THE OPTICAL PROPERTIES OF ZnO:Al FILMS DEPOSITED ON THE (0001) SURFACE OF ε-GaSe SINGLE CRYSTALS

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Abstract

ZnO:Al-GaSe:Cd heterojunctions were obtained by the thermal treatment of Cd-doped GaSe lamellae covered with a Zn nanometric layer containing different Al concentrations. The heterostructures were structurally (XRD) and optically (reflection spectra and dielectric permittivity for 1.5÷5.0 eV) analyzed.

1. Introduction

Heterojunctions based on $A^{III}B^{VI}$ stratified semiconductors and their ($A^{III}B^{VI}$) oxides, as well as oxide heterojunctions with I-II group metals optically transparent in a wide wavelength region, occupy a special place in the physics of semiconductor devices. The weak cohesion between the packings allows the cleavage of the single crystals as lamellae (parallel planes) having perfect surfaces at the atomic scale. This property, along with low concentration of the surface density of states, classify these materials as ideal objects for the elaboration of a large variety of optoelectronic devices, such as detectors of ionizing radiation, photodiodes, photovoltaic cells, and many other [1-6].

The photosensitivity curve of gallium monoselenide steeply decreases in the blue-violet spectral region regardless of the high structural quality of the surface [7]. A nanometric own oxide layer deposited in-between optical window electrode (In_2O_3) and the semiconductor results in the increase of the photosensitivity in the green-violet spectral region [8]. Multiple investigations carried out recently unambiguously demonstrate that the physical properties of the structures based on $A^{III}B^{VI}$ stratified semiconductors are mostly determined by the type and characteristics of the optically transparent oxide [9, 10]. Zinc oxide, being polycrystalline, undoped and doped with low Al concentrations is a highly conductive material [7], and it is optically transparent in the visible spectral region [11]. ZnO has a certain amount of properties widely used in various devices (acoustic cells, varistor, gas sensors, etc. [12-17]). Nanocrystalline ZnO layers obtained by various technologies (spray pyrolysis, CBD, pulsed laser deposition, CVD, etc.) have a good adhesion to the surface of semiconductor or dielectric substrates. This fact is widely used in optoelectronic and solar energy conversion devices [15], photodetectors of UV radiation [16] and sources of laser radiation [17]. The characteristics of the devices based on ZnO and ZnO:Al are highly influenced by the properties of semiconductors used as a substrate.

This paper presents the investigations on some optical properties of nanometric ZnO doped with aluminium (0.05÷5.0 at %) deposited onto GaSe substrates.

2. Experimental

p-GaSe single crystals undoped and doped with Cd (0.01 at %) were grown by Bridgman-Stockbarger method using the material synthesized from elementary components (Ga (5N) and Se (4N) in stoichiometric ratios). Plane parallel lamellae were prepared by the cleavage of bulk single crystal material perpendicular to the C_6 crystallographic axis. Their thickness was 20÷50 μm, and the surface area was 1.5÷2.0 cm^2. Indium electrodes used in electrical measurements were obtained by thermal evaporation in vacuum ($5 \cdot 10^{-5}$ torr). The hole concentration of $1.3 \cdot 10^{15}$ cm^{-3} was determined from the Hall and electrical conductivity measurements at room temperature. Thermal evaporation in vacuum ($p=5.0 \cdot 10^{-5}$ torr) was used for Zn doped with Al (0.05; 0.5; 1.0 and 5.0 at %) deposition onto as-cleaved surfaces of ε-GaSe lamellae. The thickness of the Zn:Al layer was 80÷110 nm. The primary material Zn:Al was obtained by melting the Zn and Al (5N) elementary components in vacuum at 690÷720ºC. The aluminum content in the primary Zn:Al material and in thin films deposited onto the (0001) surface of GaSe:Cd lamella was determined from atomic-emission spectroscopy. The Al content in thin layers did not differ by more than 10 % of the concentration of the source material used for evaporation. The Zn:Al was deposited onto SiO_2 substrate as well during the same technological step. The oxidation of the metal layers deposited on the (0001) surface of the GaSe:Cd lamellae and from the SiO_2 plates was carried out at 420ºC for 15 min in normal ambient.

