Contributed paper

Irreversible gigantic modification of II-VI and III-V semiconductors optical properties

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The irreversible gigantic modification (IGM) process in semiconductors under simultaneous action of strongly polar liquid, with acceptors dissolved in it, and the influence of the optical radiation in the region of fundamental absorption were investigated.

During the IGM process the reflection and transmission coefficients are gradually varying in a modified near-surface semiconductor region. This enables to reduce controllably the real part of the complex refractive index in a near-surface semiconductor region (maximum down to 0.8), and vary both its chemical composition (by impurity redistribution) and the luminescence spectrum. After IGM process the modified semiconductor region gains and ability to modulate a monochromatic light beam (having wavelength in the region of semiconductor transparency) by another light beam with different wavelength (in the region of fundamental absorption).

The IGM phenomenon was used to fabricate elements and devices of the integrated semiconductor optics (input/output diffraction gratings, channel waveguides and input horns, directional optical couplers, ohmic contact areas, etc.). The IGM phenomenon enables to make antireflective optical elements (input and output butts of infrared lightguides, lenses, prisms, etc.).

1. Introduction

The topical tasks of today's integrated optics, micro- and quantum electronics are connected with the search and investigation of new mechanisms for irreversible modification of physical properties of semiconductors as well as development of new cheap technologies based on them.

This paper describes a new kind of modification of II–VI and III–V semiconducting compounds which occurs in them under simultaneous action of band-to-band-absorbable radiation onto the crystals plunged into strongly polar liquid containing dissolved acceptors [1–3].

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2. Experimental

We have carried out an investigation of the irreversible gigantic modification (IGM) of refraction with bulk and lamellar crystals of cadmium sulphide, cadmium telluride, and gallium arsenide. The experimental lay-out is shown in Fig. 1. The samples under the study were placed in the quartz cuvette with bidistilled water and then were irradiated by band-to-band-absorbable radiation of the He-Cd or Ar^+-laser with varying power density, using the neutral filter 21 (see Fig. 1) and lens 6, from 10 to 700 mW/cm^2.

The probing beam from the He-Ne laser 13 with the wavelength $\lambda = 6328$ Å was focused by the lens 15 in a 50 μm diameter spot on the sample 7. The photodiodes 17 and 26 recorded output power of the lasers 13 and 1, respectively. The photodiodes 12 and 23 recorded the beams reflected from the modified sample 7 at the

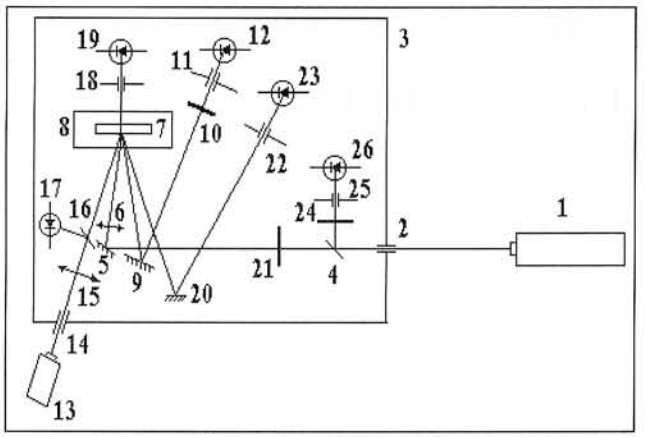

Fig.1. Experimental lay-out for modification of II-VI and III-V semiconductors.1 is He-Cd- or Ar^+-laser; 2, 14 are diaphragms in the light-protective screen 3; 4,16 are glass light-splitting plates; 5, 9, 20 are rotary mirrors; 6, 15 are lenses; 7 is a sample immersed in polar liquid (distilled water); 8 is a quartz cuvette; 10, 21, 24 are neutral attenuating filters; 11,18,22,25 are diaphragms; 12, 19, 17, 23, 26 are photodiodes FD-24K; 13 is He-Ne laser.

wavelengths $\lambda = 6328$ Å and $\lambda = 4416$ Å ($\lambda = 4488$ Å), respectively.

