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Simulation of structural and electrical parameters of CdS thin films

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Based on calculations from the first principles, we obtained the result of the calculations of the density of valence electrons and electronic energy spectra for CdS film with different oxygen content. According to the results of the calculations, it was established that oxygen atoms, adsorbing to the CdS surface, act as negatively charged ions taking electrons from the surface of the film, therefore oxygen atoms increase the catalytic activity of the CdS.

Keywords: nanostructures, density of state, the method of the theory of functionality of electronic density, pseudopotential, solar cells, nanoparticles, transition metals.

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I. Problem statement

In recent years, A_2B_6 connections have been actively used in optoelectronic technology as solar panels, fluorescent screens, scintillation sensors, photo receivers, laser structural elements. CdS is also used in combo with other semiconductors to create various devices on hetero-transients, for example in quantum-cascading lasers, photo receivers for solar panels [1-6]. The use of a thin CdS film in the structure of solar cells is indicated by its generation of media due to its high photosensitivity [7].

CdS, as well as all other compounds of group A_2B_6, is characterized by the content of isoelectron oxygen impurities – at the level of 1018-1020 cm^{-3}. This fact has been known for a long time, but the role of oxygen in the optical properties of CdS films remains unknown [8, 9]. Thus, a deeper understanding of the controlled optimization of thin CdS:O films require a deeper understanding of the effects of oxygen inclusions in the atomic layers of thin films of CdS and their impact on the structure.

II. Models and methods of calculations

The passive effect was studied in calculations from the first principles. The results were obtained using the author's program code [10], which implements the quantum-mechanical dynamics of Car-Porinello using the local approximation of the functionality of electronic density and the normalizing pseudopotential from the first principles of Becelet, Hemenn, Schleter [11]. The main states of electron-nuclear systems were detected by the algorithm of quantum dynamics. While optimizing the variables of electronic and nuclear subsystems, or by diagonalizing the Cohn and Shem matrix [12], if only electronic variables were determined at fixed atomic arrays. Following Cohn and Shem, electron density was recorded in terms of busy orthonormal single-part wave functions:

$$n(\bar{r}) = \sum_i \left|\psi_i(\bar{r})\right|^2 \qquad (1)$$

The point on the surface of potential energy in the approximation of Born-Oppenheimer was determined by a minimum in relation to the wave functions of the energy functionality:

$$E\left[\{\psi_i\},\{R_j\},\{\alpha_v\}\right]=\sum_i\int_\Omega d^3r\,\psi_i^*(\vec r)\left[-\frac{\hbar^2}{2m}\nabla^2\right]\psi_i(\vec r)+U\left[\{n(\vec r)\},\{R_j\},\{\alpha_v\}\right] \qquad (2)$$

where $\{R_j\}$ - the coordinates of the atomic backbone, $\{\alpha_V\}$ - all possible external influences on the system.

In general, the formulation of minimization of energy functionality (2) in relation to single-part orbitals when imposing additional orthonorming conditions on them leads to single-part equations of Cohn and Shem:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2+\frac{dU}{dn(\vec r)}\right\}\psi_i(\vec r)=\varepsilon_i\psi_i(\vec r) \qquad (3)$$

In these calculations, the single-part wave function decomposed into a row behind flat waves, the length of the series was chosen so that about 30 flat waves came to the base atom. In the case of searching only electron variables at fixed atomic athes, the Cohn and Shem matrix was calculated for the equation (3) at a certain value of the wave vector from the Briluen zone of an artificial super-grid with a tetragonal elementary cell to be studied. The matrix consisted of elements on the operators of kinetic energy and ionic pseudopotential, which is shielded by a dielectric function in the approximation of Thomas-Fermi [13].

Cadmium sulfide belongs to the A_2B_6 group of semiconductors. Cadmium sulfide crystals can be of two structural types: the cubic structure of zinc deceit (sphalerite) and the hexagonal structure (wurtzite), which are characterized by the tetrayedric arrangement of atoms. In the synthesis of semiconductor films CdS, by chemically surface deposition in large areas and at low temperatures, the formation of cubic rather than hexoganic structures [14, 15] is most likely. Therefore, in this work, calculations were made for the cubic CdS grid, with a constant value of 583 microns. According to the selected cubic structure of the crystal lattice, we took two basis atoms Cd: (0, 0, 0) and S: (0,25, 0,25, 0,25), on the basis of which the CdS film was built Fig. 1.

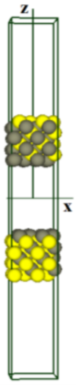

Fig.1 CdS film.

