UDC: 621.315.592

INFLUENCE OF THERMAL ANNEALING ON PHOTOELECTRICAL PROPERTIES OF GaS MONOCRYSTALS WERE IMPLANTED PROTONS

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Abstract: The proposed work is devoted to the influence of protons with 70 keV energy using the method of ion implantation $1 \cdot 10^{15}$ sm⁻² dose on the optical and photoelectrical properties of the GaS monocrystal. The photoconductivity rise was observed in the 490 nm – 900 nm wavelength interval as the passage of time. In the 505 nm wavelength photosensitivity was increased to 1.66 times, but in the 670-750 nm wavelength it was increased to 5,3 times. The location of the maximum peak which compatibe to the GaS monocrystal in the $1 \cdot 10^{15}$ sm⁻² dose whit 70 keV energy protons the "improvement" of the photosensitivity crystal is due to order of the regulary increase which was happened in the sturucture.

Keywords: single crystal, ion implantation, nanostructure, photoconductivity.

In recent years, the application of nanotechnology in microelectronics, photonics and information technology requires the synthesis and study of nanostructured materials with novel properties. The existence of quantum size effects in semiconductor nanostructures creates the conditions for the construction on their basis new structural elements with a wide range of functional capabilities. One way to fabricate such structures is the ion implantation method, widely used in the manufacture of LEDs and microchips based on Si. Under implantation is particularly important a process of thermal annealing, carried out to eliminate defects that are forming in different depths depending on the ions energy. Thus, simple stable defects generated during the thermal annealing process allow to control the photoelectric and optical properties of the crystal. Due to the fact, that in layered A^3B^6 type semiconductors a concentration of structural defects is equal ~ 10^{17} cm⁻³, in order to compensate them and purposefully control their properties, the ion implantation method and create local nanostructures in the near-surface regions[1-3].

In the present work the effect of thermal annealing on the defect layer formed in the nearsurface region of the layered GaS single crystals under implantation of hydrogen ions was studied.

The layered GaS single crystal was grown by the Bridgman method. The resistivity of the obtained single crystal at room temperature in the direction perpendicular and parallel to C axis was $2 \cdot 10^9$ Om cm and $1 \cdot 10^8$ Om cm, respectively. The dimensions of the single crystals studied were 0.65x0.5x0.028 cm. ESU-2 accelerator was used to irradiate GaS crystal with protons in the direction along the C axis. The proton energy was 70 keV, current density 0.15 μ A/cm² and the whole surface of the sample was irradiated with a dose 1×10^{15} proton/cm². To study the photoelectric properties of the crystals under study, the current contacts on the straight (implanted) and opposite (unimplanted) sides of the sample were applied using a silver paste. In measurements spectrophotometer MDR-23 was used to experimental obtain the photoconductivity spectrum of GaS single crystal. To study the optical properties spectrometer

VarianScan UV50 was used. Experimental measurements were carried out at room temperature. Thermal annealing of the implanted crystals was carried out at a temperature 200-400 °C for 30-90 minutes. After the thermal annealing process the photoelectric and optical properties of the samples were repeatedly measured[4-5].

Fig. 1 shows the spectral characteristics of the layered GaS crystals irradiated with protons $(1 \times 10^{15} \text{ cm}^{-2})$ before irradiation, after irradiation and spectral characteristics obtained from the irradiated (upper) surface of samples, thermally annealed at a temperature 473 K for 30 and 90 minutes.



Fig. 1. Spectral distribution of photoconductivity in the forward direction (1 - initial state, 2 - after implantation protons with energy 70 keV and dose 1×10¹⁵ sm⁻², 3 - after thermal annealing at the temperature 473 K for 30 minutes, 4 - after thermal annealing at the temperature 473 K for 90 minutes.

From Fig. 1 it can be seen that after irradiation with protons $(1 \times 10^{15} \text{ sm}^{-2})$ (curve 2) the spectral characteristics of the photosensitivity in the intrinsic and impurity regions of the spectrum change sharply with respect to the original sample (curve 1). Thus, an increase is observed in the photosensitivity corresponding to the maximum of the spectrum ($\lambda_{max} = 505$ nm) by 1.66 times, and 5.3 times in the 670-750 nm wavelength region. This fact shows that the radiation defects created under the irradiation have vacancy character that is consistent with the results obtained elsewhere. After the thermal annealing of the irradiated samples for t = 30 min the photosensitivity corresponding to $\lambda_{max} = 505$ nm of the spectrum decreases and simultaneously shifts to the long-wave region, and increases in the 670-750 nm wavelength region. But with the annealing time t = 90 minutes no photosensitivity is observed in the samples. The decrease in the short-wavelength region of the spectrum is the result of a decrease in the sulfur concentration in the near-surface region when irradiated with protons, and this result was observed in and in Rutherford backscattering (RBS) spectra [4]. A wide maximum, observed in the spectral range 600-800 nm shows an increase in the concentration of Ga vacancies. Thus, it can be said that the increase in photosensitivity after the action of protons occurs as a result of compensation by donor-type defects, created under irradiation the initial acceptor-type defects of the crystal.

Fig. 2 shows the spectral characteristics of the layered GaS crystals irradiated with protons $(1 \times 10^{15} \text{ sm}^{-2})$ prior to irradiation, after irradiation and spectral characteristics obtained



from the non-irradiated (lower) surface of samples, annealed at 473K for 30 and 90 minutes.

