First principle study of electronic properties of ZnO nanoclusters with native point defects during gas adsorbtion

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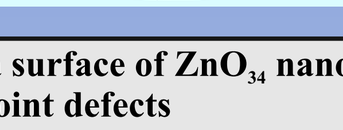
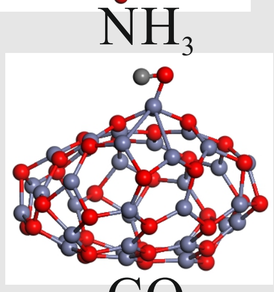
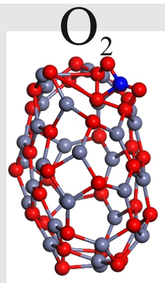
1. Introduction

Zinc oxide is a very promising material for semiconductor device applications, as well as, optoelectronic systems in the blue and UV regions of the spectrum, light-emitting diodes, spintronics, photocatalysts and other devices of new generation. Among other applications, zinc oxide was largely studied as a material for gas sensors. Special interest is given to the nanoclusters of ZnO, which with their variety of interesting physical and chemical properties are quite unique. Previous density functional theory studies of the structural and electronic properties of $(ZnO)_n$ (n = 34, 60) nanoclusters with native point defects (oxygen and zinc vacancies, zinc antisites and oxygen antisites) showed that intrinsic defects can strongly influence the electrical and optical properties of a semiconductor and often induce occupied states in the band gap. In this study we present the results of ab initio density functional theory studies of the adsorption of molecules of different gases (O_2, CO, NO_2, NH_3) on the surface of "magic" clusters $(ZnO)_n$ (n = 34, 60) with native point defects.

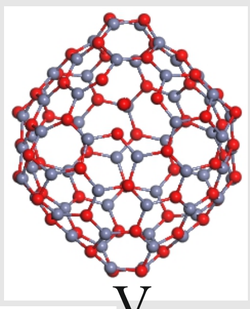
Adsorbtion of gas molecules on a surface of ZnO_{34} nanoclusters with native point defects

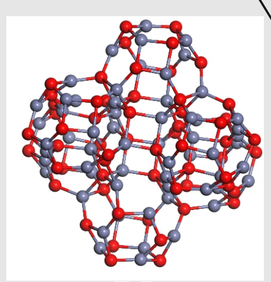


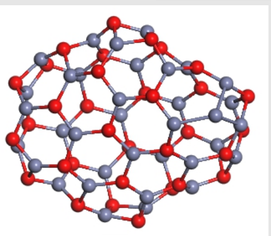


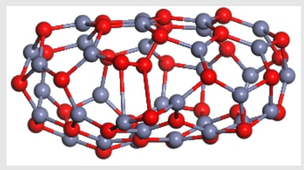


Optimized ZnO_n (n= 34, 60) nanocluster structures with native point defects

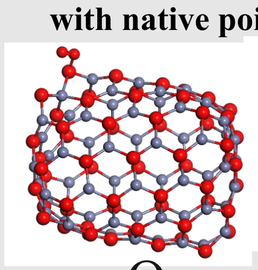


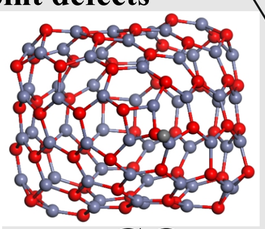


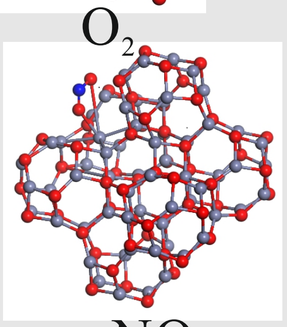


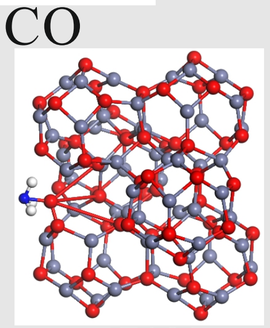


Adsorbtion of gas molecules on a surface of ZnO_{60} nanoclusters with native point defects







