

Study of the Clusterization of CdO Phase in ZnCdO Alloys by Modeling Fullerene-Like $Zn_{44}Cd_4O_{48}$ Cluster

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The structural, cohesive and electronic properties of fullerene-like isolated $Zn_{44}Cd_4O_{48}$ cluster with consideration of CdO phase clusterization are studied in the frames of density functional theory B3LYP/3-21G(d). It is revealed that an enlargement of CdO phase content in $Zn_{44}Cd_4O_{48}$ cluster leads to nonlinear rapid increase in cohesive energy and cluster stability, as well as band-gap energy shrinkage.

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1. Introduction

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 of the significant progress in the growth technologies for ZnO-based thin films and nanostructures, the problems of the controllable change of a band structure and an introduction of defects in these materials are still unsolved [1–3]. In particular, the main bottleneck is associated with the characterization of the prepared samples, especially in the case of nanoclusters formation inside the material. Experimental studies supplemented by theoretical modeling allow to find out a correlation between optical, electronic and magnetic properties on one side and nanoscale structure of the semiconductor materials on the other side. Such complementary approach gives a possibility to reduce the cost of fabrication of materials with new performance characteristics.

Earlier, it was reported the possibility of implementing the first-principles quantum chemical methods in calculation of the band-gap energy of the isolated Cd-containing ZnO atomic clusters [4–6]. It was demonstrated that the size increase of fullerene-like Zn_nO_n cluster (where $n = 12, 36, 48, 60$) causes the improvement of its stability (increase in the cohesive energy) and band-gap energy shrinkage. The further study of Zn-by-Cd substitution effect on the electronic properties of $Zn_{n-x}Cd_xO_n$ clusters in the frames of DFT with B3LYP approach and basis functions 3-21G(d) revealed that the increase in Cd content leads to lowering the cluster stability and monotonic decrease of the band-gap energy.

In this work, the model of the fullerene-like $Zn_{44}Cd_4O_{48}$ cluster with sp^2 bonds (8.33 at.% Cd) is proposed for investigation of the effect of the clusteriza-

tion of CdO phase in ZnCdO on the stability, electronic structure and band-gap energy of ZnCdO ternary alloys.

2. Model construction and theoretical framework

A basis structure for investigation of CdO phase clusterization was chosen in manner similar to that in our previous work [6], where isolated fullerene-like $Zn_{36}O_{36}$ cluster with Zn atoms substituted by Cd ones was used for study Cd doping effect on electronic structure and band-gap energy of ZnCdO ternary alloys. It should be mentioned that the results of calculation for $Zn_{n-x}Cd_xO_n$ clusters ($n = 2, 4, 6, 8, 12$) with Cd content of 5.5, 11, 16.7, 22 and 33 at.%, respectively, showed that the calculated band-gap energy (2.827 eV) for $Zn_{34}Cd_2O_{36}$ cluster (with ≈ 6 at.% Cd) is in agreement with experimental value of E_g (2.87 eV) for $Zn_{0.94}Cd_{0.06}O$ films grown by dc magnetron sputtering [7]. Therefore, we investigated the CdO phase clusterization in ZnCdO alloys within the Cd content range not exceeding 6 at.% using the cluster model with the size larger than that of the conventional $Zn_{36}O_{36}$ cluster.

Earlier, within the framework of density functional theory (hybrid B3LYP functional) with basis set 6-31G(d) it was shown that both $Zn_{36}O_{36}$ and $Zn_{48}O_{48}$ clusters could be used as models for investigation of the Cd doping effect on the electronic properties of $Zn_{n-x}Cd_xO_n$ clusters. Results of computation presented in Ref. [6] confirm the preliminary prediction of the stability improvement (increase in cohesive energy) and band gap energy shrinkage with increase in the cluster size (see Fig. 1) [4], although no clear trend to reduce of the band-gap with increase in cluster size is observed. The value of the band-gap energy for all clusters does not only depend on the size of the cluster. It can be affected by other factors such as cluster's geometry [8].