At the same time, the parameters of the basis of the primitive super-grid of tetragonal type were such that in the directions X and Y it is possible to simulate an infinite surface of the film, and in the direction of Z – free surfaces (100) with a passivating coating. To study the mechanism of dissection of oxygen atoms on the surface of CdS (100), we created 5 calculated models:1) impurity-free CdS; 2) CdS film with O_2 molecule on the surface (above Cd atoms (100); over inter-atom void of surface atoms Cd (100)); 3) adsorption of the O_2 molecule into the cavity between the surface layers of CdS; 4) CdS film with a change in the concentration of oxygen atoms (above the Cd atoms (100); over the inter-atom void of surface atoms Cd (100)); 5) adsorption of oxygen atoms into the cavity between the surface layers of CdS. Models of calculations are presented in Fig. 2 and Fig. 3.

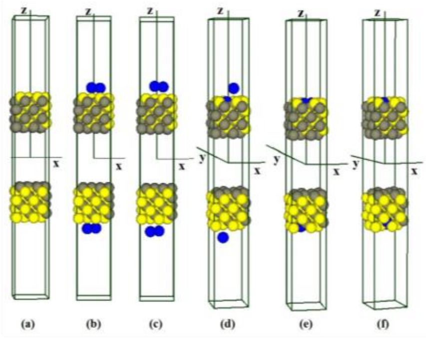

Fig. 2 The mechanism of dissetion of the O_2 molecule on the surface of CdS (100): (a) impurity-free CdS; CdS film with O_2 molecule over Cd atoms ((b) at a distance of 4.1 Å, (c) at a distance of 4.36 Å; (d) disorbation of the O_2 molecule with partial replacement of surface atoms Cd oxygen atoms, (e) replacement of surface atoms Cd adsorbed oxygen from dissociated molecule O_2, (f) partially adsorbed oxygen from dissociated O_2 molecule in the cavity between the surface layers of CdS.

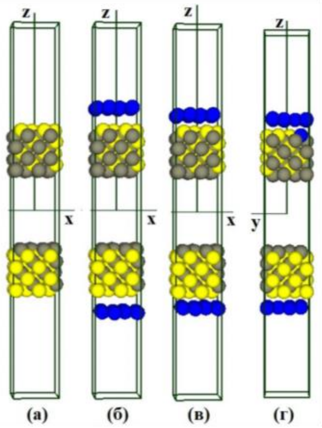

Fig. 3 Oxygen adsorption mechanism on CdS surface (100): (a) impurity-free CdS; CdS film with oxygen over Cd atoms ((b) at a distance of 5.8 Å, (c) at a distance of 4.36 Å); (d) CdS edible film partially substitution of Cd surface atoms with oxygen from dislociated O_2 molecule.

III. Results of calculation and their discussion

For comparative analysis, we obtained distributions of valence electrons by energy zones and their intersections in planes (100) and (110) of an eight-layer CdS film without oxygen, and CdS film with different oxygen content. In the following figures (Fig.4, Fig.6), the distribution of electrons by energy zones for the G-state is given. At the same time, energy in atomic units is deposited along the horizontal axis, and vertically the number of states per elementary energy interval. Figure 5 shows the spatial distribution of electron density for a impurity-free CdS film, and with the addition of the O_2 molecule over Cd surface atoms at a distance of 4.36 Å from the surface atoms of Cd.

According to Fig. 4, when the O_2 molecule is located on the CdS surface in different positions, the probability of finding this atom corresponds to the position above the Cd atoms at distance of about 4.1 Å. This result is obtained from the comparative characteristics of the total energy for the film systems described above. From Fig. 4 (c) the minimum diapason corresponds to the value from E = -178.64 a.u.e. to E = 15.84 a.u.e. with the maximum population of the states of the valence zone 16. The number of allowed states was determined by half the number of electrons (spin of the electron is not considered). When the O_2 molecule enters the CdS surface (100) and replaces the surface atoms of Cd (Fig. 6(b)), the energy range takes the minimum value from E= -161.63 a.u.e. to E = 11.62 a.u.e. The maximum settlement of the valence zone states in this case is 22. Comparing these two values of the intervals of energy with the energy diapason for the CdS film without the addition of oxygen atoms, we can conclude that an increase in catalytic activity occurs when replacing surface atoms with oxygen atoms and increasing the concentration of oxygen from 3.125% to 12.5%. Figure 5 shows the intersections of the spatial distributions of the density of valence electrons in mutually perpendicular planes (110) and (100) for a CdS film without impurities and with the location of the O_2 molecule above the surface atoms Cd with a viewing radius of 5.8 Å. It can be assumed that oxygen, due to its high electron agility, is adsorbed on the surface of the CdS as a negatively charged ion, taking electrons from the surface atoms of the CdS film [16, 17]. With an increase in the concentration of oxygen more than 12.5%, there is a decrease in the number of free bonds, which leads to a decrease in catalytic activity, that is, the degradation of the CdS film and a decrease in the photocurrent [18-20].

