Electronic Structure, Optical and Sensor Properties of ZnO Nanowires

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Density functional theory calculations of structural, electronic and optical properties of ZnO nanowires were performed. It was established that the band gap of ZnO nanowires increases with decreasing nanowire size. The calculated dielectric functions of ZnO nanowires show a significant blue-shift compared with that of bulk ZnO. Our results provide some information for real understanding of the optical properties of ZnO and also enable more precise monitoring and controlling during the growth of ZnO materials. Moreover, the theoretical calculations of adsorption of different gas molecules on the surface of ZnO nanowires were carried out. In order to define the donor or acceptor character of molecular adsorption, the degree of charge transfer to nanowires was determined.

Keywords: ZnO nanowires, Density functional, Electronic structure, Optical properties, Adsorption.

1. INTRODUCTION

Zinc oxide (ZnO) is a typical wide band semiconductor ($E_g = 3.37$ eV) with high exciton binding energy (60 meV) and, as known, is one of the most important functional oxides. The properties of ZnO attract more and more attention of researchers in recent years to its potential use in the production of electronic, optoelectronic and photoelectronic nanodevices, as well as of sensors [1-5]. ZnO nanostructures, such as nanowires, nanotubes, nanoribbons, nanorods are promising functional elements in optical and electronic devices due to the potential use in short-wavelength laser diodes, solar batteries, transparent and conductive electrodes in solar batteries, surface acoustic wave devices, as well as in chemical and biological sensors [6-8]. A number of experimental and theoretical studies reported the use of ZnO nanowires in various optoelectronic devices [9-11]. Currently, there are not many systematic theoretical studies of the size-dependent properties of ZnO nanowires. In particular, the influence of surface effects of electronic states, due to the side wall of ZnO nanowires, on their electronic and optical properties, remains unclear.

In the paper, theoretical studies of electronic, optical and adsorption properties of ZnO nanowires of various sizes are presented based on the first-principle calculations.

2. MODELS AND CALCULATION TECHNIQUES

The theoretical calculations within the density functional theory (DFT), which was successfully used for the study of nanosized structures, such as, nanorings, nanotubes and nanoribbons, are performed in the work [12-15].

The ultrasoft Vanderbilt pseudopotentials [16] in the plane wave basis were used for the ionic potentials. In order to describe the exchange-correlation energy of the electronic subsystem, the functional in the generalized gradient approximation (GGA) in the Perdew, Burke and Ernzerhof (PBE) parameterization [17] was applied. The integration in the first Brillouin zone was carried out in special k-space points generated by the Monkhorst and Pack scheme [18].

While within this approach the calculated structural parameters of the system are reproduced well compared with experimental data, the electronic structure suffers from the known problem of understatement of the band gap because of partially constrained electron density functionals. In the case of a bulk ZnO crystal, this error is pronounced, since the calculations give the band gap value of 0.98 eV that greatly underestimates the experimental value of 3.4 eV. One of the reasons for this underestimation is an inaccurate description of the location of zinc $3d$-zones, which lie higher on the energy scale of about 2 eV compared with the experiment; however, this does not affect the general trend of electronic and structural properties that is confirmed by a number of previous electronic calculations [14-15, 19-21].

In order to avoid the problem of understatement of the band gap in our calculations, we used DFT together with the Hubbard method U (DFT + U). The deviations in the calculation of the band structure when using this method is within 1 % of the experimental values. For a more precise description of the exchange-correlation potential in this work, an adapted method of calculations DFT + U_d + U_p is used. It is assumed in [22] that the value of $U_{p,O}$, which is equal to 7 eV for oxide materials, is well suited for the first-principle calculations. In this work we consider both values: $U_d = 10$ eV for Zn $3d$-orbitals and $U_p = 7$ eV for O $2r$-orbitals. The calculated band gap of a bulk ZnO crystal is equal to 3.37 eV for the specified parameters U_d and U_p. These results are in a good agreement with the experimental data.

To minimize the surface interactions between nanowires, they were located in the structural models at a distance of 10 Å from each other.

