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Optical and photoelectrical properties of GaS and CdTe thin FILMS, components of GaS/CdTe heterojunctions

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In the paper, experimental results concerning the absorption and photosensibility spectral dependence of GaS and CdTe thin film components of GaS/CdTe heterojunctions are presented. GaS films (d = 0.06 μm – 2.8 μm) were deposited onto ITO substrate by laser light pulses. CdTe films (d = 3.6 μm) were deposited onto GaS films by close-spaced sublimation technique. At the fundamental absorption edge, the absorption coefficient of CdTe layers increases of five orders of magnitude in a narrow 40 – 100 meV energy range, up to 4 10^4cm^{-1}. At room temperature, the energy band of GaS/CdTe heterojunctions photosensitivity is 1.45 eV-2.75 eV, the photocurrent having a constant value up to 2.0 eV photon energy.

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1. Introduction

CdTe thin films are widely used in optoelectronic devices technology as generator of non-equilibrium charge carriers [1–3]. Due its high absorption coefficient (> 10^4 cm^{-1}) and optimum direct band-gap of about 1.5 eV which well matches with the solar spectrum, CdTe thin films are one of most promising photovoltaic materials. Polycrystalline thin film CdS/CdTe heterojunctions have been extensively investigated with respect to their potential application for low-cost and high-efficiency thin film solar cells. The reported efficiency of about 16% [4, 5] of these solar cells is lower than the theoretical calculated maximum value of about 28% [6, 7]. For the further improvement of performance of such solar cells, the study regarding the optimization of the properties of device component films is still necessary.

Beside other physical properties, the optical and photoelectrical properties of device component films are widely used for characterization of quality of respective devices. The results obtained by different researchers revealed that the photosensitivity band of CdS/CdTe heterojunctions is localized in the 1.4 eV ÷ 2.4 eV energy range, but is constant only in a narrow interval (1.55 eV ÷ 1.85 eV) and decreases for the remaining range [8].

The widening of the photosensitivity band of CdTe-based solar cells to higher energy region is one of the possibilities to increase their efficiency. This can be obtained by the substitution of CdS thin films having a direct optical band gap with larger band gap semiconductor thin films having both indirect and direct optical transitions. The GaS thin films are one of such materials due to its high band gap value (≈ 2.5 eV) and specific character of crystallization as layers [9 – 12]. However, until now, very few data are available in literature on physical properties of GaS/CdTe heterojunctions.

In the present paper, the optical and photoelectrical properties of GaS and CdTe thin films, components of ITO-GaS/CdTe-Metal structure in the fundamental absorption band edge, at the 78 K and 293 K are investigated.

2. Experimental

The GaS thin films have been deposited by "flash" evaporation of initial compound synthesized from elementary Ga (000) and S of spectral purity. The evaporation was performed by using a solid state laser focalized light pulses (λ = 1.06 μm, τ = 20 ns). The CdTe thin films have been deposited by close-spaced sublimation technique. The CdTe (1 % at. Sb) single crystal, grown by Bridgmann method, has been used as material for evaporation.

For the study of the optical and photoelectrical properties, the GaS layers with thicknesses ranged from 60 nm to 2.8 μm have been grown on the surface of ITO, and then the CdTe (d = 3.6 μm) has been grown onto GaS films.

The layer thickness d > 0.2 μm has been determined from absorption and reflection interference spectra whereas the thicknesses of thinner films were determined by ellipsometric measurements.

The optical transmittance, T, and reflectance, R, were recorded in the 1.3 eV- 3.2 eV spectral range using a spectrophotometric set-up based on diffraction grid monochromator (1200 mm^{-1}, 600 mm^{-1}). The monochromatic light beam has been recorded by a electronic photomultiplier with a multialcaline photocathode, with a 0.15 ÷ 0.9 μm sensitivity spectral region. The energetic resolution for R and T measurements was 0.5 meV.

Considering that in the absorption band edge region for GaS and CdTe, $n^2 >> k^2$, the absorption coefficient, α, were calculated based on the reflectance and transmittance data using the relation [13]:

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)} \quad , \qquad (1)$$

where d is samples thickness.

The photoconductivity spectral dependence has been measured using the same equipment. The 1000 W Xe lamp was used as light source. The spectral dependence has been measured by a VTH-1 thermoelement with 4 V/W sensitivity. The amorphous quartz cryostat was used for low temperature measurements. The sample was placed in liquid nitrogen vapors.

