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Gettering effect in Cr/$4H$-SiC UV photodetectors under ptoton irradiation vith $E = 15$ Mev

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The mechanism of structure transformation in Cr/$4H$-SiC UV photodetectors, which is responsible for the cyclic gettering of radiation defects, under repeated proton irradiation, is proposed in this work..

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Introduction

Silicon carbide of the $4H$ polytype, due to its unique properties, is currently the most promising material used in devices intended for operation in outer space. Numerous studies in the field of detecting cosmic radiation in the ultraviolet (UV) range have shown that UV detectors based on $4H-$SiC have significant advantages over detectors based on other semiconductor materials such as Si, Ge, GaAs , GaP [1–3]. Since the radiation activity in space is high, the problem of the radiation resistance of such devices is urgent, in particular, it is of great importance to study the processes occurring in the $4H-$SiC structure and the resulting changes in the electrophysical and optical characteristics under the influence of high-energy particle bombardment of the devices. Of particular interest is the study of the effect of proton irradiation on the characteristics of $4H-$SiC devices, since solar particle radiation is 90% protons. It was shown in Refs. [4,5] that one of the main radiation defects due to proton irradiation are vacancies in carbon and silicon sublattices and more complex complexes based on them. It was also suggested that microdomains of single-crystal silicon carbide with a high concentration of vacancies appear in the structure of the material irradiated by protons.

In the present paper, we study the structural changes and quantum efficiency of Cr/$4H-$SiC UV photodetectors upon their step-by-step irradiation with 15 MeV protons. The results of studies are presented by the example of a sample with Nd−Na= $1 \cdot 10^{14}\,\mathrm{cm}^{-3}$ (Nd, Na being the concentrations of donors and acceptors, respectively) in CVD -epitaxial layer after each of the seven stages of proton irradiation with a fluence of $1 \cdot 10^{12}\,\mathrm{cm}^{-2}$. Thus, the total proton fluence was $7 \cdot 10^{12}\,\mathrm{cm}^{-2}$.

1. Experiment

The photodetectors were formed on $n-4H-$SiC-epitaxial layers grown by chemical vapor deposition (CVD) with a thickness of $5\,\mu$m and a concentration of $N_d - N_a = 1 \cdot 10^{14}\,\mathrm{cm}^{-3}$ on commercial n^+-4H-SiC substrates with concentration $N_d - N_a = 3 \cdot 10^{18}\,\mathrm{cm}^{-3}$. Irradiation of photodetectors with high-energy protons was carried out in seven stages with fluences $1 \cdot 10^{12}\,\mathrm{cm}^{-2}$, amounting to a total fluence of $7 \cdot 10^{12}\,\mathrm{cm}^{-2}$.

To study the structural transformations in the $4H-$SiC CVD layer at each stage of proton irradiation, the X-ray diffraction method was used. Since the influence of point defects arising upon irradiation with protons primarily affects the „tails" of the double-crystal X-ray rocking curve, it was important to analyze these regions in the most detail. A detailed study of these regions is possible by obtaining distribution patterns of X-ray reflection intensity in two scanning directions (ω and 2ω). The measurements were carried out on the double-crystal spectrometer assembled based on a DRON-3 industrial diffractometer in both scanning modes in symmetric reflection (0008) $4H-$SiC. Scanning in the 2ω direction was carried out step by step manually by shifting the detector with a slit 0.05mm wide with a step of 0.005° with respect to the exact Bragg reflection both in the direction of increasing 2ω and in the direction of decreasing it. The rocking curves (ω-scanning) at each detector shift were measured in the range of 0.2° with a step of 0.001°. The detector was shifted until the reflection intensity at the maximum of the double-crystal rocking curve measured at a given position of the counter became negligible.

The quantum efficiency spectra of the samples were measured by comparison with a monochromator based on SF-16 spectrophotometer. The source of UV radiation in the wavelength range 200−400 nm was a DDS-30 deuterium lamp. A Keithley 6485 picoammeter was used to record the currents. An SPD-100UV photodiode calibrated in the range of 40−400 nm was taken as a secondary sensitivity standard.