The diameter of the investigated structures is up to 2 nm that is less than in the synthesized experimentally ZnO nanowires (20-100 nm). Since the first-principle calculations of the nanostructures of 20-100 nm diameter require significant computer resources, the results below represent the role of the surface curvature and the radial size effect in the properties of nanostructures.
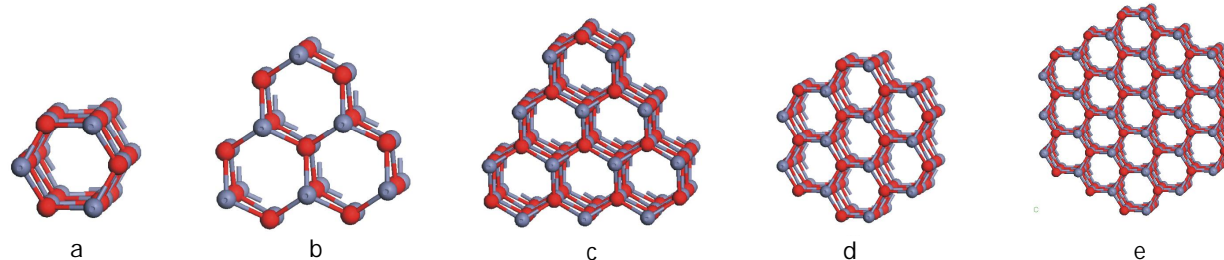
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Fig. 1 – Structural models of ZnO nanowires: the number of atoms in the unit cell a) $n = 12$; b) $n = 26$; c) $n = 44$; d) $n = 48$; and e) $n = 108$ (grey atoms are Zn, red ones – O)

The models of ZnO nanowires were formed from a bulk ZnO crystal with the wurtzite structure along the (0001) crystal axis (Fig. 1). The obtained nanowires had a triangular or hexagonal shape (three or six faces of the non-polar $(10\bar{1}0)$ crystal, respectively) and were composed of 12, 26, 44, 48, 108 atoms in the unit cell.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

At first, all models of ZnO nanowires were optimized, i.e. the search for equilibrium ionic coordinates, at which the total electron energy of the system is minimal, was carried out by an efficient algorithm of delocalized internal coordinates [23]. After structural optimization, all oxygen atoms of the outer nanowires layers are shifted outward, while zinc atoms are shifted inward (Fig. 2). The relaxation of the surface atoms in ZnO nanowires has the same mechanism of change as on the $(10\bar{1}0)$ ZnO surface [24].

In Table 1 we give the values of the binding energy and band gap of the studied ZnO nanowires.

As seen from the results obtained, the binding energy decreases and the band gap increases with decreasing nanowire size. The largest of the studied structures by its properties approaches to a bulk ZnO crystal. An increase in the band gap with increasing ratio of the surface area
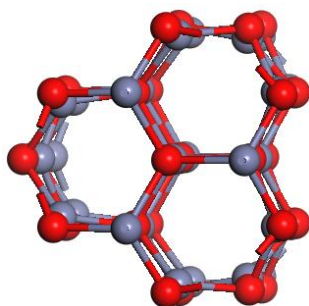

Fig. 2 – The model of ZnO nanowire with $n = 26$ after optimization of the structure model

Table 1 – Structures, binding energies per one atom (eV) and band gaps (E_g, eV) of ZnO nanowires

Structure Number of atoms	Binding energy, eV	E_g, eV
a) $n = 12$	6.458	4.42
b) $n = 26$	6.751	4.11
c) $n = 44$	6.96	3.56
d) $n = 48$	7.011	3.54
e) $n = 108$	7.22	3.48

to the nanostructure volume confirms the dependence of the electronic properties of ZnO on its sizes. It should be noted that the dispersion of the electronic bands in the valence band is not practically changed with changing nanowire diameter. The band gap varies on account of the motion of delocalized states of the conduction band bottom in the energy band.