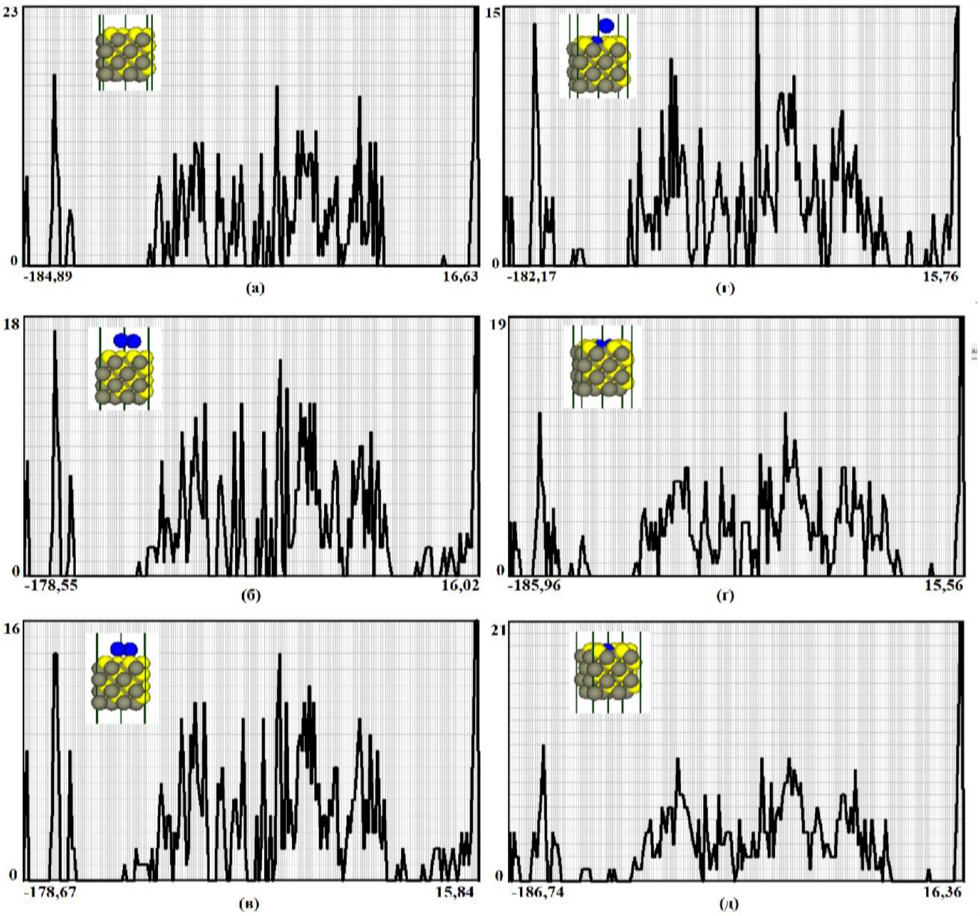

Fig.4 Distribution of valence electrons by energy zones for molecular oxygen on CdS surface (100): (a) impurity-free CdS film; CdS film with O_2 molecule over Cd atoms ((b) at a distance of 4.36 Å, (c) at a distance of 4.1 Å); (d) disorbation of the O_2 molecule with partial replacement of surface atoms Cd oxygen atoms, (e) replacement of Cd surface atoms with adsorbed oxygen from the dissociated O_2 molecule, (f) partially adsorbed oxygen from the dissociated O_2 molecule in the cavity between the surface layers of CdS.