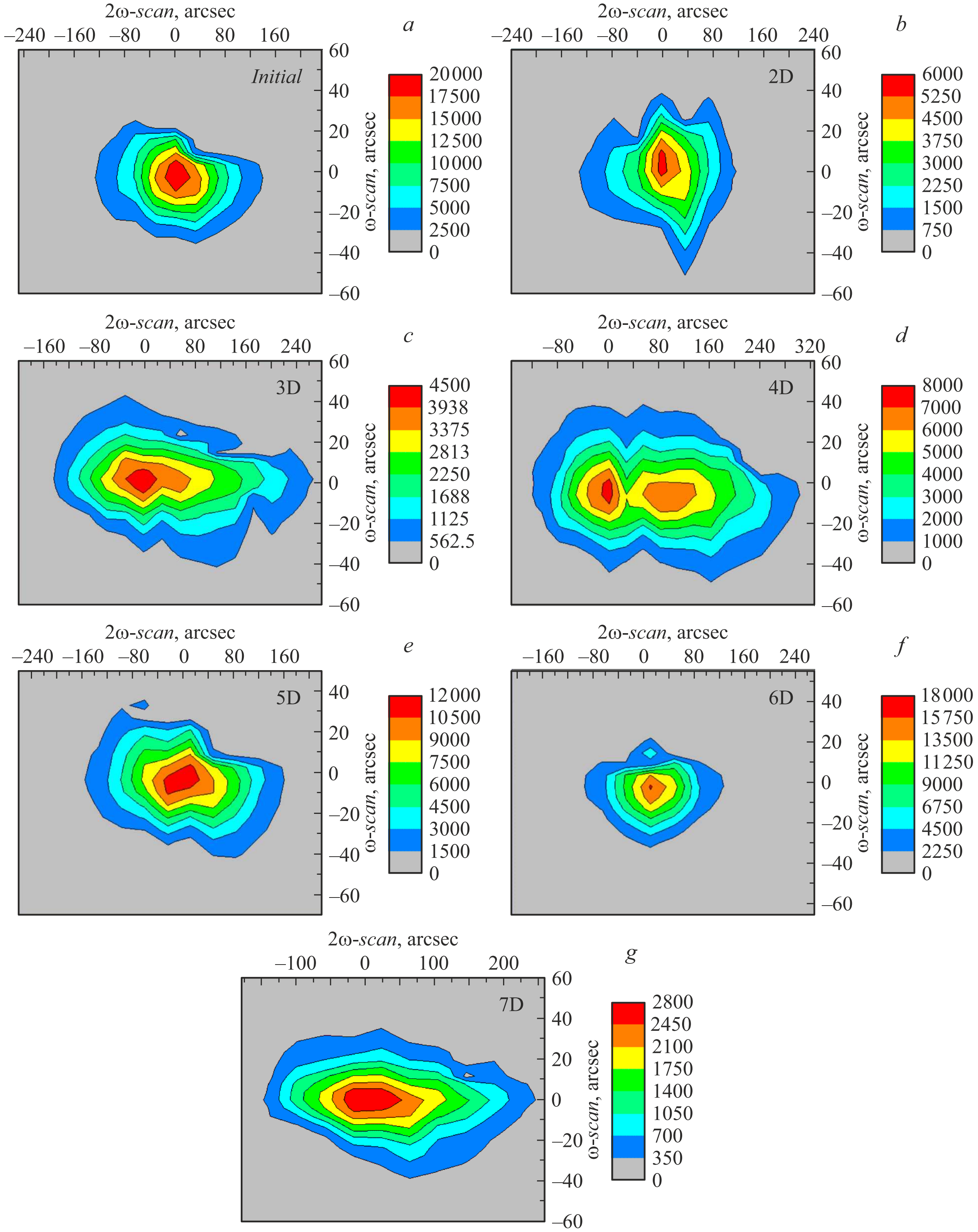

Figure 1. Distribution maps of X-ray reflection intensity (reflection (0008) $4H$–SiC) from the initial sample (a) and after (2–7) exposures ($b-g$), respectively.