As seen from Fig. 3, ZnO nanowires possess a direct energy band gap at a relatively high dispersion along the high-symmetry line $\Gamma(0, 0, 0) – F(0, 0, 0.5)$ in the Brillouin zone. The conduction band bottom goes down on the energy scale, and the optical band gap narrows with increasing nanowire size, as shown in Fig. 3 a-c. The values of the calculated energy gaps of ZnO nanowires are higher than for a bulk ZnO crystal (3.37 eV). The reasons for this can be explained by as follows: on the one hand, the lowest occupied state of ZnO nanowires corresponds to the surface atoms, and the main contribution is from free $2p$-oxygen bonds. On the other hand, the interactions between electric charges are the result of their delocalized character, and electrons have greater mobility along these surfaces.

The spectra of the imaginary part of the dielectric function ε_2 are obtained from the results of the energy band calculations of wave functions and eigenvalues of the energy of valence and virtual states. On their basis, the absorption spectra are determined by the Kramers-Kronig relation. The calculated absorption spectra and spectra of the imaginary part of the dielectric function are illustrated in Fig. 3, Fig. 4. The use of the GGA + U method allowed to obtain a coincidence of the band gap and the absorption edge that agrees well with the experimental results, according to which the absorption edge is located at 377 nm at room temperature [25].

As seen from Fig. 4, the fundamental absorption edge undergoes a substantial blue shift with decreasing nanowire size. These characteristics are of great interest due to their significant potential applications in optoelectronic nanodevices.

Fig. 5 presents the calculated dielectric functions ε_2 of ZnO nanowires for the incident radiation polarization along the polar axis in the direction [0001]. The spectrum of ε_2 can be divided into two main groups: low-energy from 2.9 eV to 5 eV and high-energy from 5 eV to 10 eV.

The interband transitions, which form the absorption edge of nanowires, start from 2.9 eV to 4 eV and correspond mainly to the transitions from the valence band top to the conduction band bottom. The corresponding intense peak in the low-energy region is shifted toward the high-energy region with decreasing nanowire size. In the high-energy region, three intense peaks come from the inter-
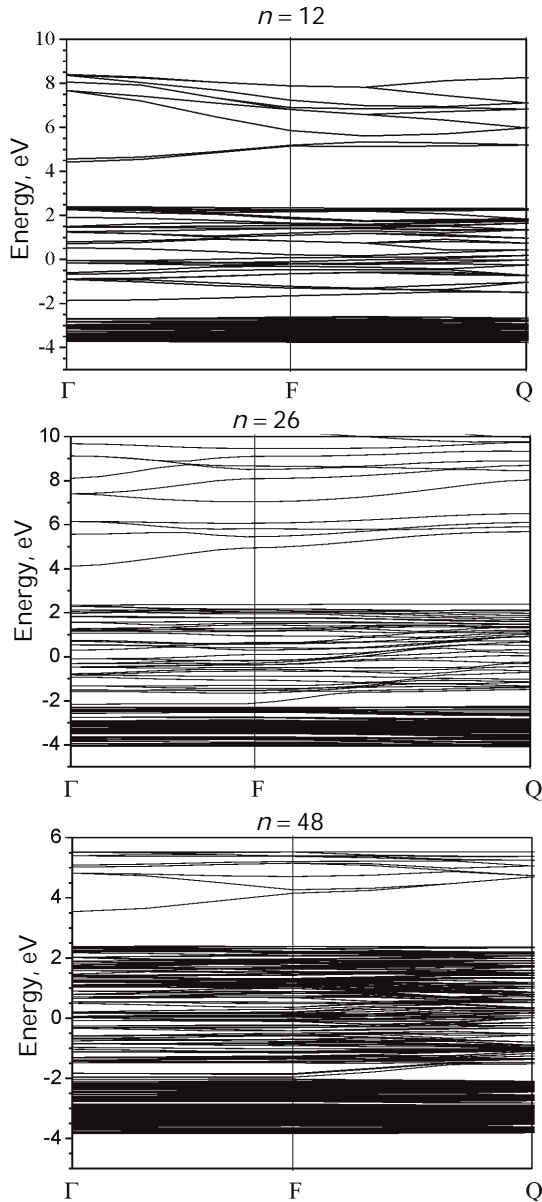
$n = 12$

