

L.I. Ovsiannikova, G.V. Lashkarev, V.V. Kartuzov, D.V. Myroniuk,
M.V. Dranchuk, A.I. Ievtushenko

The Study of the Behavior of Al Impurity in ZnO Lattice by a Fullerene Like Model

Frantsevich Institute for Problems of Materials Science, NASU, Kyiv, Ukraine, earsen@ukr.net

The fullerene like $Zn_{32}Al_4O_{36}$ clusters were investigated and the oxygen interstitial O_i acceptor intrinsic defect formation energy as well as Al ionization energy were calculated. The effect of lattice packing defects on the electroactivity of Al impurity in ZnO was investigated. Analysis of the defects formation energies shows the smaller formation energy of interstitial O_i in a comparison with a formation of Zn vacancy. This allows us to formulate recommendations of technological conditions for films deposition, with improved electroactivity of Al donor.

Keywords: fullerene like model; zinc oxide; Al ionization energy; native defects formation energies; ZnO packing defects.

Received 5 March 2021; Accepted 5 April 2021.

Introduction

For the development of deposition technology and for control the properties of ZnO films doped by Al or other donor impurities as well as for their applications in photovoltaic and optoelectronic devices, the minimization of donor impurities compensation by native acceptor defects (V_{Zn} , O_i etc.) is strongly required. An exponential dependence of defects concentration on their formation energy results in the situation when almost only defects with minimal energy are presented in any semiconducting material. For determination the thermodynamic properties of defects we started series of computational experiments.

The effectivity of semiconductor doping by donor impurity (for example Al in ZnO) is determined by its electroactivity (EA). The electroactivity means the number of conductivity electrons which donor impurity atom delivers to conduction band (1 electron in the case of Al doped ZnO means $EA = 1$). The real Al electroactivity in ZnO lower than 1, because of different reasons. The main of them is aluminum compensation by acceptor native defects: zinc vacancies (V_{Zn}) or oxygen interstitials (O_i) [1].

The purpose of this article is the determination of the

influence of the intrinsic O_i defects and packing defects of ZnO on the Al electroactivity in the ZnO lattice using a fullerene-like model i.e. FL $Zn_{36}O_{36}$ cluster. The choice of such cluster as a model for *ab initio* quantum chemical study is due to the fact that isolated $(ZnO)_n$ clusters exist really and have been synthesized experimentally [2].

The information about formation of isolated clusters $(ZnO)_n$, where $n = 1 - 100$, was published in [2, 3]. The authors reported that zinc oxide clusters have been processed by laser ablation of zinc peroxide in vacuum and investigated by time-of-flight (TOF) mass spectroscopy. Experimental results revealed unpredicted and hitherto unknown $(ZnO)_n$ clusters of enhanced stability (“magic clusters”). Cage-like structures for the magic clusters have been suggested and supported by first-principles calculations.

We fulfilled our own *ab initio* study of a number of $(ZnO)_n$ clusters [4] and came to the decision that the most suitable for investigating behavior of the impurity in ZnO lattice are clusters $Zn_{36}O_{36}$ and $Zn_{48}O_{48}$ because of their stability and high symmetry, which leads to saving of computation resources.

We successfully used fullerene like (FL) cluster model earlier for a solution of band engineering problems in $Zn_{1-x}Cd_xO$ alloys and precipitation of CdO phase in

these alloys (spinodal decomposition) [4-7]. The investigations showed that a substitution of Zn atoms by Cd ones [7] leads to the reduction of cluster stability and monotonous decrease of energy gap with growing Cd content. The CdO phase inclusion to FL $Zn_{44}Cd_4O_{48}$ cluster leads to non-monotonic rapid increase of cohesive energy i.e. cluster stability followed by band-gap energy shrinkage. The energy advantage belongs to a cluster with a nonhomogeneous distribution of Cd impurity.

I. Model and computation technique

As the basis of the model, an isolated FL $Zn_{32}Al_4O_{36}$ cluster was chosen to study its cohesive and electronic properties with different distribution of Al-O pairs [2, 8], the defect formation energies of V_{Zn} [8], effect of intrinsic O_i defects [1], and packing defects on the electroactivity of the Al impurity in the ZnO lattice. Qualitative results for the behavior of Al impurity in FL cluster based on ZnO were obtained [8]. Al impurity tends to homogeneous distribution in such cluster. Analysis of the defects formation energies shows the smaller formation energy of

interstitial O_i in a comparison with a formation of Zn vacancy. The FL $Zn_{36}O_{36}$ cluster was investigated also to study packing defects in the ZnO lattice.