3. Experimental results

The typical IGM dynamics process is presented in Fig. 2 for a CdS single crystal. Curves 1 and 2 show, respectively, how the reflection R and transmission T

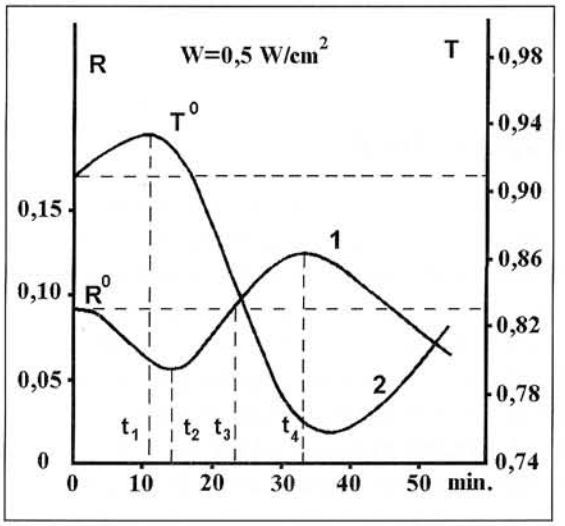

Fig. 2. Dynamics of low-temperature photohydromodification of the CdS single crystal. Dependence of the reflection R (curve 1) and transmission T (curve 2) coefficients at the wavelength of 6328 Å on the time of irradiation the CdS single crystal at the wavelength 4416 Å. Bulk CdS single crystal. (0001)A surface. Irradiation power density: 500 mW/cm^2.

coefficients depend on time in the case of 6328 Å wavelength radiation probing the near-surface region of the CdS modified single crystal. It is seen that at the first stage ($0 < t < t_2$) the reflection coefficient R decreases monotonously and the transmission coefficient T almost with the opposite phase, slowly increases during $0 < t < t_1$ period. At $t = t_1$ it achieves a maximum value and then smoothly decreases. It is also explicitly seen from Fig. 2 that the transmission coefficient T reaches a maximum earlier than the reflection coefficient comes to its minimum. Such behaviour is always observed for an IGM process and is its characteristic feature. It was found experimentally that the difference value ($t_2 - t_1$) depends on the resistivity of modified single crystals and it can reach up to 8 – 10 min.

In the reflected light, when $t > t_2$, a glittering film with characteristic metal glitter slowly appeared. At the same time in the interval of decreasing transmission the irradiated part of single crystal gradually acquired tints of brown passing light. By the moment of achieving a maximum (time t_4 in Fig. 2, curve 1) the reflection coefficient R (in water) of some bulk single crystals increased up to 0.2 that significantly exceeds the initial value of the CdS single crystal reflection coefficient in water, $R^0 = 0.091$.

In the case of high-resistivity ($\rho \propto 10^8$ to 10^9 Ωcm) lamellar single crystals of CdS the IGM process was qualitatively similar to that of low-resistance crystals. However it was characteristic that the maximum value achieved by the reflection coefficient R (by the time t_4 in Fig. 2) in all our experiments was lower than its initial value R^0 and a film glittering in reflected light (observed always under IGM of the low-resistance bulk samples) was weakly noticeable in this case.

Investigation of the angular dependence of the Brewster angle (Θ) in the case of layer-by-layer removing of the modified surface enabled to determine the refraction index profile (Fig. 3). As seen from Fig. 3, the modified region propagates in the single crystal down to depth of 1.2 μm while the strongest modification occurs in the 0.5 μm thick layer. The higher irradiation intensity was the stronger n_{eff} decreased; and for some low-resistance samples the effective refraction index of the near-surface region decreased down to 1.7.

We consider this as the strongest kind of known irreversible variations of the real part of the optical medium refraction index. Therefore, we refer to such variations of the refractive index as gigantic.

Using the methods of Auger spectroscopy and electron microprobe it was shown that under IGM a chemical composition of semiconductors in the 1.2 μm thick near-surface layer strongly changes.