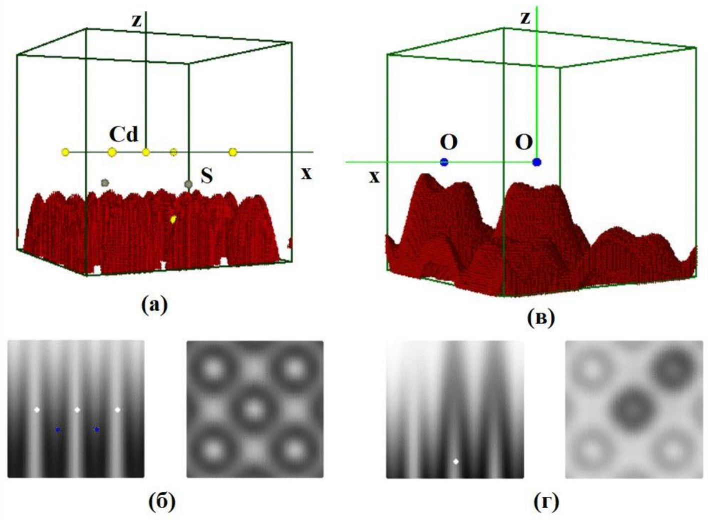

Fig.5 Spatial distribution of the electron density for CdS film without impurities and with the addition of the O_2 molecule over surface atoms Cd: (a) the range of values of 0.9 - 1.0 from the maximum, radius of view 5.8 Å; (c) the range of values of 0.7 - 0.8 from the maximum, viewing radius 5.8 Å; intersections of the spatial distribution of valence electrons in mutually perpendicular planes (110) and (100) for the non-finished CdS film (b) and with the addition of the O_2 molecule (d).

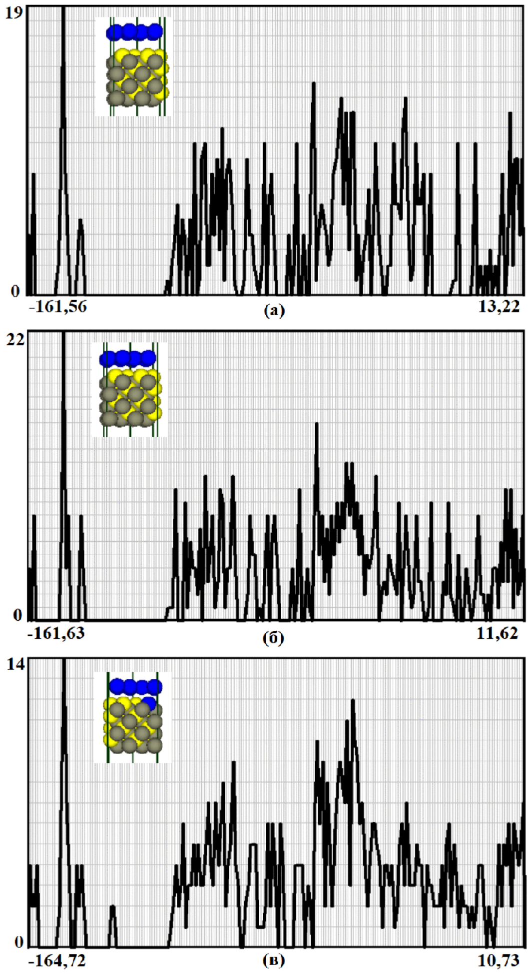

Fig. 6 Distribution of valence electrons by energy zones for oxygen on cds surface (100): CdS film with oxygen over Cd atoms ((a) at a distance of 5.8 Å, (b) at a distance of 4.36 Å); (c) adsorbed oxygen from the dissociated O_2 molecule in the cavity between the surface layers of the CdS.

Conclusion

To study the mechanism of dissociation of oxygen atoms on the CdS surface, we obtained the distributions of valence electrons by energy zones and the intersections of spatial distributions of the density of valence electrons in planes (100) and (110) of an eight-layer CdS film without oxygen, and CdS film with different oxygen concentration content.

It has been shown that the inclusion of oxygen atoms affects the structural and electrical parameters of a thin film of CdS. It was found that when oxygen atoms adsorption to the CdS surface, oxygen taking electrons from the surface atoms of the CdS film increases its catalytic activity. In this case, the concentration of oxygen should not exceed 12.5%.

The results give a deeper understanding of catalytic processes to control the optimization of electron and energy parameters of thin films of CdS:O for solar panels, etc.

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Моделювання структурних та електричних параметрів тонких плівок CdS

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На основі розрахунків з перших принципів нами отримано розподіли густини валентних електронів та електронні енергетичні спектри для плівки CdS з різним вмістом кисню. Згідно результатів розрахунків встановлено, що атоми кисню при адсорбції на поверхню CdS, виступають як негативно заряджені іони. Забираючи електрони з поверхні відповідної плівкової системи, атоми кисню підвищують каталітичну активність плівки CdS.

Ключові слова: наноструктури, густина станів, метод теорії функціоналу електронної густини, псевдопотенціал, сонячні елементи, наночастинки, перехідні метали.