The crystalline structure of the ZnO:Al thin layers from the surface of the GaSe lamellae and SiO_2 amorphous plates was analyzed using an XRD-6000 Shimadzu diffractometer. The ellipsometric investigations of the ZnO:Al films in the UV spectral region were carried out by use of a complex device based on a UV-vis VSU-2 spectrophotometer. Two Glan-Thomson prisms made of quartz and optically contacted (polarization degree was 95%) were used as analyzer and polarizer. The Rochon prism (deviation angle of 2^o) and a Glan-Thomson prism made of $CaCO_3$ were used as an analyzer and a polarizer in the visible and near IR spectral regions. The optical signal was recorded by a multialkaline cathode (Na-K-Sb-Cs). A 120-W Xe lamp was used as a light source. The spectral resolution of the measurement system did not exceed 5 Å in the UV and 12 Å in the yellow-orange spectral regions.

3. Results and discussion

3.1. Crystalline structure

The X-ray diffractogram from the ε-GaSe lamella (Fig. 1) for the 2θ angles from 10º to 90º consists of high intensity lines at 2θ=11.14º and 22.22º corresponding to the (002) and (004) planes, respectively, and 4 lower intensity diffraction peaks at 45.51º, 57.82º, 70.87º, 85.11º, corresponding to diffraction from the (008), (0010), (0012), and (0014) systems of atomic planes, respectively.

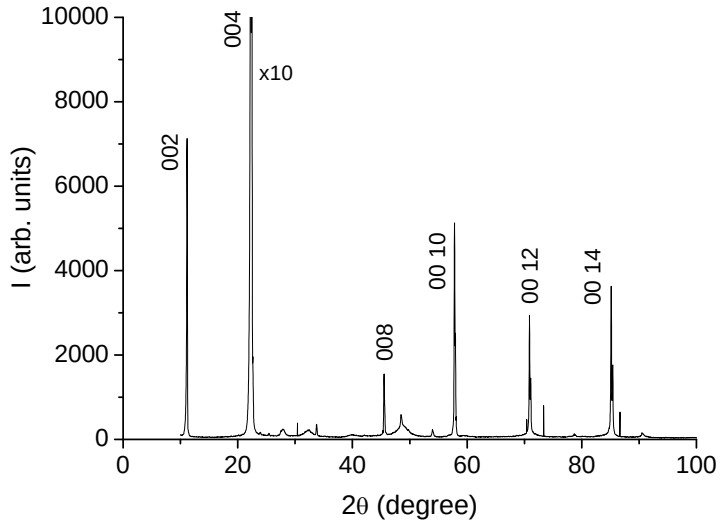

Fig. 1. XRD pattern of as-deposited sample of GaSe doped with Cd (0.01 at %).

The XRD pattern for ZnO:Al–GaSe heterojunction contains a diffraction band having a complex contour and average intensity localized in 2θ angles interval starting with 35.5º and going up to 37.5º, with peak intensity at 2θ=36.27º, along with high intensity lines caused by GaSe substrate (Fig. 2). This band is identified as diffraction from the (101) planes of the ZnO:Al crystallites. It is known [18] that, for this angle interval, the peak corresponding to diffraction from the (002) ensemble of the planes of Zn crystallites is localized at 2θ (36.25º). Considering that the XRD pattern from the ZnO:Al–GaSe heterojunction does not contain a peak from the (101) planes (2θ=43.4º) of the Zn crystallites, one can conclude that a thermal treatment at 420ºC for 15 min results in the complete oxidation of the Zn:Al film from the surface of the microlamelae of ε-GaSe lamella.

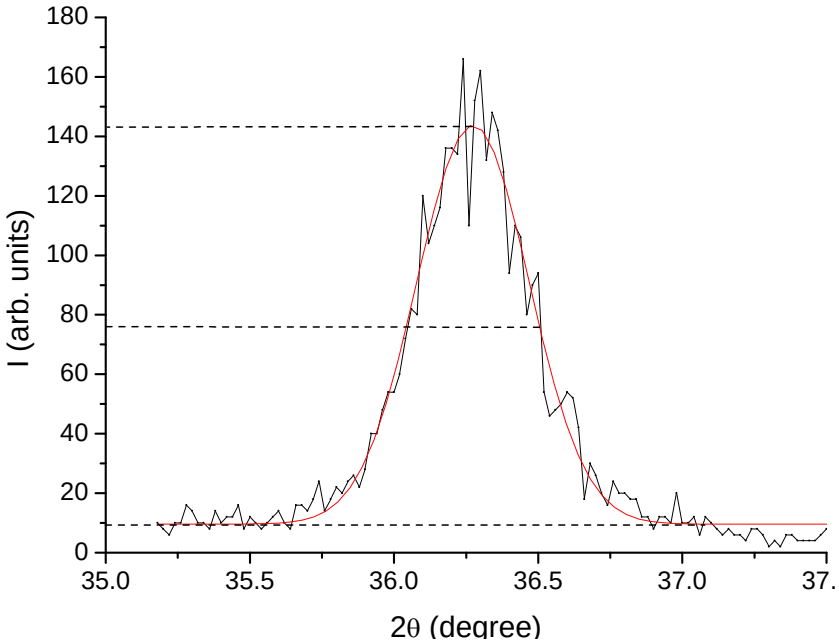

Fig. 2. Contour of the diffraction line corresponding to the 2θ=36.27º for the(101) oriented ZnO:Al crystallites.