Geometrically, the $Zn_{36}O_{36}$ cluster is a polyhedron with 72 vertexes, which is restricted by 6 square and 32 hexagonal facets, at the vertexes of which Zn and O atoms are located. Each Zn atom is surrounded by 3 O atoms and vice versa. As a macromolecule, the $Zn_{36}O_{36}$ cluster is a single-layer hexagonal ZnO plane folded into the sphere, which consists of 6-membered Zn-O rings. The folding of the ZnO plane into the sphere occurs as a result of the replacement of a series of 6-membered rings by 4-membered rings. Four-membered rings provide the convolution of the ZnO plane into a sphere, similar to the case when 5-membered rings ensure the convolution of the graphene plane into fullerene. As a result, the $Zn_{36}O_{36}$ FL cluster consists of six 4-membered rings and thirty two 6-membered Zn-O rings. Four-membered rings are centers of structural stresses in the $Zn_{36}O_{36}$ cluster, because of distortions of the electron population on atoms, valence angles and the length of the interatomic bond Zn-O in them (Tab. 1, Fig. 1).

In this paper, we consider the 4-membered ring in

Table 1

Characteristics of $Zn_{36}O_{36}$ cluster: Bond Zn-O is the length of interatomic Zn-O bond, Angles are valence angles, Mull.pop. is the number of electrons on atoms by Mulliken* in electron amount (calculated in approximation B3LYP/6-31d).

Ring type	Bond Zn-O length (Å)	Angles O-Zn-O (deg)	Angles Zn-O-Zn (deg)	Mull.pop. on Zn (e)	Mull.pop. on O (e)
6-membered	1.88	115.55	119.7	29.08;	8.99
4-membered	1.94	89.4	89.97	29.05	8.94
6-membered adjacent to the 4-membered	1.88 - 1.89	124.77	114.02	29.03	8.99

* The analysis of the electron populations of the orbitals according to Mulliken is a procedure for determining the electron charges of atoms in a molecule and the electron populations of the overlapping orbitals. It is performed by equal distribution of the overlap between two atomic orbitals of chemically bound atoms. The electron density associated with the diffuse orbital is attributed to the atom on which this orbital is centered. Electron population on Zn and O ions testifies to ionic-covalent bond in ZnO.

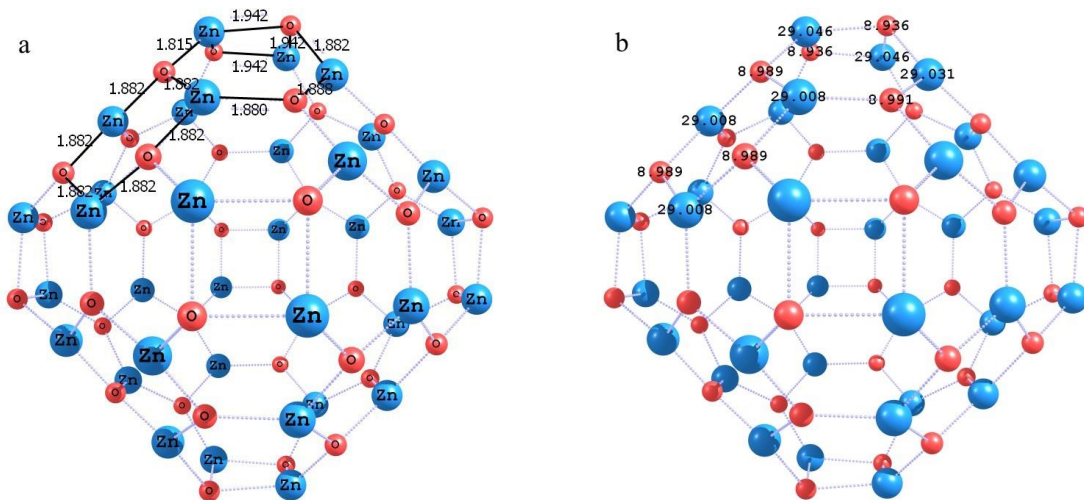


Fig. 1. The $Zn_{36}O_{36}$ cluster characteristics: a) lengths of interatomic bonds (Å), black color denotes the bonds in the 6- and 4-membered rings; b) electron populations on atoms.

cluster as a model of a local structural feature in the ZnO lattice similar to a partial dislocation (packing defect). The substitution of the Zn atom by the Al atom in the 4-membered ring we consider as a model for the replacement of Zn atoms by the Al impurity in the region of the packing defect in the ZnO lattice.