2. Experimental results

2.1. X-ray measurements

Figure 1 shows maps of the X-ray reflection intensity distribution (reflection 0008) from the initial (Fig. 1, a) $4H-$SiC sample with $N_d - N_a = 1 \cdot 10^{14}\,\mathrm{cm}^{-3}$ in the CVD-epitaxial layer and after each exposure, starting from the second one (Fig. 1, $b-g$).

A comparative analysis of the intensity distribution maps shows that the modes of proton irradiation used by us begin to noticeably affect after the third exposure. The reflection intensity pattern at this stage is blurred on both sides of zero in the 2ω direction and becomes sharply asymmetric (Fig. 1, c). Nonzero intensity values dominate from the side of larger 2ω angles. This means that after the third irradiation, defects of the vacancy type begin to dominate in the structure. The inhomogeneity of distribution of point defects leads to the appearance of elastic stresses in the structure of irradiated silicon carbide. It is possible that already at this stage small vacancy clusters are formed, which do not manifest themselves clearly in the reflection intensity distribution patterns. In the distribution pattern after the fourth irradiation, along with the main maximum at $2\omega = 0$, a second powerful maximum is observed from the side of larger 2ω angles, due to the formation of a large localized region with negative deformation, i.e. oversaturated with vacancy defects (Fig. 1, d). As a result of the next fifth exposure, the destruction of localized regions is observed (Fig. 1, e). After the sixth exposure, the intensity distribution map again becomes practically symmetric along the 2ω axis with respect to zero. Along the ω axis, the appearance of a small additional maximum is observed, which indicates the formation of a coarse-block structure at this stage (Fig. 1, f). As a result of the seventh exposure, a small asymmetry along the 2ω axis towards larger angles is again found in the intensity distribution map, i.e., defects of the vacancy type again begin to predominate in the structure (Fig. 1, g). For a more visual representation of the changes in the distribution of point-type radiation defects at each stage of proton bombardment, the dependences of the maximum reflection intensity on the double Bragg angle (2ω) at $\omega = 0$ were plotted (Fig. 2).

Previously [4] we have shown that no other silicon carbide polytypes are observed in the structure irradiated with protons, i.e. the formation of the second maximum in the distribution pattern after the fourth exposure cannot be associated with other silicon carbide polytypes. The formation of an amorphized layer in the structure at this stage was also demonstrated there.

2.2. Optical measurements

Figure 3 shows the results of measuring the external quantum efficiency in the spectral range $200-400$ nm in the initial sample and after each act of irradiation with protons. As can be seen, there is no monotonic degradation of the quantum efficiency as the number of exposures increases. So, after a sharp drop following the first and second exposure, an increase in the external quantum efficiency by 8 times is observed as a result of the third exposure, and after the fourth one by 12 times, almost to the values inherent in the original sample. At the next fifth and sixth stages, the value of the quantum efficiency at the maximum changes little, revealing a slight tendency to decrease. After the seventh exposure, a significant decrease in the external quantum efficiency is again observed. What is the reason for such a jump-like change in the external quantum efficiency and the lifetime of charge carriers associated with it? The involvement of the X-ray diffraction method in the study of this issue made it possible to reveal the relationship between the dynamics of the transformation of the sample structure at each stage of irradiation and the nature of the change in the external quantum efficiency.