The diffraction peak intensity from the (101) planes of the ZnO is localized at 2θ=36.25º [19], and the substitution of the Zn atoms with Al ones in the ZnO crystalline lattice results in its shift to a higher diffraction angle.

At submicronic sizes of crystallites, the XRD diffraction line contour represents narrow bands, and their width increases along with decrease of the crystallites' linear dimensions. The average size of the crystallites d_m in a ZnO thin film can be estimated using the formula [20]:

$$d_m = \frac{0.94\lambda}{\Delta\theta \cdot \cos\theta}, \quad (1)$$

where θ is the diffraction angle, λ is the X-ray wavelength, and Δθ is the width of the diffraction bands at half intensity.

The halfwidth of the X-ray band (CuK_α=1.5405 Å) which has the peak intensity localized at 2θ=36.27º for ZnO:Al thin films in ZnO:Al–GaSe heterojunctions with an Al content of 0.05, 0.5, 1.0, and 5.0 at % lies in an interval of 2.1º÷2.9º. The average crystallites sizes corresponding to the above mentioned halfwidth are about 3.0÷4.5 nm.

3.2. Optical reflection properties

The reflection spectra recorded from the as-cleaved surface of undoped ε-GaSe, the one doped with 0.01 at % Cd, and from the surface of ZnO:Al thin film, component of ZnO:Al–GaSe heterojunction, with two concentrations of Al in zinc oxide layer, in the 1.5÷4.5 eV energetic interval are given in Fig. 3. The peculiarity weakly revealed at about ~2.0 eV in the reflection spectra R(hν) of the ε-GaSe crystal (curve 1) and of the ZnO (0.5 at % Al)–GaSe heterojunction (curve 3) is determined by electronic transitions between the valence band top and the conduction band bottom at the center of the Brillouin zone of the GaSe crystal. Due to spin-orbit interaction in the valence band top, in the center of Brillouin zone, the superposition of the Γ_4^- state (corresponds to the ground state of the Ga atom) and one state of the four bands (Γ_5^+, Γ_5^-, Γ_6^+, Γ_0^-) localized approx. 0.5 eV lower than Γ_4^- occur [21]. The slopes in the 3.3÷3.4 eV region of the reflection spectra of GaSe primary crystals (curve 1) and of ZnO:Al–GaSe heterojunctions (curves 3, 4, Fig. 3) correspond to electronic transitions between the first valence subband and the conduction band at the center of the Brillouin ($\Gamma_5^+ \leftrightarrow \Gamma_3^+$) zone.

The reflection spectra R(hν) of the GaSe crystals and GaSe (Cd) crystals are localized for hν > 4.25 eV is determined by electronic transitions between extremities of the valence and conduction bands in the K point of the Brillouin zone [21].

The presence of the polycrystalline ZnO layer doped with 0.5 at % Al (Fig. 3, curve 3) results only in a decrease in the reflection coefficient in the visible spectral region. The reflection coefficient of the ZnO (5.0 at % Al) layer of the heterojunction increase (curve 4) for hν > 3.5 eV is determined by the presence of the crystallization seed of the aluminum oxide structurally having a trigonal lattice along with the ZnO nanocrystallites having a hexagonal lattice. The mixture of the two phases, i.e., zinc oxide and aluminum oxide, results in the formation of high defect concentration in GaSe at the interface of the ZnO (5.0 at % Al)–GaSe heterojunction and in the attenuation of the reflection bands "deep" in the fundamental absorption region of gallium monoselenide at 3.30 and 4.25 eV.

The increase of the reflection coefficient from the surface of the ZnO:Al film of the heterojunctions which have 5.0 at % Al with increasing photon energy for hν > 3.5 eV is the result of optical transitions in crystallization seeds of the aluminum oxide in ZnO layer.