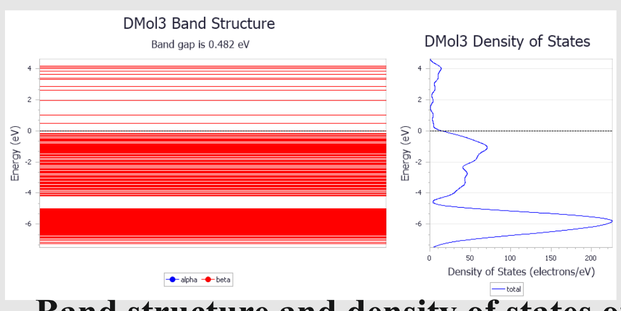


2. Methods

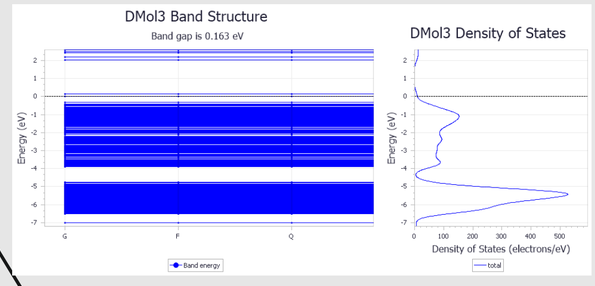
Ab initio calculations within density functional were performed, which have been successfully used in previous studies [1, 2]. For structural models the optimization (relaxation) of the geometry (finding the equilibrium of ions coordinates, in which the full electronic energy of the system is minimal) was carried. Optimization was calculated using the effective algorithm of delocalized internal coordinates. The convergence of the relaxation procedures deemed reached when the magnitudes of forces acting on atoms were less than 0.05 eV/Å. The geometry optimizations were followed by vibrational frequency analysis. The vibrational frequency analysis confirmed that the structures are at true local minima.

For describing the exchange-correlation energy of the electronic subsystem the generalized gradient approximation with Hubbard pseudopotential (GGA+U) in a parameterization of Perdew, Burke and Ernzerhof was used. Electronic functions of electrons were divided in the basis of atomic orbitals, including d-orbitals. Core electrons had been described using effective potential with regard to relativistic corrections. Integration in the first Brillouin zone was conducted in the Monkhorst-Pack k-point set.

Band structure and density of states of ZnO_{34} nanocluster during adsorbtion of O_2 gas molecule



Band structure and density of states of ZnO_{60} nanocluster during adsorbtion of O_2 gas molecule



3. Results

We performed geometry optimization for a number of isomers of $(ZnO)_{34}$ and $(ZnO)_{60}$ nanoclusters with oxygen (V_O) and zinc (V_{Zn}) vacancies, as well as, zinc (Zn_O) and oxygen (O_{Zn}) antisites, and then the molecules of O_2, CO, NO_2, NH_3 had been added to the surface at the location of each defect. The calculations of electronic properties of these clusters were performed and then we compared the results with the values obtained in our previous studies for ZnO nanoclusters with defects [3]. The nature of intermolecular interaction is discussed in the light of consideration of the distributions of the density of electronic states and the form of the highest filled molecular orbital (HOMO) and the lowest unfilled molecular orbitals (LUMO) of adsorbate molecules. Two mechanisms of charge transfer were considered: a) charge transfer occurs depending on the relative location on graph of the density of states of the system of HOMO and LUMO orbitals of the adsorbate. If the HOMO is above the Fermi level of a nanocluster without the gas molecule, then the charge is transferred to the adsorbed molecule; ; b) charge transfer between the adsorbate molecule and the ZnO cluster is determined by hybridization of HOMO and LUMO orbitals of the molecule with electronic orbitals of the cluster.