In this article the isolated FL $Zn_{32}Al_4O_{36}$ cluster was chosen to study the effect of intrinsic defects (O_i), and packing defects on the electroactivity of the Al impurity in the ZnO lattice. In this cluster four zero charged three-valent Al impurity atoms substitute four two-valent Zn atoms in cation sublattice of $Zn_{36}O_{36}$ cluster (Fig. 2).

The calculations of optimized geometry, full energy and electronic structure were fulfilled in the frames of electronic density functional theory with B3LYP hybrid functional (in which the exchange energy was calculated using the Hartree–Fock method) with the MINI [9] basis set. Inasmuch as the used computational resources were restricted only the relative data were calculated in this paper which magnitudes can be compared (larger–smaller). The cohesive energy of cluster was computed as a difference between the total energy of the cluster and the total energy of noninteracting constituent atoms without taking into account the energy of zero vibrations. The cohesive energy of FL $Zn_{32}Al_4O_{36}$ cluster is equal 208.8 eV.

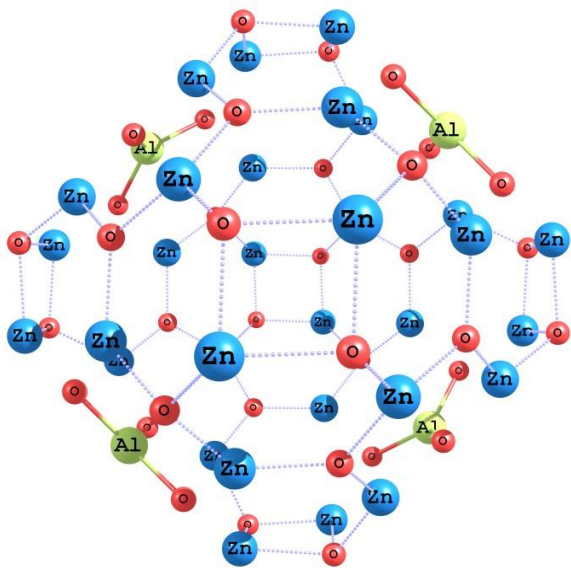


Fig. 2. Geometry of the FL $Zn_{32}Al_4O_{36}$ cluster with homogenous distribution of Al-O pairs; yellow ball – Al, blue ball – Zn, red ball – O.

At substituting Zn atoms by four Al atoms in $Zn_{36}O_{36}$ FL cluster with a formation of $Zn_{32}Al_4O_{36}$ the hybridized molecular levels associated with Al arise. The energy gap between the highest occupied level associated with Al (E_{HOMO}) and the lowest unoccupied level of the conduction band (E_{LUMO}) was evaluated as 0.71 eV. In this paper this energy gap we consider further within the terminology of semiconductor physics band structure as relative ionization energy of Al donor $E_i = 0.71$ eV.

At the application of calculation results obtained in the frames of cluster model to solid state it is necessary to take into account that energy gap E_g of solid state is

impossible to estimate at calculations of clusters containing several dozens of atoms. Only at the number of atoms aspiring to the infinity the magnitude of calculated energy gap will approach to experimental data [10]. The calculation method and the set of basic functions limit the accuracy for absolute magnitudes of energy parameters also. But for the comparison estimations for basic $Zn_{32}Al_4O_{36}$ FL cluster and studying clusters with different space distribution of Al which were fulfilled at similar conditions the satisfactory qualitative relative results may be obtained.

On the basis of the developed model the calculations of the following energy characteristics for the mentioned $Zn_{32}Al_4O_{36}$ FL clusters were performed: the most energy preferable Al impurity distribution; energies of zinc vacancy and oxygen interstitial formation, relative magnitudes of Al ionization energies.