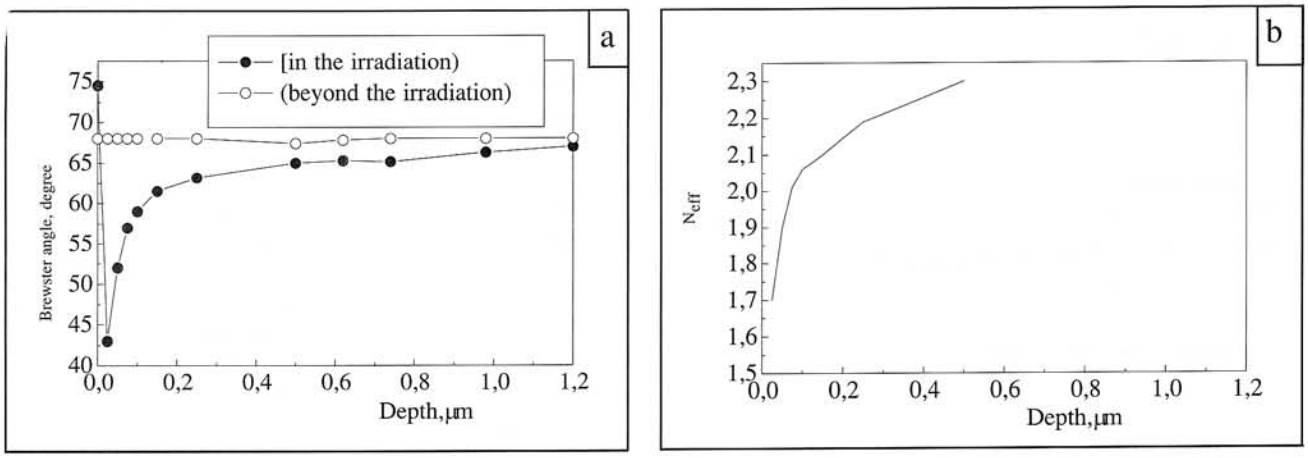

Fig. 3. Dependences of the Brewster angle for the CdS single crystal in the irradiated region and beyond it (a), and the effective refractive index in the irradiated region (b) on the removed layer thickness.

Physical properties of the 1.2 μm thick near-surface region in the II-VI and III-V compounds change so strongly (e.g., the refractive index real part for the CdS single crystal at the wavelength 6328 Å decreases from 2.48 down to 1.7) that it seems to be appropriate to refer to these materials as IGM-semiconductors. For example, during the process of gigantic modification the CdS single crystal surface acquires ability to change reversibly the reflection coefficient at a wavelength λ_1 due to action of light with another wavelength λ_2 (in the region of band-to-band absorbable radiation of a single crystal). A magnitude of the reflection coefficient variation at a probing light wavelength λ_1 depends on the irradiating light intensity at a wavelength λ_2. It was experimentally found that the wavelengths λ_1 and λ_2 are within the limits from 0.4 to 0.7 μm and from 0.4 to 0.51 μm, respectively. The lay-out of the set-up to measure the effects of additional illumination on the reflection R and transmission T coefficients of the CdS single crystal near-surface region is presented in Fig. 4. The single crystal 1 with the modified region 1' was mounted on the movable micrometric table 2. The probing radiation 3 with the wavelength (λ = 6328 Å was focused by the long-focus lens 9 at the investigated single crystal irradiated with the beams of the He-Cd laser 4 (power: 15 mW; power density averaged over the beam: 0.3 W/cm^2) with the wavelength λ = 4416 Å through the optical mechanical chopper 5 in a 50 μm diameter spot and it was directed to crystal at the 10° angle. The probing beam (50 μm diameter spot) overlapped in the modified region of the single crystal with the illuminated region or was removed to a distance ***l*** from it (just that very case is shown in Fig. 4). When the probing and illuminating beams were separated from each other by a distance ***l*** (***l*** was measured from the centre of the illuminating beam) the screen 6 was used (to eliminate additional illumination of radiation of the beam 4 in the region of incidence of the probing beam 3). The photodiodes 7' and 7 recorded intensity of the probing radiation beams 3' and 3 reflected and passed through the single crystal, respectively. Investigations of this phenomenon, which is referred to as the gigantic photoreflection (GP), have shown that changes of the reflection and transmission coefficients are very large.

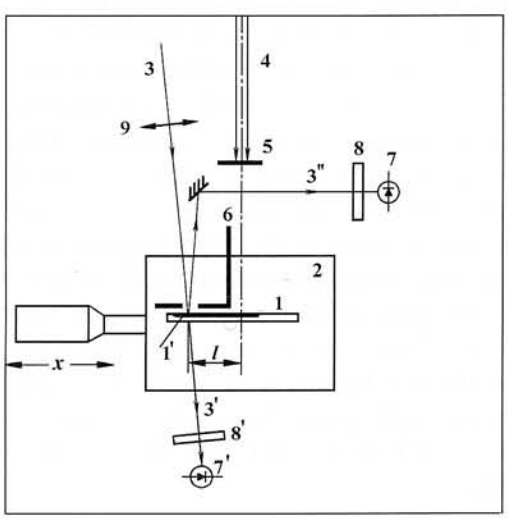

Fig. 4. Lay-out of measurements of illumination effects on the reflection, R, and transmission, T, coefficients of the modified near-surface region in the CdS single crystal. 1 is a CdS single crystal under modification; 2 is an micrometric table; 3 is an probing radiation with λ = 6328 Å; 3',3'' are reflected and passed probing radiation; 4 is an illumination beam with λ =4416 Å; 5 is an electromechanical chopper; 6 is an light-protective screen; 7',7'' are photodiodes; 8',8'' are light filters.