3. Results and discussion

In Fig.1 the absorption spectra at 293 K for GaS films component of GaS/CdTe heterojunction are given (curve 1). Also, the dependences $\lg \alpha = f(\hbar\omega)$ (curve 2) and $\alpha^{1/2} = f(\hbar\omega)$ (curve 3) are plotted in the same figure. The specific aspects of curves (2) and (3) from Fig.1 indicate the presence both of indirect and direct transitions in respective sample. Indeed, the GaS crystal (D_{6h}^4 symmetry) is characterized by indirect optical transition [12,14]. The valence band top is localized in the center of Brillouin zone and has Γ_2^- symmetry whereas the minimum of the conduction band is placed at the edge of the zone in K point (K_3^+ symmetry) [15]. The indirect transitions between these energy states can take place when optical radiations are absorbed. For such indirect allowed transitions, the dependence of the absorption coefficient, α, versus incident photon energy $\hbar\omega$ is given by the relation [16]:

$$\alpha\hbar\omega = A(\hbar\omega - E_g^i)^2 \quad , \qquad (2)$$

where A is a parameter independent of $\hbar\omega$ and E_g^i is the indirect band-gap.

As one can see from Fig. 1 (curve 3), the dependences $\alpha^{1/2}$ *vs.* $\hbar\omega$ is linear in the 2.8 eV ÷ 3.0 eV spectral range. This indicates that in the studied GaS films the indirect transitions take place. The indirect band gap of GaS layers, determined from the extrapolation of linear segment of $\alpha^{1/2} = f(\hbar\omega)$ dependence to α= 0 is 2.5 eV. This value is in good agreement with the data quoted by other researchers [9,12].

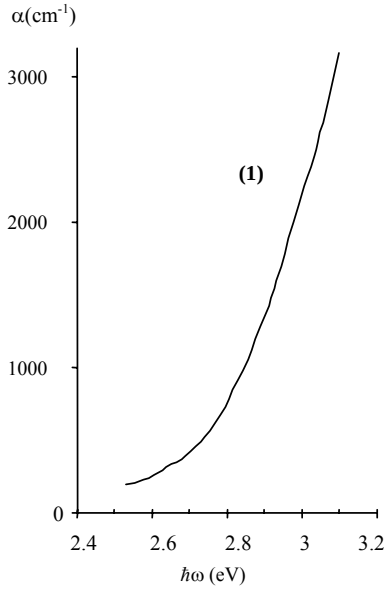
From Fig.1 also one results that in the vicinity of the fundamental absorption edge, the plot $\lg\alpha = f(\hbar\omega)$ (curve 2) is linear. This indicates that the dependences $\alpha = f(\hbar\omega)$ in respective spectral range can be described by the Urbach rule [17]:

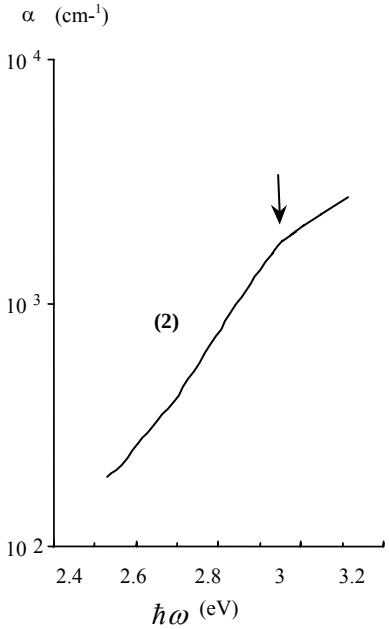
$$\alpha = \alpha_0 \exp\left[\frac{\gamma(\hbar\omega - E_0)}{kT}\right] \quad , \qquad (3)$$

where E_o denotes the optical band-gap and parameters α_o and γ depend on the semiconductor nature.

The modification of the slope of curve (2) beginning with photon energy of 2.95 eV indicates that along with indirect optical transitions, other electron transitions appear in the spectral range of 2.95 eV-3.1 eV. These can be the optical direct transitions that can take place between the electronic states in the center of Brillouin zone. Indeed, the energy gap between the valence band top and the minimum of the conduction band in the center of Brillouin zone in GaS single crystals is ~ 3.0 eV [15].

From Fig. 1 results that at photon energy of 2.95 eV, the value of the absorption coefficient due both to direct and indirect transitions is about 1.7×10^3 cm^{-1}.