Fullerene-like isolated $Zn_{44}Cd_4O_{48}$ cluster with four Cd atoms (8.33 at.% Cd) was chosen for modeling the CdO phase clusterization in ZnCdO.

Three cases of distribution of Cd–O atomic pairs in cluster were studied (Fig. 2). In the first case, the cluster

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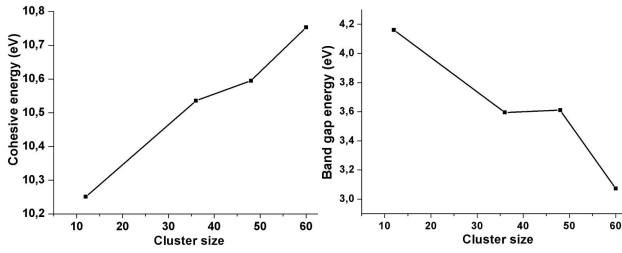


Fig. 1. The dependence of cohesive energy and band gap energy of the $(\text{ZnO})_n$ clusters ($n = 12, 36, 48, 60$) on cluster size.

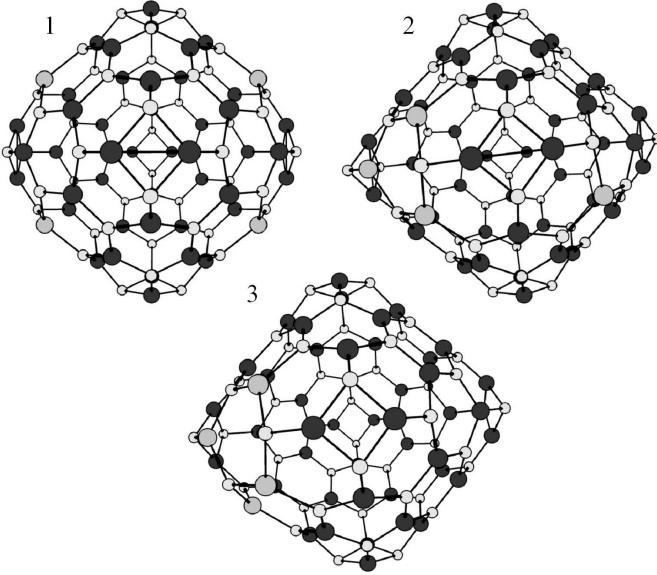


Fig. 2. Optimized geometry of the $\text{Zn}_{44}\text{Cd}_4\text{O}_{48}$ clusters with different degree of clusterization of CdO phase: Cd–O atomic pairs are not merged (1), three Cd–O atomic pairs are combined in clusters (2), four Cd–O atomic pairs are grouped together (3); gray ball — Cd, black ball — Zn; white ball — O.

has four regions, where Cd–O pairs are not adjacent to each other. In the second case, three Cd–O pairs are merged in cluster. In the last case, all four Cd–O pairs are grouped together.

Optimized geometry, the total energy and band-gap energy of the clusters were determined using the hybrid B3LYP functional with basis set 3-21G(d). The cohesive energy was calculated as the difference between the total energy of the cluster and the total energy of its constituent non-interacting atoms without regard for the energy of zero vibrations.

GAMESS'09 [9], ChemCraft and Molekel 5.4 [10] programs were used for computations.

3. Results and discussion

As a result of computation procedure, the potential energy surface scan was performed and optimized geometry and electronic structure of the clusters were deter-

mined. The minima of the potential energy surface suggest that optimized geometry is stable and the isolated Cd-containing fullerene-like ZnO cluster is formed. Energetic parameters of the (cohesive energy, band gap energy) $\text{Zn}_{44}\text{Cd}_4\text{O}_{48}$ clusters are presented in Table I and Fig. 3.

TABLE I

Energetic parameters in [eV] of $\text{Zn}_{44}\text{Cd}_4\text{O}_{48}$ clusters for different distributions of CdO atomic pairs: E_{tot} is the total energy, E_c is the cohesive energy of cluster, E_e/CdO is the cohesive energy increase per one Cd–O pair, E_g is the band gap energy.