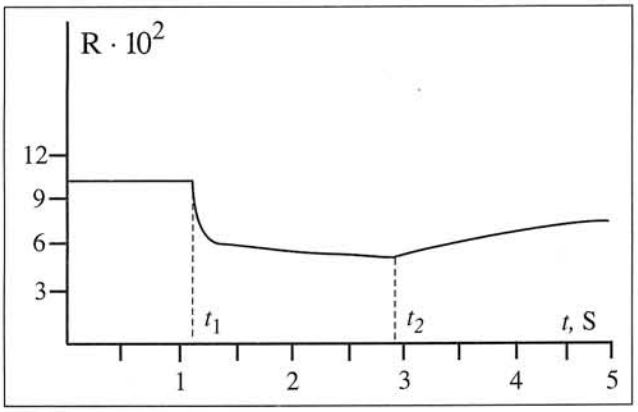

Fig. 5. The oscillogram of gigantic photoreflection for the modified near-surface region of the CdS single crystal (the GP sign is negative) at the wavelength λ =6328 Å with illumination of it in the interval t_2-t_1 by the 10 mW radiation with wavelength λ = 0.4416 μm. (1120) surface; l = 0.

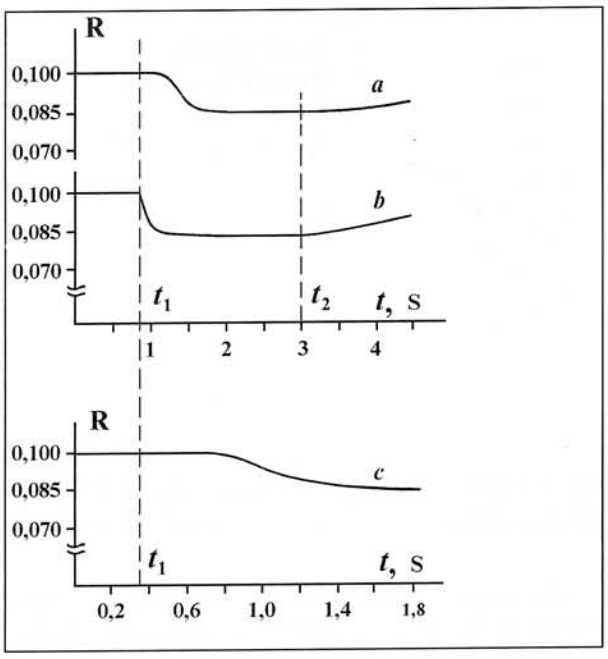

Fig. 6. Dependence of the gigantic photoreflection at the wavelength λ =6328 Å on the distance l between centres of the probing and illuminating beams: b is for l = 0 mm (overlapped beams), a and c are for l = 4.5 mm (non-overlapped beams). Total illumination power, P = 10 mW; illumination wavelength, λ = 4416 Å; illumination duration-(t_1–t_2).

For example, Fig. 5 shows the oscillogram of GP where the absolute variation of the reflection coefficient is 0.33 and its relative value is $\Delta R/R = 0.33$. For comparison it should be noticed that the maximum value of $\Delta R/R$ in the photoreflection effect in semiconductors of the II–VI compound type was achieved only in a narrow region of the exciton resonance and it was equal to 10^{-2}, i.e., under GP a relative variation of the reflection coefficient is at least two orders of magnitude as large as compared that of usual photoreflection. The GP changes for all the samples were reversible.

The time τ_σ of transition from the dark reflection coefficient, R_D, to its value with illumination, R_C, was for various samples within the limits from 10^{-2} to 1s while the recovery time of the reflection coefficient after switching off illumination to its initial value was longer than τ_σ, not exceeding, however, 10 s. We have found that for investigated samples, before and after their modification, within the studied range of intensity the time of the stationary photocurrent establishing, τ_σ, does not exceed 1–2 ms. It is much less than the transition time τ_σ.

When illuminating the single crystal surface at some distance from the probing zone ($l \neq 0$ in Fig. 4), the reflection coefficient R variation occurs with some time delay in regard to the front edge of the illumination pulse (the front edge duration of the illumination pulse did not exceed 1 ms), which is seen from Fig. 6 where the R(t) oscillograms for the lamellar single crystal with dimensions: $2 \times 0.05 \times 0.15$ mm^3 under illumination by the 10 mW and 1 mm diameter beam directly in the probing zone (l = 0) at the distance l = 4.5 mm from it are presented. In the case of spatial separation of the probing beam from the illuminating one the reflection coefficient of the near-surface region in the point of observation (l = 4.5 mm) begins to change with a large time delay (400 ms) in regard to the front edge of the illumination pulse while the front edge of transition from R_D to R_C is more prolonged. The longest distance of the illumination zone from the probing one when illumination still influenced the value of R in the probing zone was equal in our experiments to 17 mm. At the same time the delay τ_3, increased in fact linearly with increasing distance between the probing and illumination zones within the limits from 1 to 17 mm with the coefficient 100 ms/mm.

4. Summary

The carried out experiments have shown that irreversible gigantic modification of the II–VI and III–V semiconducting compounds causes irreversible changes of refraction coefficient and chemical composition of their near-surface region and this region acquires new physical properties.

5. References

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