Energy gap values for $(ZnO)_{34}$ nanoclusters

Nanocluster	E_g, eV				
	no gas	O_2	CO	NH_3	NO_2
$(ZnO)_{34}$ V_{Zn}	1.86	0.482	1.963	2.122	2.178
$(ZnO)_{34}$ V_O	2.3	1.628	1.794	1.453	1.352
$(ZnO)_{34}$ Zn_O	1.426	1.065	1.194	1.347	1.410
$(ZnO)_{34}$ O_{Zn}	2.184	1.296	1.762	1.591	0.909

Energy gap values for $(ZnO)_{60}$ nanoclusters

Nanocluster	E_g, eV				
	no gas	O_2	CO	NH_3	NO_2
$(ZnO)_{60}$ V_{Zn}	2.081	0.163	2.041	2.179	2.26
$(ZnO)_{60}$ V_O	2.05	1.782	1.967	1.627	1.594
$(ZnO)_{60}$ Zn_O	1.314	1.195	1.239	1.568	1.649
$(ZnO)_{60}$ O_{Zn}	1.882	1.264	1.498	1.349	0.854

Adsorption of molecules caused, in most cases the reducing of the band gap of nanoclusters. Molecules of CO and NH_3 are the donor types during charge transfer, and the O_2 and NO_2 are the acceptors. Analysis of the obtained results showed that the molecules of CO, NO_2, NH_3, increase the concentration of the main charge carriers (electrons) in sensor systems, whereas molecule O_2, reduce their concentration. The sharpest decrease of the band gap was observed for O_2 molecule during adsorbtion on all for types of defects. For zinc antisite defect (Zn_O) the biggest change of the band gap for donor molecules was observed during adsorbtion of CO molecule, for the oxygen antisite defect (O_{zn}) during adsorbtion of NH_3 molecule. The adsorbtion of NO_2 molecules showed increase of the band gap both for V_{Zn} and Zn_O defects. The sharp decrease of the band gap for O_{Zn} can be explained by the mixing of the HOMO-orbitals of the nanocluster with the orbitals of the molecule of a toxic gas and the acceptor level of NO_2 appearing in the forbidden zone. The LUMO- orbital level of the nanocluster shifts on the energy scale up.

4. Conclusions

We present the results of ab initio density functional theory studies of the adsorption of molecules of different gases (O_2, CO, NO_2,NH_3) on the surface of "magic" clusters $(ZnO)_n$ (n = 34, 60) with native point defects. We performed geometry optimization for a number of isomers of $(ZnO)_{34}$ and $(ZnO)_{60}$ nanoclusters with oxygen and zinc vacancies, as well as, zinc and oxygen antisites, and then the molecules of O_2, CO, NO_2, NH_3 had been added to the surface. Adsorption of gas molecules leads to change geometry of nanoclusters and promotes electron exchange between the adsorbed molecules and the surface of the clusters. It was found that molecules of CO, NH_3, increase the concentration of basic carriers (electrons) in the sensory system, while molecules of O_2 and NO_2 decrease their concentration. Adsorption of molecules causes the reducing of the band gap of nanoclusters. The sharpest decrease is observed for O_2 molecules, and among donor molecules the greatest impact was observed with CO and NH_3 molecules.

5. References

1. Bovgyra O.V., **Bovhyra R.V.**, Popovych D.I., Serednytski A.S. **The Density Functional Theory Study of Electronical Properties of (ZnO)12 Clusters During Gas Adsorption** // Journal of Nano- Electronic Physics. – 2015. – **V.7**, №4. – P. 04090(6).

2. **Bovhyra R.V.**, Popovych D.I, Bovgyra O.V., Serednytski A.S. **Ab Initio Study of Structural and Electronic Properties of (ZnO)n "Magical" Nanoclusters n = (34, 60)** // Nanoscale Research Letters. – 2017. – **12**. – P.76(5).

3. **R.Bovhyra**, D.Popovych, O.Bovgyra, A.Serednytsky **First principle study of native point defects in (ZnO)n nanoclusters (n = 34, 60)** // Applied Nanoscience. – 2019. – **9(5)**. – P. 1067-1084.