GAMESS'09 [11], ChemCraft and Molekel 5.4 [12] programs were used for computations.

Table 2

Energy parameters of $Zn_{32}Al_4O_{36}$ clusters with different space distribution of Al: E_c - the cohesive energy of cluster; E_i - ionization energy of Al.

Variants	Position of Al	E_c (eV)	E_i (eV)
1	Al impurity atoms are located in the 4-membered ring	203.73	0.86
2	Al impurity atoms are located in the 6-membered ring	204.99	1.11

II. Results and discussion

2.1. The influence of the Al spatial distribution in the $Zn_{32}Al_4O_{36}$ cluster on its cohesive energy and the ionization energy of Al

The influence of packing defects in the ZnO crystal lattice on the electroactivity of the Al impurity was studied. The cohesion energy of clusters and the electroactivity of the Al impurity were calculated in the following cases: 1) the substitution of a Zn atom belonging to the 4-membered ring by an Al impurity; 2) the substitution of Zn atom belonging to the 6-membered ring by an Al impurity (Tab. 2). The arrangement of the Al atom in the 4-membered ring leads to a little bit smaller cohesion cluster energy and to significant decrease of the ionization energy of Al in comparison with the location in the 6-membered ring. Figure 3 shows electron density distribution on cluster atoms of the upper filled molecular orbital (HOMO).

It is seen from the Fig. 3 that the electron density is concentrated mainly on Al impurity atoms located in the 4-membered rings and in the neighboring 6-membered one.

As a result, an increase of the number of packing defects in the ZnO lattice leads to a decrease in cluster stability and an increase of the Al electroactivity.

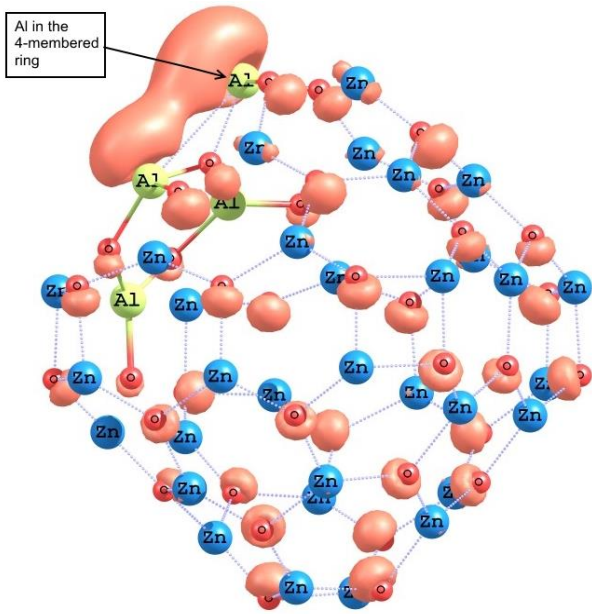


Fig. 3. The electron density distribution on cluster atoms for the higher occupied molecular orbital (HOMO); orange spheres - distribution of electron density.

2.2. The effect of the spatial allocation of oxygen interstitial relatively to Al on the formation energy of O_i and energy of Al ionization in the $Zn_{32}Al_4O_{36}$ cluster

In $Zn_{32}Al_4O_{36}$ cluster oxygen interstitial can be situated in two types of locations – near the Al atom and remotely to it. The calculations showed (Tab. 3, variant *a*, *b*) that the O_i defect formation energy near Al is essentially smaller than at their remote location, respectively 0.44 and 3.13 eV. For these cases Al ionization energy is about 0.47 and 0.97 eV. Thus, at the O_i location in the vicinity of Al the formation energy of this defect becomes more than 7 times lower and Al ionization energy diminishes about 2 times comparatively to the case of their remote disposition. Thus, the compensation of Al donor increases in this case.

