

Effect of oxidation method of cadmium and zinc chalcogenide substrates on physical properties of CdO and ZnO heterolayers

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Formation of CdO and ZnO heterolayers on cadmium and zinc chalcogenide substrates by oxidation and effect of the formation method on physical properties of the oxides are discussed.

Обсуждаются методы получения гетерослоев CdO и ZnO окислением подложек халькогенидов кадмия и цинка и влияние способа получения на физические свойства оксидов.

Most modern electronic devices are based on heterojunctions [1]. The more and more importance therein is taken by the oxide layers of wideband semiconductors, especially ZnO and CdO [2, 3]. Their physical properties (optical, electro-optical, piezoelectric) provide the potential for the use of such materials in solar cells, electroluminescent and liquid-crystal displays, different type of light-emitting diodes, spin-functional devices, etc. Therefore, besides of further improvement and development of single-crystal growth methods, a great attention is given to the layer formation methods of these materials.

At present, the main widely used formation methods of ZnO and CdO are the well-approved processes of epitaxy (molecular-beam, vapor-phase, MOC hybrid technology, etc.), different electrochemical methods and especially magnetron sputtering [2–5]. However, even the latter one is rather difficult and expensive. Therefore, actual is the search for new methods to prepare ZnO and CdO and especially heterolayers thereof as active elements of different sensors. Such layers can be provided by thermal annealing

in air which allows to get, in particular, ZnO layers on ZnTe substrate [6]. In this work, studied was the formation of ZnO layers on zinc chalcogenides (ZnTe, ZnSe, ZnS) and CdO on cadmium chalcogenide (CdTe, CdSe, CdS) by that method and the properties of heterolayers obtained.

Our investigations have shown that ZnO and CdO heterolayers can be obtained by oxidation of cadmium and zinc chalcogenide single crystals used as substrates [7, 8]. As the base substrates, bulk crystals were selected grown from the melt by the Bridgman technique [9]. Plates $4 \times 4 \times 1$ mm³ size were cut out of the crystals and treated mechanically and chemically. The high quality of surface layer is confirmed by efficient volume luminescence in an appropriate spectral region characteristic for each of the used materials. The heterolayers were formed by isothermal annealing of base substrates in air at 700–1100°C [7, 8]. The layer thickness amounts 0.1–0.2 mm and is checked by luminescence and optical reflection studies and by visual microscopic observation of oblique micro sections of the obtained samples.

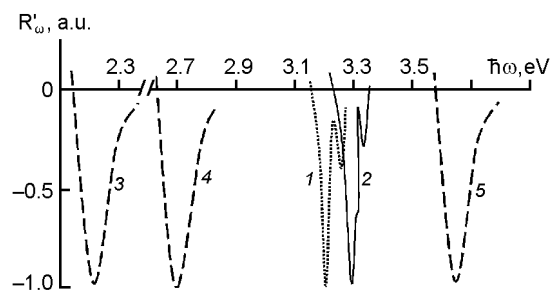


Fig. 1. Differential reflection spectra of β -ZnO (1) and α -ZnO (2) heterolayers synthesized on ZnTe (3), ZnSe (4), ZnS (5) substrated at 300 K.

The annealing method is the main factor defining the properties of the layers obtained. Two basic oxidation techniques were used, using molecular and atomic oxygen. In the latter case, the oxygen molecules were activated using a DRSH-250 mercury lamp with the radiation penetrating through the transparent quartz furnace walls.

As the band gap of ZnO and CdO heterolayers exceeds the similar parameter of cadmium and zinc chalcogenide substrates (except for ZnS), its width was determined from the optical reflection spectra. Those were studied using the λ -modulation method [10]. Measurements of differential spectra R'_ω , made it possible to set important dependences of the oxide properties on the above-mentioned oxidation methods and also to identify the crystal lattice modification. It has been established that ZnO heterolayers can be obtained on all types of substrates by oxidation both in molecular and atomic oxygen, Fig. 1. Each of the methods provides formation of cubic or hexagonal ZnO modification, respectively. This is confirmed by measuring the band gap width. In the case of oxidation in molecular oxygen, this value is $E_g = 3.2$ eV and does not depend on the substrate type. That value is in accordance with the known study results of cubic zinc oxide, β -ZnO [2]. The formation of this structure type is due to the isovalent substitution of chalcogen atoms with oxygen, as well as in the case of other VI group elements in wideband II–VI compounds [11]. It has been shown [12, 13] that such process is of diffusion character and the corresponding solid solution is formed between the heterolayer and substrate that eliminates completely the parameter mismatch of the materials in contact. As a result, the crystal structure of heterolayers is cubic and identical with those of ZnSe, ZnS, and

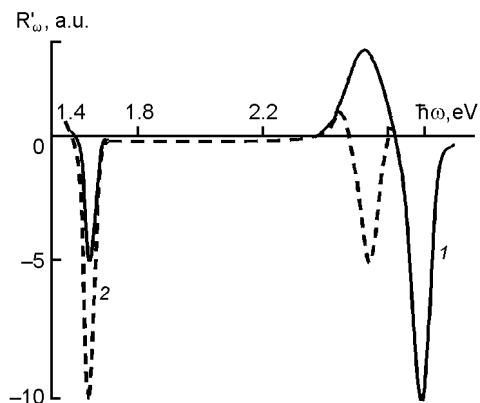


Fig. 2. Differential reflection spectra of CdO heterolayer (1) and CdTe substrate (2) at 300 K.