3. Discussion of results

The analysis of the results obtained here in the study of structural transformations at each stage of proton irradiation in the selected modes confirms the assumptions made in Refs. [5,6] about the possible formation of clusters of point defects during proton bombardment. At the initial stages of irradiation (up to the third stage), point defects of both types (vacancies and interstitial atoms) and their combinations are formed, which are almost uniformly distributed in the structure (Fig. 1, b). This process is accompanied by the formation of energy states in the band gap, leading to a sharp drop in the quantum efficiency (Fig. 3, curve $2D$). The inhomogeneity of distribution of point defects at the third stage of irradiation (Fig. 1, c) leads to the appearance of elastic stresses in the structure of irradiated silicon carbide. At this stage, when the structure becomes stressed as a result of the predominance of vacancy-type defects in the structure, two competing processes begin: partial relaxation of the resulting stresses through the formation of dislocation loops [7] and the predominant process of the formation of small vacancy clusters, leading to the growth of stresses in the structure. Both the dislocation loops and the resulting small clusters act as sinks for radiation defects. This leads to a slight increase in the quantum efficiency at this stage (Fig. 3, curve $3D$). At the next, fourth, stage of irradiation, under the influence of growing stresses, radiation defects of the vacancy type, on the one hand, take part in the formation of dislocation loops, and on the other hand, they form a localized single-crystal region oversaturated with these defects (Fig. 1, d). The coexistence of the initial matrix and the cluster with negative deformation leads to even higher elastic stresses in the structure of the irradiated material. Thus, after the fourth irradiation, the structure of the irradiated material becomes sharply inhomogeneous, and the effect of radiation defects uniformly distributed in the structure becomes negligible. This is the reason why the quantum efficiency at the fourth stage sharply