The calculations of the defect O_i formation energy and the Al ionization energy were carried out to determine the effect of the defect O_i location near the packing defect of the ZnO lattice on the electroactivity of the Al impurity (Fig. 4, Tab. 3, variant *c* – O_i adjacent to Al and 4-membered ring). For this case, Fig. 4 shows the electron density distribution for the HOMO molecular orbital. The electron density is concentrated mainly on the atoms of embedded oxygen, and O atoms situated in the neighborhood. It can be seen from the Tab. 3, variant *c* that the location of O_i near 4-membered ring (the packing defect of the ZnO lattice) leads to a significant decrease in the formation energy of the defect O_i (0.1 eV), compared with variants *a* and *b*. Thus, from the analysis of the formation energy of the O_i defect, the most probable is the variant *c*, then *a*, and then *b*. Defect O_i formulated near the packaging defect becomes the leading one. In this case (*c*), the ionization energy increases in comparison with the case *a* and decreases insignificantly in comparison with the case *b*.

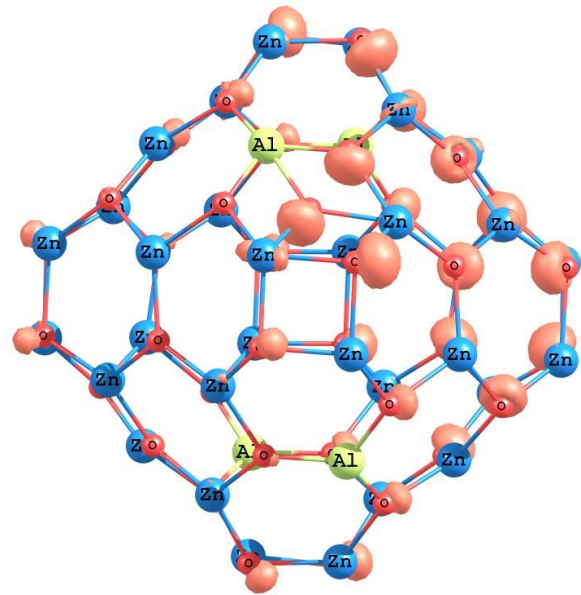


Fig. 4. The distribution of electron density on cluster atoms for the higher occupied molecular orbital (HOMO); the displacement of an oxygen atom (for variant *c* in the Tab. 3) where O_i adjacent to Al and 4-membered ring; orange spheres are the distributions of electron density on cluster atoms for the higher occupied molecular orbital (HOMO).

Table 3

Energy parameters of $Zn_{32}Al_4O_{36}$ clusters with different space distribution of Al: E_{O_i} - defect formation energy; E_i - ionization energy of Al. Variants: a) O_i adjacent to the aluminum atom; b) O_i is not adjacent to aluminum; c) O_i adjacent to Al and 4-membered ring

Variants	E_{O_i} (eV)	E_i (eV)
a	0.44	0.47
b	3.13	0.97
c	0.1	0.75

Conclusions

Fullerene Like Model demonstrated its capability of living, what allows to use it in the future for the control of the electroactivity of donor impurities of the third group due to their compensation by intrinsic acceptor defects of ZnO crystal lattice and to look for technological ways for improving electroactivity of donor impurities in ZnO. The results of theoretical calculations of Al ionization energy with adjacent V_{Zn} and O_i allowed us to formulate recommendations to the conditions of technological processes for deposition ZnO films with improved conductivity

The presence of packing defects in the ZnO lattice at the O_i presence leads to an increase of Al ionization energy.

The O_i location near the packing defect of the ZnO lattice and the Al impurity leads to a significant decrease of the formation energy for the O_i defect, the defect becomes the leading one.

The presence of packing defects in the ZnO lattice leads to the predominant location of the Al impurity in the

defect region and to the increase of the Al electroactivity.

At summarizing the results, it should be mentioned that E_i increasing at V_{Zn} acceptor defects formation increases the compensation rate of Al impurity. This means that Al will pass its excess electron not to the gas of free carriers but to the nearest V_{Zn} acceptor center. Inasmuch as V_{Zn} is equivalent to oxygen excess, the ZnO films growth is necessary to carry out in the gas media with a lack of the oxygen. This will cause troubles to the V_{Zn} acceptor defects formation. Another way is annealing ZnO films in vacuum.

Al diminishes the formation energy of O_i acceptor defect, what increases a compensation of the Al donor impurity. Thus, in this case the lack of oxygen at ZnO film deposition is required also for Al electroactivity improving. The confirmation of this conclusion is the publication [13] where increasing of electrical conductivity for ZnO:Al films was observed at

diminishing partial oxygen pressure in working chamber at magnetron technology of film deposition.

