ANNOTATION

of the dissertation for scientific degree of
doctor philosophy (PhD)

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First principles calculations of atomic and electronic properties of zinc oxide

Topicality of the Work

Over the past decade, the study of atomic and electronic structure of zinc oxide (ZnO) has attracted much attention, because this was a relatively inexpensive semiconductor material with good optoelectronic properties, and can replace more expensive optoelectronic materials. Modern technology makes it possible to obtain ZnO his doping, creating p-n junctions, as well as its use in heterojunctions. This implies the importance of understanding the effect of various impurities on the atomic and electronic structure of zinc oxide. In this regard, hydrogen as a impurity is especially important, since it is always present in the ZnO during its growth by magnetron sputtering, and according to preliminary experimental data increases electron conductivity ZnO, which is essential for creating transparent conductive layers in microelectronics. Understanding the role of hydrogen requires atomistic simulations.

In this paper we describe the crystal structure and electronic properties of zinc oxide doped with hydrogen at the atomic level, carried out quantum-chemical modeling using density functional theory.

Work purpose: The purpose of this study is the hydrogen impurity effect on atomic and electronic properties of ZnO in bulk and on surface.

The subjects of the work are:

1) Optimization of the basis set of the atomic orbitals and the geometrical parameters using the model of ZnO supercell;
2) The quantum-chemical calculations of the hydrogen impurity in the interstitials;
3) The quantum-chemical calculations of the hydrogen impurity in the oxygen vacancies;
4) Modeling of defect-free non-polar surfaces of ZnO;
5) The quantum-chemical calculations of hydrogen adsorption on the non-polar ZnO surface.

Object of research a semiconductor crystal of zinc oxide (ZnO) doped with hydrogen. The object of study corresponds to the topic of the thesis, the goal and objectives of the study.

The subject of the research is a theoretical study of the effect of atomic hydrogen on the bulk and surface properties of ZnO

Scientific novelty consists from following research results:

1. Hydrogen is effectively creates donor levels near the bottom of the conduction band;
2. On the surface of ZnO hydrogen is adsorbed mainly on the surface oxygen ions;
3. Get another strong presence of hydrogen adsorption on the surface;
4. Hydrogen adsorption reduces the surface energy relaxation;
5. Diffusion into the crystal requires considerable energy costs.

Main protected definitions of the work:

1. Energetically favorable position of the hydrogen atom in ZnO is a position near the oxygen atom ($AB_{O,\perp}$). Between the impurity atom of hydrogen and oxygen ions formed a regular connection with the length of 0.978 Å. Hydrogen in the bulk ZnO is a shallow donor, giving part of the electron density at the closest neighboring Zn atoms and O (delocalization of the charge);

2. Calculations for defect-free non-polar surfaces showed that covalent contribution Zn-O bonds on the surface than in the bulk. Additional non-polar surfaces, and is more stable surface.

3. Found that the adsorption of hydrogen on the surface of ZnO is energetically favorable in position above the surface oxygen ion and causes it to «metallization». Weak physical adsorption is observed in interstitial positions (hollow). As a result, the surface energy of adsorption decreases.

Scientific and practical significance: The results of these ab initio calculations explain the physical and chemical properties of pure and mixed with hydrogen ZnO crystal at the atomic level, and can be used to make transparent conductive coatings for microelectronics in the production of solar cells and transistors.

The volume and structure of the thesis: The thesis consists of content, an introduction, four chapters, conclusions and bibliography. Scope of the thesis was 108 pages, including 31 Figures, 14 Tables, 173 literary sources.

Conclusion:

Carried out quantum- chemical calculations of the properties of ZnO crystals with hydrogen , which inevitably gets into the material of the plasma during growth by magnetron sputtering demonstrate the capabilities of modern theoretical methods of modeling and reliable prediction of the effects of doping process materials . In particular, we are:

1. It was found that the energetically favorable position of the hydrogen atom in ZnO is a position close to the oxygen atom ($AB_{O,\perp}$), which formed a strong chemical bond OH;
2. It was showed that the hydrogen inside the crystal ZnO is a shallow donor, giving part of the electron density at the nearest neighboring atoms of Zn and O (delocalization of the charge);
3. It was showed that covalent contribution Zn-O bonds on the surface than in the bulk. Additional non-polar surfaces , and is more stable surface.
4. It was revealed that the hydrogen adsorption is energetically favorable in position above the surface oxygen atom. Also, weak physical adsorption is

observed in interstitial positions (hollow). As a result, the surface energy of adsorption decreases.

5. It was found that the adsorption of hydrogen on the surface of ZnO leads to its "metallization" as in the case of surface ZnO. As the concentration of hydrogen impurities on the surface band structure of the surface disappears, and the complete saturation of the dangling bonds of the Zn atoms and O, the crystal becomes an insulator again.

Approbation and publications:

As a result of these calculations, we have been published 19 publications, including two in a Thomson Reuters base, one in Scopus base, 6 publications recommended by Committee of the Control in Education and Science MES RK, 10 theses in International conferences.