Fig. 2. Spectral distribution of the photoconductivity in the opposite direction (1 - initial state, 2-after implantation protons with energy 70 keV and dose 1×10^{15} sm⁻², 3-after thermal annealing at the temperature 473 K for 30 minutes, 4-after thermal annealing at the temperature 473 K for 90 minutes

From the comparison of Fig. 1 (curves 1 and 2) and Fig. 2 (curves 1 and 2), it can be seen that the spectral characteristics obtained from irradiated and non-irradiated surfaces of the samples, irradiated with protons $(1 \times 10^{15} \text{ sm}^{-2})$, differ quantitatively, but in character they have the same features. That is, there is an increase in photosensitivity in the range 500-700 nm. However, after the thermal annealing process (Fig. 2, curves 3 and 4) the photosensitivity of the samples changes abruptly. It was found that the spectrum obtained from the non-irradiated surface of samples thermally annealed for 30 and 90 minutes, the photosensitivity corresponding to $\lambda_{\text{max}} = 505$ nm is the same as initial photosensitivity before irradiation. However, in the range 500-700 nm the photosensitivity after annealing for t = 30 min is higher than the photosensitivity that is observed after annealing for t = 90 minutes. This shows that the structural and radiation defects are different in nature.

Fig. 2. shows the spectral characteristics of the crystals irradiated with protons, measured from the non-irradiated (bottom) surface of samples thermal annealed at the temperature 473K for 30 and 90 minutes. From Fig. 2 it can be seen, that the photosensitivity of samples irradiated with a dose 1×10^{15} sm⁻² completely corresponds to the photosensitivity of the irradiated surface, that is, the photosensitivity increases throughout the spectrum. After annealing these samples for 30 minutes photoconductivity throughout the spectrum, including corresponding to $\lambda_{max} \sim 505$ nm, sharply decreases (curve 3). Under these conditions, when samples are annealed for t = 90 minutes, the photosensitivity decreases again in the spectral range 600 nm - 900 nm, and the photosensitivity corresponding to a wavelength 505 nm approaches to its initial value. And this fact once again proves that the sulfur atoms leave the crystal and they diffuse to the surface. For this reason, thermal annealing affects the highest photosensitivity corresponding to the bandgap (505 nm) of the single crystal.

Fig. 3. Absorption spectra for proton-implanted and thermal annealed at a temperature of 473K for 30 and 90 minutes GaS crystal (1 - initial state, 2 - after implantation with protons with an energy 70 keV and dose 1×10^{15} sm⁻², 3 - after thermal annealing at the temperature 473K for



30 minutes, 4 - after thermal annealing at the temperature 473K for 90 minutes).

Fig. 3. shows absorption spectra for proton-implanted and thermal annealed at the temperature 473K for 30 and 90 minutes GaS crystal.

From Fig. 3 it can be seen that before irradiation (curve 1) an absorption coefficient (α) increases exponentially with increasing photon energy (hv). The width of the forbidden band, determined from the plot is 2.45 eV and corresponds to the results obtained elsewhere [1]. When are irradiated with protons, the absorption coefficient in the region of intrinsic absorption of the spectrum decreases, and at wavelengths 668 nm (1.85 eV) and 739 nm (1.68 eV) additional transitions are observed. The values of the energy levels corresponding to these peaks were 0.59 eV and 0.77 eV. As a result of our measurements, it was found that the energy corresponding to the transitions observed in the α -(hv) dependence corresponds to the peak energies on the spectral characteristic (Fig. 1).

Acknowledgment

This work was financed by the Science Development Foundation under the President of the Republic of Azerbaijan Grant № EİF-KETPL-2-2015-1(25)-56/03/1

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ВЛИЯНИЕ ТЕРМИЧЕСКОГО ОТЖИГА НА ФОТОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА МОНОКРИСТАЛЛОВ Gas имплантированных протонами

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Резюме: Предложенная работа посвящена влиянию протонов с энергией 70 кэВ с использованием метода ионной имплантации $1 \cdot 10^{15}$ см⁻² дозы на оптические и фотоэлектрические свойства монокристалла GaS. Повышение фотопроводимости с течением времени наблюдалось в интервале длин волн 490 нм - 900 нм. При длине волны 505 нм фоточувствительность была увеличена до 1,66 раза, но при длине волны 670-750 нм она была увеличена до 5,3 раз.

PROTONLARLA İMPLANTASİYA EDİLMİŞ GaS MONOKRİSTALLARININ FOTOELEKTRİK XASSƏLƏRİNƏ TERMİK DƏMLƏMƏNİN TƏSİRİ

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Xülasə: Təqdim olunan iş, ion implantasiya metodundan istifadə etməklə $1 \cdot 10^{15}$ sm⁻² dozada 70 keV enerjili protonların GaS monokristalının fotoelektrik xassələrinin təsirinə həsr olunmuşdur. Baxdığımız halda fotokeçiriciliyin zaman keçdikcə 490nm-900nm dalğa oblastında artımı müşahidə edilmişdir. 505nm dalğa uzunluğunda fotohəssaslıq 1.66 dəfə, lakin 670-750nm dalğa uzunluğunda 5.3 dəfə artmışdır. Qadağan olunmuş zolağa uyğun gələn pikin maksimumunun yeri λ =490 nm-dən 505nm sürüşmüşdür. GaS monokristalı enerjisi 70 keV olan protonlarla $1 \cdot 10^{15}$ sm⁻² dozada implantasiya etdikdən sonra kristalın fotohəsasslığının «yaxşılaşması» strukturda baş verən nizamlılığın artması ilə bağlıdır.

Açar sözl r: monokristal, ion implantasiyası, nanosturuktur, fotokeçiricilik.