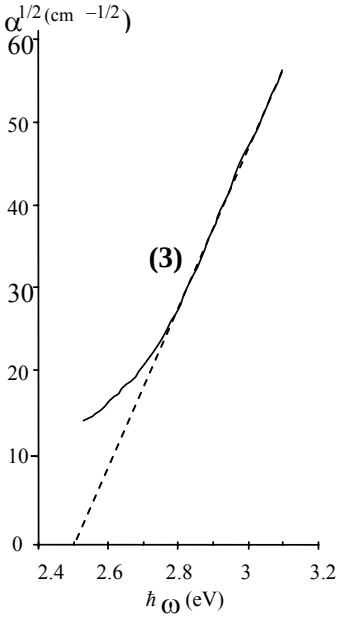


Fig. 1. Typical absorption spectra for GaS thin films at 293K. curve (1): $\alpha = f(\hbar\omega)$; curve(2): $\lg\alpha = f(\hbar\omega)$; curve (3): $\alpha^{1/2} = f(\hbar\omega)$.

The above conclusions are sustained by the obtained results regarding the spectral dependences of the photosensitivity of GaS thin film, plotted in Fig. 2. As one can observe, the GaS thin films have a great photosensitivity in the 300 nm (4.1 eV) – 500 nm (2.48 eV) spectral range. The energies corresponding to A' ($\hbar\omega_1$ = 2.5 eV) and B' ($\hbar\omega_2$ = 2.95 eV) particularities can be attributed to indirect and direct optical transitions of the electrons from the valence band top in the center of Brillouin zone (Γ point) to conduction band (K point and Γ point), respectively. The D maximum from Fig. 2 corresponds to $M_2^- \leftrightarrow M_1^+$ electronic transitions in M point of Brillouin zone, whereas the C particularity can be attributed to $\Gamma_2^- \leftrightarrow \Gamma_1^+$ electronic transition in the center of Brillouin zone [18].

The strong decrease of GaS film photosensitivity for λ > 500 nm $\hbar\omega < E_g^i = 2.5eV$ indicates that the studied GaS layers have a relative low concentration of the surface states. This fact can be due both to the used preparation technique of GaS films and to the particular characteristic of lattice bonding in the layer-type semiconductors of III-VI family at which belong the GaS crystal. In such materials, the inter-layer bonding is very weak (of van der Waals type) whereas the bonding inside layers is strong covalent [10, 19]. The laser light pulses technique used for film preparation determines a growth of GaS films having such sub-layers parallel to substrate surface. In this way, samples with lower concentration of unsatisfied chemical bonds at layer surface were deposited.

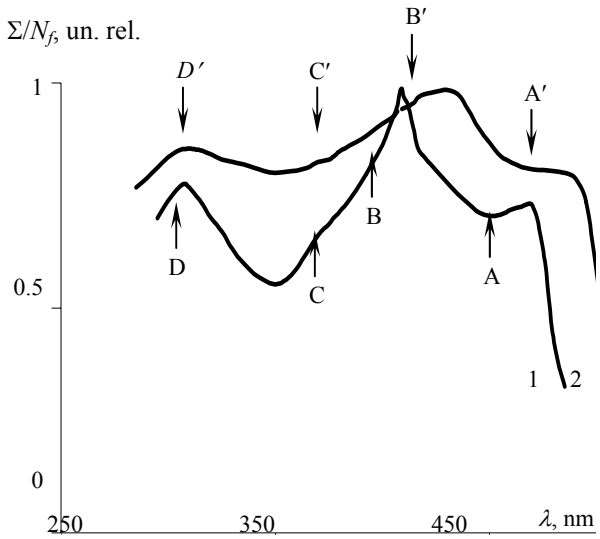


Fig. 2. The normalized spectral dependence of the photosensitivity for GaS films, at 78 K (1) and 293 K (2); (Σ/ N_f denotes the photocurrent/number of incident photons).

Besides GaS thin films, the optical and photoelectrical properties of CdTe thin films, component of GaS/CdTe junction have been also studied. In Fig. 3 the absorption spectra at the fundamental absorption edge of CdTe grown on GaS polycrystalline substrate are presented. As one can see, at room temperature, the optical absorption begins with photon energy of 1.34 eV, lower than the CdTe energy band gap (of 1.52 eV).