ZnTe substrates. In other words, their structure forms and stabilizes the atomic arrangement in the crystal lattice of β -ZnO. A quite other process takes place at oxidation in the photoactivated oxygen. In this case, the zinc oxide is formed by growth of layers on the crystal lattice of zinc chalcogenide substrates. Its components are formed due to diffusion of the metal atoms from the substrate volume to its surface and oxygen atoms from the vapor phase [14]. Such formation and growth process of ZnO can be considered as a quasi-epitaxial one. The spectral studies show formation of heterolayers with $E_g = 3.3$ eV. This value is in agreement with the band gap width of α -ZnO [2, 3].

Thus, it can be stated that ZnO heterolayers can be obtained on all types of zinc chalcogenide substrates, and modification of the crystal structure thereof depends only on the preparation method, the isovalent substitution or quasiepitaxial growth. The formation of cubic or hexagonal heterolayers is confirmed by the E_g value as well as by the features of band structure characteristic for each of those. So in the differential optical reflection spectra of β -ZnO, there is a singularity due to only spin-orbit interaction, $\Delta_{so} \approx 0.065$ eV. For α -ZnO, optical transitions are also observed involving the subband split by the crystalline field, namely, $\Delta_{cr} \approx 0.017$ eV. In this case, the spin-orbital split value diminishes insignificantly and makes $\Delta_{so} \approx 0.055$ eV. The results obtained agree well with the known literature data [2, 3]. It is to note that at the study of base substrates, their differential reflection spectra give the typical E_g values [9, 14].

In contrast to zinc oxide, the CdO heterolayers are formed only at oxidation of cadmium chalcogenides in atomic oxygen

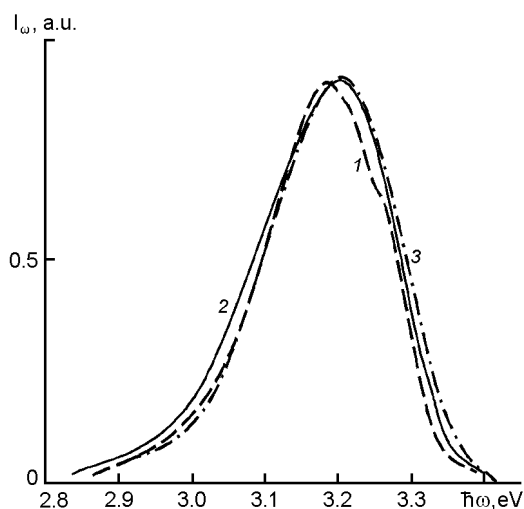


Fig. 3. Photoluminescence spectra of ZnO heterolayers obtained by isovalent substitution on ZnTe (1), ZnSe (2) and ZnS (3) substrates.

(quasi-epitaxial growth). The formation of CdO layer at the isothermal annealing in photoactivated oxygen is confirmed by λ -modulated reflection spectra. A peak is observed at photon energy of ~ 2.6 eV. This value agrees with literature data identifying the CdO band gap width at 2.5–2.7 eV [15]. A typical example of differential spectra are the reflection curves of cadmium oxide heterolayers on CdTe substrates, Fig. 2. Note that the spectra also contain singularities at 1.5 eV and 2.4 eV. They are explained by optical transitions in CdTe substrates, since the CdO heterolayers are optically transparent in this region. The value $E_{gA} = 1.5$ eV corresponds to the band-to-band transitions, while $E_{gc} = 2.4$ eV, to those involving the valence subband split due to spin-orbit coupling Δ_{so} . Indeed, difference $E_{gA} - E_{gc}$ makes 0.9 eV and agrees with $\Delta_{so} \approx 0.9$ eV for CdTe [9, 14].

An important property of materials for sensors is the luminescence. In this connection, attention is to be paid to that a radiation appears only in ZnO heterolayers obtained by oxidation. An intense photoluminescence is observed in layers obtained by isovalent substitution. The photoluminescence quantum efficiency attains $\eta \sim 15\%$ at 300 K. The radiation is localized in the edge region, as well as in the case of II–VI compound heterolayers grown by isovalent substitution [11, 13]. The spectral maximum is at $\hbar\omega_m = 3.18$ eV, Fig. 3. Its position and the spectrum shape is essentially

independent of the zinc chalcogenide substrate type. Note that the photoluminescence encompasses the photon energy region $\hbar\omega > E_g$. Since for the β -ZnO heterolayers obtained, $E_g \approx 3.2$ eV, its nature can be interpreted as a consequence of radiative band-to-band transitions [7]. The final data on the luminescence mechanisms responsible for radiation, can be obtained by additional researches.

Note that the obtained ZnO and CdO heterolayers have electronic conductivity. In the case of formation thereof on p -CdTe and p -ZnTe substrates, an anisotype heterojunction are formed. Thus, this technology is of good promise in development of different sensors types. It is to note also, that annealing of zinc chalcogenides in molecular oxygen allows synthesizing ZnO heterolayers with an efficient luminescence.

Thus, the results obtained have confirmed the potential for production of ZnO and CdO heterolayers by oxidizing the single-crystals substrates of zinc (ZnTe, ZnSe and ZnS) and cadmium (CdTe, CdSe, CdS) chalcogenides. Varying the annealing method, it is possible to change purposefully the physical properties of such wide bandgap oxides of II–VI compounds.

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Вплив методу окислення підкладок халькогенідів кадмію і цинку на фізичні властивості гетерошарів CdO і ZnO

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Обговорюються методи створення гетерошарів CdO і ZnO окисленням підкладок халькогенідів кадмію і цинку та вплив способу отримання на фізичні властивості оксидів.