$n = 26$

$n = 48$

Fig. 3 – Band diagrams of ZnO nanowires along 2 main directions in the Brillouin zone: a) $n = 12$; b) $n = 26$; c) $n = 48$
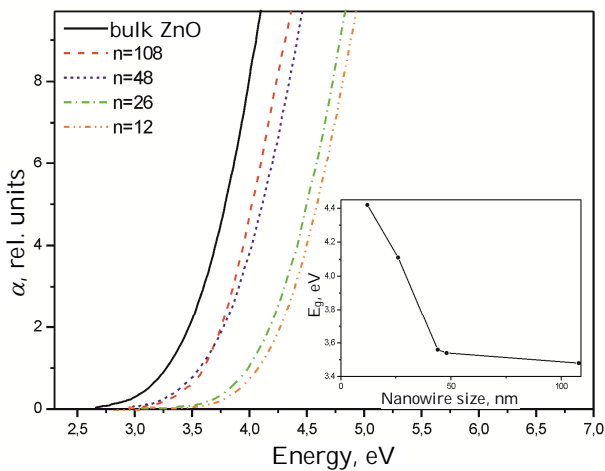

Fig. 4 – Calculated absorption spectra of ZnO nanowires in the region of the fundamental absorption edge (on the inset: dependence of the direct energy gap on the nanowire size)
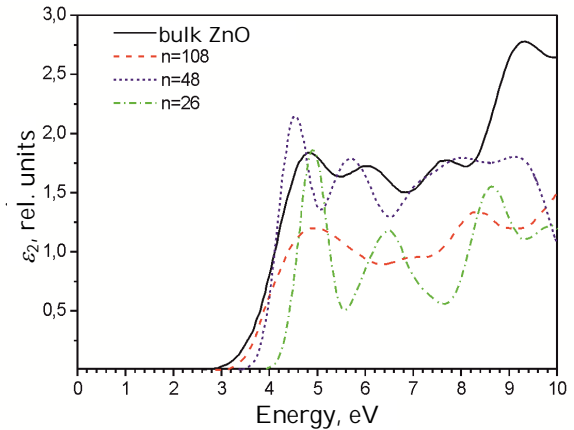

Fig. 5 – Imaginary part of the dielectric function for ZnO nanowires

band transitions between the second and the third unoccupied states and the conduction band states. Moreover, the shape of the spectra of the dielectric functions is very similar and indicates that the dielectric permittivity function of ZnO nanowires is relatively insensitive to the change of their diameter.

Investigation of adsorption of different gas molecules (O_2, H_2O, CO, NH_3, C_2H_5OH) on the surface of ZnO nanowires is also performed for the obtained models of nanowires. For the models of ZnO nanowire, the optimization of the geometric parameters was initially carried out, and then gas molecules were added to the side surface. The geometric parameters of such a system were again optimized. In Fig. 6-Fig. 8 we illustrate the results of the interaction of individual molecules (CO, NH_3, O_2) with ZnO nanowires containing 26 atoms in the unit cell.

CO and NH_3 molecules (Fig. 6 and Fig. 7) undergo molecular chemisorption on the nanowires surface and become charge carrier donors. In the case of adsorption of CO molecules, we note the dependence of the charge transfer value on the molecule orientation with respect to the nanowire surface. For the CO molecule, the states of the conduction band play a decisive role in the donor nature of binding to the sensor surface of the nanowire, since they are closer to the Fermi level of the nanowire than the states of the valence band.
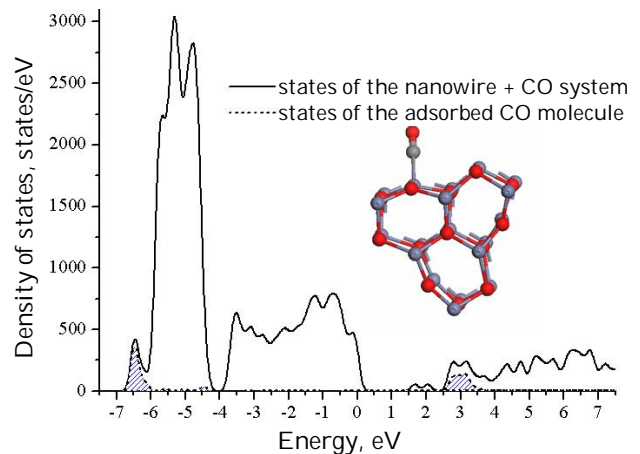