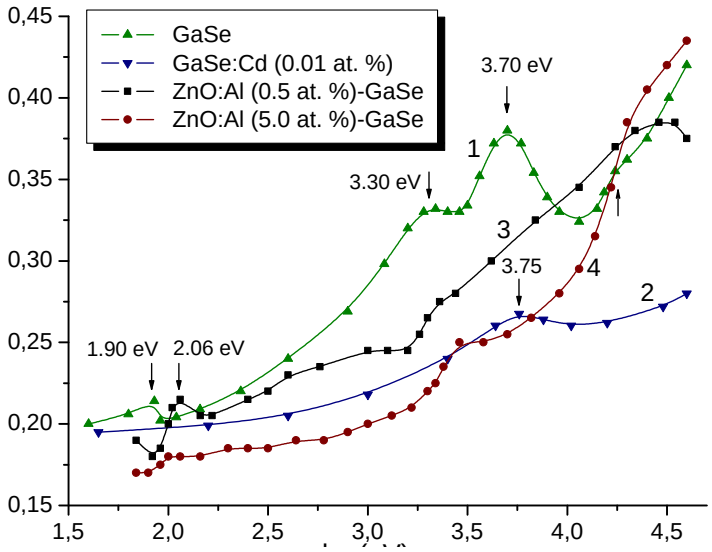

Fig. 3. Reflection spectra from the (0001) surface of the ε-GaSe undoped lamella (1), the one doped with 0.01 at % Cd (2), and from the surface of ZnO:Al layer of ZnO:Al–GaSe heterojunctions for two aluminum concentrations: 0.5 at % (3) and 5.0 at % (4).

3.3. ε_1 and ε_2 optical functions

Figure 4 presents the dielectric permittivity spectral distribution ($\varepsilon_1(h\nu)$ and $\varepsilon_2(h\nu)$) for ZnO (0.5 at % Al) films components of ZnO:Al–GaSe heterojunctions being 165 nm (curves 1a and 1b) and 112 nm (curves 2a and 2b) thick and grown on the (0001) surface of GaSe:Cd lamella.

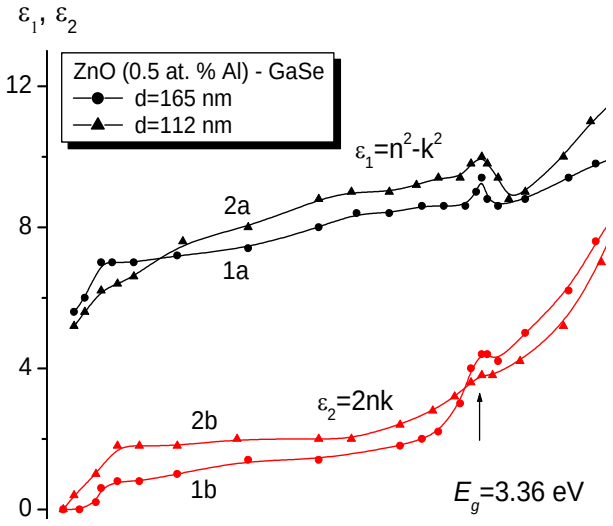

Fig. 4. Spectral distribution of the optical functions $\varepsilon_1(h\nu)$ and $\varepsilon_2(h\nu)$ for ZnO (0.5 at % Al) films having thicknesses of 165 (1) and 112 nm (2).

The highly pronounced increase of the $\varepsilon_1(h\nu)$ and $\varepsilon_2(h\nu)$ functions in 1.9÷2.0 eV region is determined by the increase in the absorption coefficient in GaSe substrate. The peculiarities of the optical functions $\varepsilon_1(h\nu)$ and $\varepsilon_2(h\nu)$ localized at 3.35÷3.50 eV are caused by the presence of the absorption band edge in ZnO:Al layers and by the nature of the electronic transitions in GaSe substrate. The bandgap of ZnO (0.5 at % Al) film determined by the edge of $\varepsilon_2(h\nu)$ function is 3.36 eV and correlates well with the one determined from the absorption spectra of ZnO:Al thin films deposited on quartz substrates.

4. Conclusions

- ZnO:Al-GaSe heterojunctions were obtained by thermal treatment at 420ºC of the GaSe (0.01 at % Cd) single crystalline plates covered by Zn nanometric layer containing 0.05, 0.5, 1.0, and 5.0 at % Al;

- The ZnO:Al layers from the (0001) surface of GaSe lamella consist of crystallites with average dimensions of 3.0÷4.5 nm.

- Dielectric permittivity ε_1 and ε_2 of ZnO:Al films, component of ZnO:Al–GaSe heterojunctions, depends on the thickness of the ZnO:Al film and monotonically increases with energy in the 2.0÷4.0 eV spectral region.

- The bandgap of the ZnO (0.5 at % Al) film determined by the edge of the $\varepsilon_2(h\nu)$ function is 3.36 eV.

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