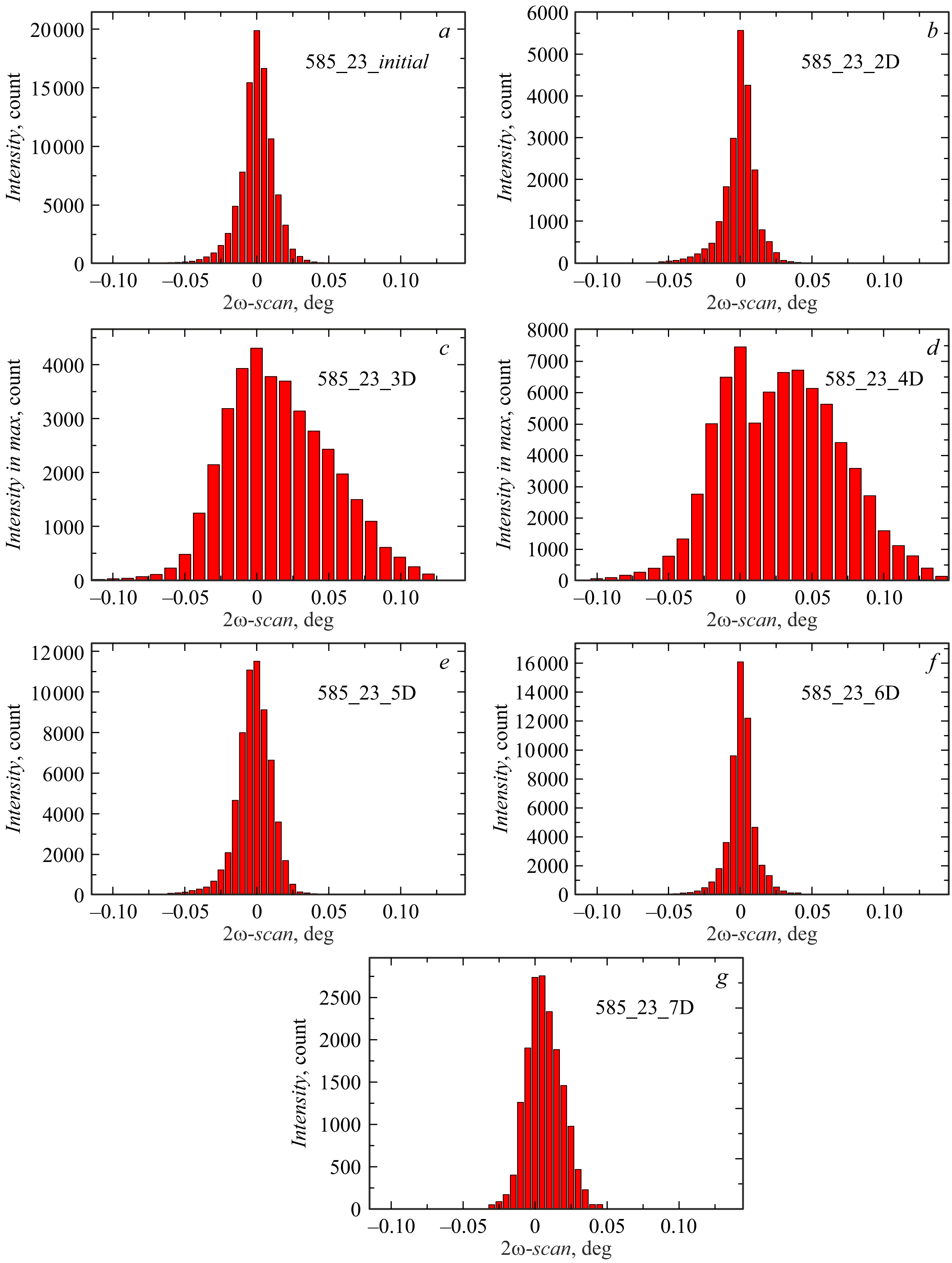

Figure 2. Dependence of the maximum X-ray reflection intensity on the double Bragg angle at $\omega = 0$ for the initial sample (a) and after each of the seven proton exposures, starting from the second one $(b-g)$.

increases and approaches the values inherent in the initial sample (Fig. 3, curve $4D$). In other words, the single-crystal cluster formed at the fourth stage, enriched with vacancy-type radiation defects, itself serves as a powerful sink for point defects formed as a result of irradiation, i.e. is a very effective gettering center for themselves. The gettering process is triggered by stresses arising in such an inhomogeneous structure due to the predominance of defects of one type over another. Elastic stresses in the structure at this stage reach critical values, at which the existence of such a configuration becomes unfavorable from the energy point of view. Therefore, at the next fifth and sixth stages, significant stress relaxation occurs due to the mass formation and enlargement of dislocation loops and their transformation into extended defects. In this case, the density of extended defects increases, and the disorder of the structure increases too, i.e., the structural perfection deteriorates compared to the original sample (Fig. 1, *e, f*). At these stages, the quantum efficiency remains high due to gettering on extended defects, the density of which has become higher (Fig. 3, curves $5D$ and $6D$). It is obvious that the proportion of the influence of extended defects on the gettering of radiation defects at the fifth and sixth stages of irradiation increases in comparison with the sample after the second irradiation. After the seventh irradiation (Fig. 1, *g*), the intensity distribution map shows smearing along the 2ω axis on both sides of zero, which indicates a reasonably uniform distribution of point defects in the structure at this stage. This leads to a significant drop in the quantum efficiency (Fig. 3, curve $7D$) compared to the previous one (Fig. 3, curve $6D$). Nevertheless, a slight asymmetry towards larger 2ω angles, found on the intensity distribution map after the seventh irradiation, indicates the beginning of a new process of formation of an inhomogeneous structure due to the predominance of vacancy-type defects in it (Fig. 1, *g*). Apparently, at the seventh stage, a new cycle of structural transformations, described above, begins. However, the structure of the new „original" pattern is significantly disordered compared to the initial one. When comparing the dependences of the maximum intensity of X-ray reflection along the 2ω direction at $\omega = 0$ after the third and seventh irradiation events (Fig. 2, *c, g*), it is clearly seen that the predominance of vacancy-type defects in the structure at the seventh stage is much less pronounced than at the third stage. This should slow down the formation of localized regions supersaturated with vacancies at the next stages of irradiation, which leads to an increase in the quantum efficiency. To summarize the comparative analysis of structural changes and the nature of the quantum efficiency behavior under multiple proton bombardment, we can conclude that with an increase in the number of proton irradiation events, the quantum efficiency changes cyclically with periodic drops and subsequent increases rather than abruptly, as it was thought at the beginning of the study. The cyclic nature of the change in the quantum efficiency is due to the also cyclic formation and subsequent destruction of powerful gettering centers of