Ovsianikova L.I. - Candidate of Physical and Mathematical Sciences, Senior Researcher;

Lashkarev G.V. - Doctor of Physical and Mathematical Sciences, Professor, Head of Department;

Kartuzov V.V. - Candidate of Physical and Mathematical Sciences, Senior Researcher, Head of Department, Scientific Secretary;

Myroniuk D.V. - Candidate of Physical and Mathematical Sciences, Senior Researcher

Dranchuk M.V. - junior researcher;

Ievtushenko A.I. - Candidate of Physical and Mathematical Sciences, Senior Researcher, Head of Department.

- [1] A. Ievtushenko, O. Khyzhun, I. Shteplyuk, and et. al., Journal of Alloys and Compounds 722, 683 (2017) (<https://doi.org/10.1016/j.jallcom.2017.06.169>).
- [2] A. Dmytruk, I. Dmitruk, A. Kasuya, Materials Science & Engineering Technology, 40(4), 265 (2009) (<https://doi.org/10.1002/mawe.200800438>).
- [3] A. Dmytruk, I. Dmitruk, I. Blonsky, and et. al., Microelectronics Journal 40, 218 (2009) (<https://doi.org/10.1016/j.mejo.2008.07.010>).
- [4] L.I. Ovsianikova, Acta Physica Polonica A 122, 1062 (2012) (<https://doi.org/10.12693/APhysPolA.122.1062>).
- [5] L.I. Ovsianikova, Acta Physica Polonica A 126 1090 (2014) (<https://doi.org/10.12693/APhysPolA.126.1090>).
- [6] L. Ovsianikova, V. Kartuzov, I. Shteplyuk and et. al., Acta Physica Polonica A 129, 41 (2016) (<https://doi.org/10.12693/APhysPolA.129.A-41>).
- [7] I. Shteplyuk, V. Khranovskyy, G. Lashkarev and et. al., Solid-State Electronics 81, 72 (2013) (<https://doi.org/10.1016/j.sse.2013.01.015>).
- [8] L. Ovsianikova, M. Dranchuk, G. Lashkarev and et. al., Superlattice and Microstructures 107, 1 (2017). (<https://doi.org/10.1016/j.spmi.2017.03.054>).
- [9] S. Huzinaga, J. Andzelm, M. Klobukowski and et. al., Gaussian basis sets for molecular calculations Elsevier (Amsterdam, 1984).
- [10] R.P. Messmer, G.D. Watkins, Phys. Rev. B 7, 2568 (1973) (<https://doi.org/10.1103/PhysRevB.7.2568>).
- [11] M.W. Schmidt, K.K. Baldridge, J.A. Boatz and et. al., J. Comput. Chem. 14, 1347 (1993) (<https://doi.org/10.1002/jcc.540141112>).
- [12] S. Portmann, H.-P. Lüthi, CHIMIA International Journal for Chemistry 54, 766 (2000).
- [13] A.I. Ievtushenko, O.I. Bykov, L.O. Klochkov and et. al., Physics and Chemistry of Solid State 16(4), 667 (2015) (<https://doi.org/10.15330/pcss.16.4.667-674>).

Л.І. Овсяннікова, **Г.В. Лашкар'єв**, В.В. Картузов, Д.В. Миронюк,
М.В. Дранчук, А.І. Євтушенко

Дослідження поведінки домішки Al у ґратці ZnO за допомогою фулереноподібної моделі

Інститут проблем матеріалознавства ім. І.М. Францевича, НАН України, Київ, Україна, earsen@ukr.net

Шляхом дослідження фулереноподібних кластерів $Zn_{32}Al_4O_{36}$ було розраховано енергію утворення власних дефектів акцептора кисню O_i та енергію іонізації Al в оксиді цинку. Досліджено вплив дефектів ґратки на електроактивність домішки Al. Встановлено, що аналіз енергій утворення дефектів показує меншу енергію утворення міжвузлового кисню O_i у порівнянні з енергією утворення вакансії Zn. Проведені розрахунки дозволяють сформулювати рекомендації щодо технологічних умов осадження плівок ZnO із покращеною електроактивністю донорної домішки Al.

Ключові слова: фулереноподібна модель; оксид цинку; енергія іонізації алюмінію; енергії утворення власних дефектів; дефекти упаковки ZnO.