Fig. 6 – Optimized configuration and distribution of the density of states of the CO molecule on the ZnO nanowire surface
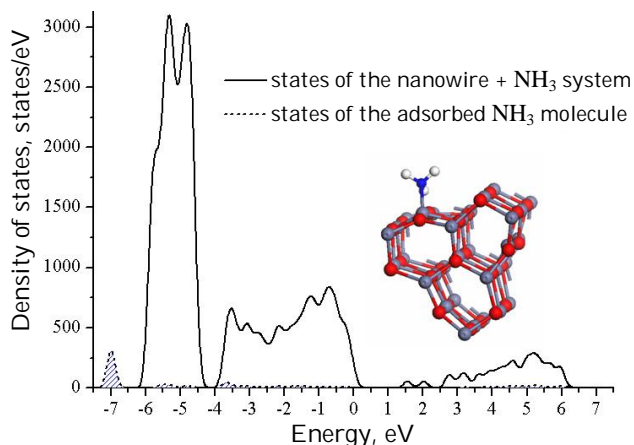
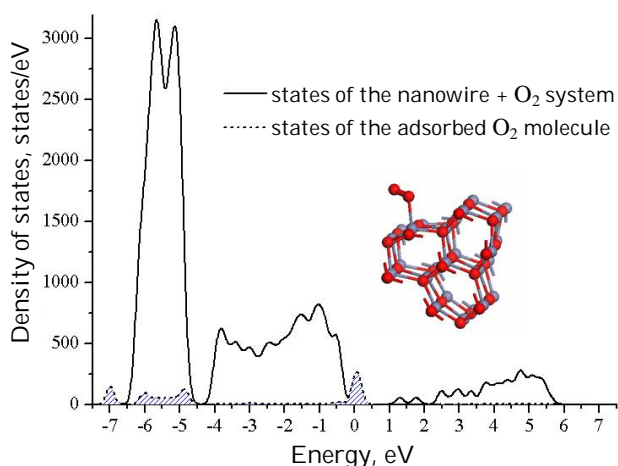Fig. 7 – Optimized configuration and distribution of the density of states of the NH₃ molecule on the ZnO nanowire surface

Fig. 8 – Optimized configuration and distribution of the density of states of the O₂ molecule on the ZnO nanowire surface

In the case of adsorption of CO and NH_3 molecules on the surface of nanowires, the situation is similar to the adsorption on the surface of nanotubes [14].

The interaction of molecular oxygen with the surface of ZnO nanowire is described by the process of physical adsorption; the acceptor level of O_2 appears in the band gap (see Fig. 8). As a result, the oxygen molecule gets a charge, i.e. the charge transfer occurs from the nanowire surface to the molecule O_2. Such an acceptor nature of charge transfer from the nanowire to the molecule O_2 is confirmed by experimental studies of sensor properties of ZnO nanowires [26].

In the general case, the adsorption properties of thin ZnO nanowires are very close to the properties of the surfaces of nanotubes. However, since ZnO nanowires are experimentally more accessible, they are more practical for the use as chemical sensors.

4. CONCLUSIONS

Theoretical investigation of the electronic structure and optical properties of different size ZnO nanowires is carried out. The calculation results show that all ZnO nanowires have a direct band gap, whose value is greater than that in a bulk crystal. A clear manifestation of the quantum size effect is established: the increase in the band gap in the 1D nanostructure with increasing surface-to-volume ratio. Correspondingly, the fundamental absorption edge undergoes a significant blue shift with decreasing nanowire size. These results favor the use of ZnO nanowires as nanodevices, nanosensors and optoelectronic devices of the ultraviolet range. Adsorption of gas molecules on the surface modifies the electronic spectrum of ZnO nanowires confirming the possibility of practical application of such nanostructures as gas sensors.

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