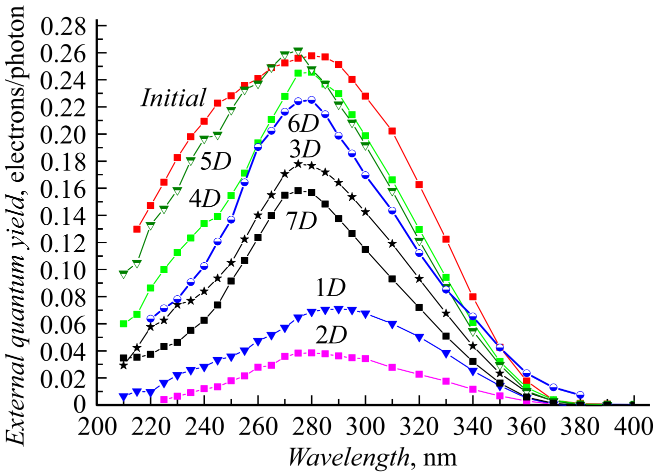

Figure 3. Quantum efficiency spectra of Cr/$4H-$SiC UV photodetectors of the initial $4H-$SiC sample with $N_d - N_a = 1 \cdot 10^{14}\,\mathrm{cm}^{-3}$ (Initial) and after seven exposures to protons with an energy of 15 MeV and fluences of $1 \cdot 10^{12}\,\mathrm{cm}^{-2}$. Exposures 1–7 correspond to the curves $1D$–$7D$.

radiation defects, i.e., transformation of the structure of the irradiated material. In this case, the main gettering center is a single-crystal cluster enriched with vacancy-type defects. With an increase in the number of irradiation events, the duration of the cycle increases and the absolute value of the quantum efficiency at the maximum decreases. It should be noted that the gettering of radiation defects due to structural disorders was noticed earlier in other semiconductors [8–10], as well as in $4H-$SiC [4,11], however, the gettering process was not described.

Of course, the mechanism of structure transformation described here and the related character of the change in the quantum efficiency of a repeatedly irradiated silicon carbide crystal is schematic. In fact, the processes initiated by proton bombardment are much more complicated. In particular, the amorphized regions found in the structure can also serve as sinks for radiation defects. However, the presented mechanism of structural transformations, in our opinion, is dominant. It can also be assumed that a similar mechanism also takes place upon irradiation by other particles, with the only difference being that the repeatability of the cycles in this case will be determined by the mass and energy of the incident particles.

Conclusion

The use of the X-ray diffraction method to study the transformations of the crystal structure made it possible to explain the evolution of the quantum efficiency of Cr/$4H-$SiC UV photodetectors under staged proton irradiation. Based on a comparative analysis of the data obtained in the study of the structure and quantum efficiency at each stage of irradiation, a mechanism for the gettering of radiation defects is proposed. It is shown that the effect of gettering is determined mainly by the formation under the influence of irradiation of localized single-crystal regions enriched with vacancy-type defects. The driving forces for the sink of radiation defects are elastic stresses arising in an inhomogeneous structure. It is assumed that the gettering effect is cyclic in nature, determined by the periodic formation and subsequent destruction of structural clusters with a predominance of vacancy-type defects in them. The process is accompanied by a gradual disordering of the initial crystal structure due to the formation of extended defects, the share of influence of which in the gettering effect increases with an increase in the number of irradiation events.

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Conflict of interest

The authors declare that they have no conflict of interest.

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