$-E_{\text{tot}}$	E_c	E_e/CdO	E_g
CdO+CdO+CdO+CdO			
2810273.558	613.382	–	2.819
(CdO)•3+CdO			
810273.633	613.456	0.0371	2.688
(CdO)•4			
2810273.707	613.530	0.074	2.582

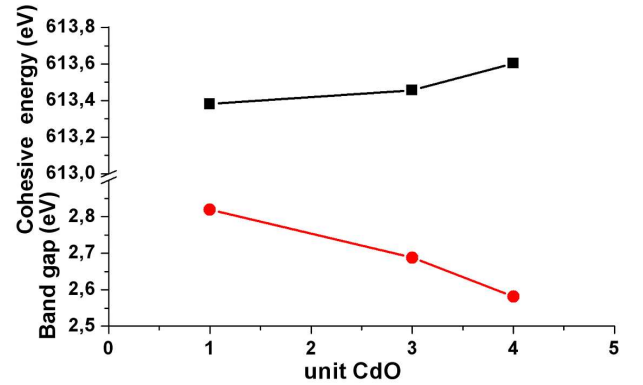


Fig. 3. Dependence of the cohesive energy and band-gap energy of $\text{Zn}_{44}\text{Cd}_4\text{O}_{48}$ cluster on the number of combined Cd–O atomic pairs.

Non-monotonic increase of the cohesive energy of the $\text{Zn}_{44}\text{Cd}_4\text{O}_{48}$ cluster with increase in a degree of the clusterization of CdO phase is observed. When three Cd–O pairs are grouped together the cohesive energy of the $\text{Zn}_{44}\text{Cd}_4\text{O}_{48}$ cluster increases by 0.07414 eV. That is, the clusterization energy is equal to 0.037 eV per one Cd–O pair. Adding to the previous CdO cluster the fourth Cd–O pair leads to an enhancement of the cohesive energy of $\text{Zn}_{44}\text{Cd}_4\text{O}_{48}$ cluster on 0.074 eV (it is equal to clusterization energy of fourth Cd–O pair). A reduction in band-gap energy from 2.82 eV (Fig. 2(1)) to 2.69 eV (Fig. 2(2)) and to 2.58 eV (Fig. 2(3)) with increase in the degree of clusterization were revealed.

The revealed phenomenon of the ZnCdO alloys transition to more stable at nonhomogeneous distribution of Cd in ZnO is the analogue of spinodal decomposition. In Ref. [11] it was demonstrated that in ZnCdO alloys the isovalent Cd component nonhomogeneous distribu-

tion is energetically beneficial. As a result the attempts of formation of ZnO–CdO solid solution meet with great difficulties. In particular, the low solubility of Cd in ZnO matrix is frequently observed experimentally. Such phenomena significantly influence on the optical properties (the Raman scattering, photoluminescence etc.) of the ZnCdO ternary alloys.

Thus cluster approach for evaluation the energetic characteristics of ZnCdO alloys is useful for understanding spinodal decomposition phenomena on nanoscale level.

4. Conclusions

The model of fullerene-like $Zn_{44}Cd_4O_{48}$ cluster with sp^2 bonds was implemented for study of the effect of CdO phase clusterization in ZnCd alloy on the stability, electronic structure and band gap energy of ZnCdO ternary alloys.

A possibility of formation of fullerene-like Cd-containing ZnO clusters was shown.

It was revealed that the increase in the contribution of CdO phase to $Zn_{44}Cd_4O_{48}$ cluster leads to nonlinear rapid increase in cohesive energy and cluster stability followed by band-gap energy shrinkage.

The present study and its further development may be used for the prediction and analysis of spinodal decomposition in ZnCdO ternary alloys and controllable synthesis of promising new ZnO-based materials with variable band gap energy.

Acknowledgments

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