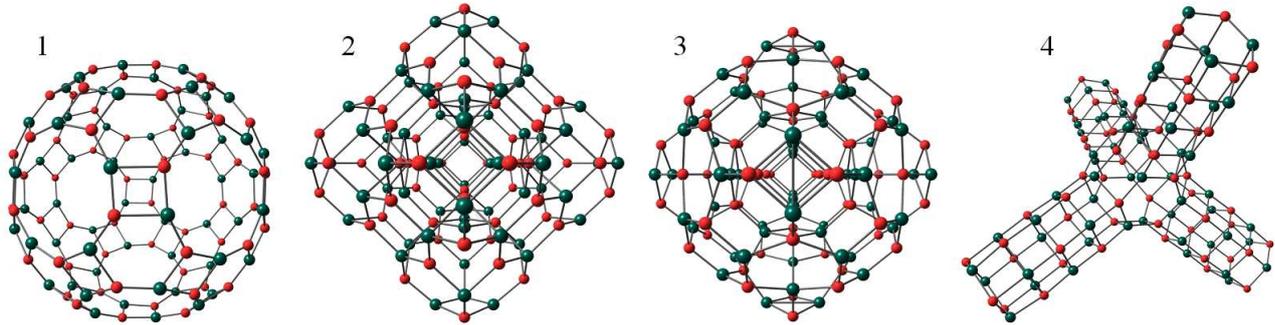

Fig. 1. Optimized geometries of clusters: (1) $Zn_{60}O_{60}$ fullerene, (2) $Zn_{12}O_{12}@Zn_{48}O_{48}$ onion, (3) $Zn_{60}O_{60}$ particle with mixed sp^2/sp^3 bonds, (4) $(Zn_{12}O_{12})_5$ coordination tetrahedron.

The $Zn_{60}O_{60}$ cluster with a fullerene-like morphology and symmetry T, consists of 30 square, 20 hexagonal, and 12 ten-member rings. The $ZnO_{12}@ZnO_{48}$ onion consists of two fullerene-like layers, namely, a $(ZnO)_{12}$ internal layer of symmetry T_h formed by 6 squares and 8 hexagons and $(ZnO)_{48}$ external layer of symmetry T_h formed by 6 squares and 40 hexagons. The model of a fullerene-like $(ZnO)_{60}$ particle with a shell of diamond-like structure with mixed sp^2/sp^3 bonds was described earlier [7]; among 120 atoms of its structure, 48 internal atoms are bound by sp^3 bonds, and 72 surface atoms are bound by sp^2 bonds (the ratio of the number of atoms with sp^3 bonds to the number of atoms with sp^2 bonds is 48/72). The model of the coordination tetrahedron was constructed from five fullerene-like $Zn_{12}O_{12}$ structural units of symmetries T_h bound along the perimeters of hexagons in such a way as to provide the alternation of the positions of zinc and oxygen atoms.

The optimized geometry, total energy, cohesive 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) and 6-31G(d) basis sets. The geometry was optimized by the method of gradient descent. The cohesive energy per ZnO unit 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 divided by the number of ZnO units in the cluster. 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 and electronic structures of the investigated clusters. The energy characteristics of the $(ZnO)_{60}$ structures are presented in Table.

TABLE

Energy characteristics of $(ZnO)_{60}$ structures: total energy per ZnO atomic per, cohesive energy per ZnO atomic pair, energy band gap.

Cluster	$-E_{total}/ZnO$ [eV]	E_c/ZnO [eV]	E_g [eV]
$Zn_{60}O_{60}$ (fullerene)	50457.985	10.432	4.106
$ZnO_{12}@ZnO_{48}$ (onion)	50458.373	10.821	3.72
$Zn_{60}O_{60}$ (with sp^2/sp^3 bonds)	50458.306	10.753	3.072
$(Zn_{12}O_{12})\times5$ (tetrahedron)	50458.028	10.474	3.513

The calculations showed that, among the investigated structures, the cluster of onion structure has the largest stability ($E_c = 10.821$ eV per ZnO atomic per), and the particle with a mixed sp^2/sp^3 type of bonds has a somewhat smaller stability ($E_c = 10.753$ eV per ZnO atomic per). The transition of bonds of some atoms from the sp^2 to the sp^3 configuration and vice versa influences the optimization process of the $Zn_{60}O_{60}$ cluster (with sp^2/sp^3 bonds) and $ZnO_{12}@ZnO_{48}$ (onion) cluster. An analysis of the values of the energy band gap indicates that the electronic characteristics of the fullerene-like $Zn_{60}O_{60}$ cluster with a shell of diamond-like structure with sp^2/sp^3 bonds ($E_g = 3.072$ eV) are the closest to those of solid-state ZnO ($E_g = 3.37$ eV). Note that the calculated value 3.072 eV is somewhat lower than the true value because of the characteristic features of the used computing method.

To investigate the influence on the electronic structure of the $Zn_{60}O_{60}$ clusters (with sp^2/sp^3 bonds) of the cadmium additive, 12 zinc atoms in sp^3-positions in the cluster shell were replaced by Cd atoms (20% substitution). The additive atoms are uniformly distributed over the cluster shell, and Cd–O pairs do not neighbor each other (Fig. 2).

Calculations performed within the framework of the D3LYP electron density hybrid functional method with
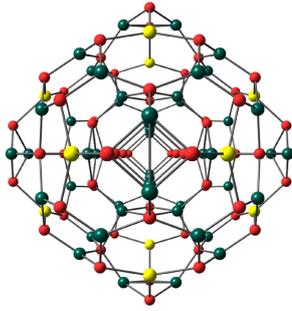
Fig. 2. Optimized geometry of the fullerene-like $Zn_{48}Cd_{12}O_{60}$ atomic cluster (20% cadmium additive); yellow ● — Cd, green ● — Zn, red ● — O.

the 3-21G(d) basis set showed that the substitution of 20% of zinc atoms by cadmium atoms led to a decrease in the band gap by 0.2 eV for the $Zn_{48}Cd_{12}O_{60}$ cluster as compared with that for $Zn_{60}O_{60}$. For the $Zn_{48}Cd_{12}O_{60}$ cluster, we obtained a band-gap width of ≈ 2.6 eV, which agrees with the data of [2].

4. Conclusions

We propose a model of a fullerene-like $Zn_{60}O_{60}$ cluster with a shell of diamond-like structure with sp^2/sp^3 bonds for the investigation of the influence of additives in ZnO-based solid-state structures on their electronic characteristics and, in particular, the influence of a cadmium additive in the ZnO matrix on the electronic structure and band-gap width of ZnCdO ternary alloys.

The results of calculations of the band-gap widths of the investigated clusters composed of the equal number of ZnO structural units but differing in cluster geometry indicate that the band-gap width of the $Zn_{60}O_{60}$ fullerene-like cluster with a shell of diamond-like structure with sp^2/sp^3 bonds is the closest to that of solid-state ZnO (≈ 3.1 eV).

The calculations showed that, as a result of the implantation of cadmium (20%) into the ZnO matrix of the $(ZnO)_{60}$ fullerene-like cluster, the band gap energy decreases down to ≈ 2.6 eV, i.e., by ≈ 0.2 eV.

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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