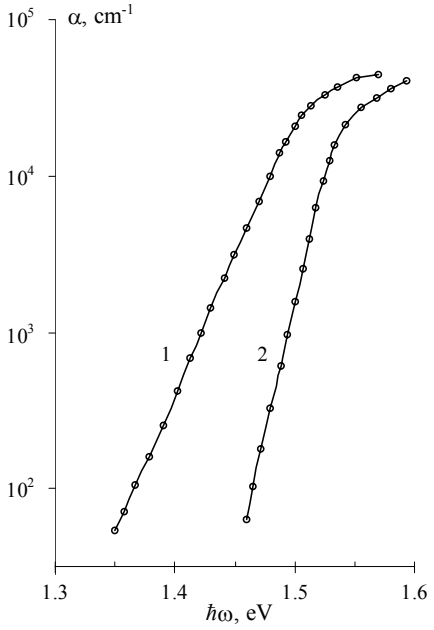
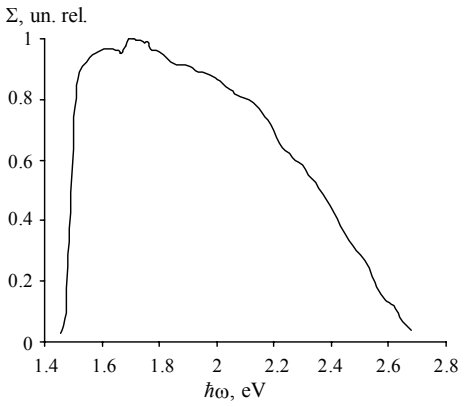


Fig. 3. The spectral dependence of the absorption coefficient at 293 K (1) and 78 K (2) for CdTe thin films deposited onto GaS substrate.

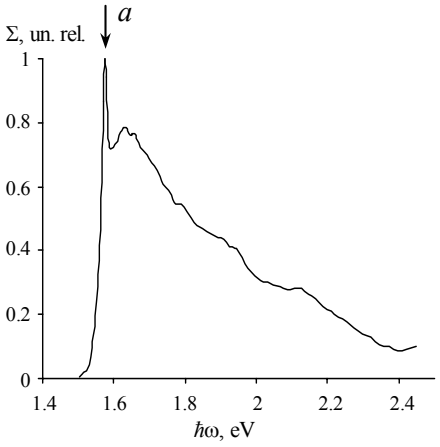
In the same figure, an increase with three orders of magnitude, up to about 4×10^4 cm^{-1} of the absorption

coefficient, in the 1.35 eV – 1.5 eV spectral range, can be also observed. The same order of magnitude for absorption coefficient have been reached in the CdTe layers grown from vapor phase on mica substrate [20] (about 9×10^4 cm^{-1} at $\hbar\omega \approx 1.53$ eV).

The exponential increase of α (vs energy) at 293 K as well as 78 K (Fig. 3) is characteristic for optical transitions with an excitons-fonons interaction in CdTe thin films [20]. In Fig.4 the normalized spectral dependence of the photocurrent for the CdTe film grown onto GaS substrate are shown. The sharp peak "*a*" in photoconductivity spectrum, at 78 K (Fig. 4b) correspond to the free exciton peak (1.581 eV) in monocrystalline CdTe layers [20].



(a)



(b)

Fig. 4. The normalized spectral dependence of the photocurrent for CdTe layers grown onto GaS substrate. (a) at 293 K; (b) at 78 K.

As it results from Fig.4b, the photosensitivity of CdTe layers at 78 K has a tendency to decrease after the excitonic band energetic position. If one assumes that with energy increase the surface states (low lifetime) lead to the decrease of the photocurrent, Σ, than one can conclude that the cooling of sample from 293 K to 78 K determines a considerable increase of the concentration of structural defects in CdTe grown on GaS layers, which creates low energy, low lifetime states.

From Fig. 4a on can be seen that at 293 K the photosensitivity spectral region of GaS/CdTe heterojunctions is 1.45 eV - 2.75 eV, Σ having a constant value up to 2.0 eV and decreasing afterwards with energy increase.

4. Conclusions

The absorption coefficient and photosensibility spectral dependence of GaS and CdTe thin films, component of GaS/CdTe heterojunctions have been investigated.

It was established that the fundamental absorption edge of the GaS thin films is determined by indirect optical transitions with value of 2.4 eV for respective optical band gap.

The absorption coefficient of GaS films slowly increases with photon energy increase, reaching its maximum value (of about 4×10^3 cm^{-1}) at the photon energy of 3.2 eV.

The spectral range of the GaS thin films photosensitivity is from 2.5 eV to 3.6 eV. In the high-energy spectral region, the GaS film photosensitivity is limited by the ITO lower optical transmittance.

At the fundamental absorption edge, the absorption coefficient of CdTe layer, component of GaS/CdTe heterojunction increases of five orders of magnitude in a narrow 40 – 100 meV energy range, up to 4×10^4 cm^{-1}.

The width of the spectral photosensitivity range of the GaS/CdTe heterojunctions is about of 1.3 eV, starting with 1.45 eV, and reaching the band edge of GaS.

The obtained results indicate that GaS films in GaS/CdTe heterojunctions determines a widening of the band photosensitivity of the heterojunction and can improve the optical quality of solar cells based on respective compounds.

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