Experimental study of the influence of laser radiation power on the reflection coefficient of germanium and silicon at a wavelength of 355 nm

T V Malinskiy¹, V Yu Zheleznov¹, V E Rogalin¹ and I A Kaplunov²*

¹Laboratory of Electric-Discharge and Laser Technologies, Institute for Electrophysics and Electric Power of Russian Academy of Sciences, 18 Dvorovaya Naberezhnaya, 191186, St. Petersburg, Russian Federation
²Department of Applied Physics, Tver State University, 33 Zhelyabova Street, 170100, Tver, Russian Federation

*E-mail: kaplunov.ia@tversu.ru

Abstract. The dependences of the reflection coefficients at a wavelength of $\lambda = 355$ nm for germanium and silicon single crystals on the energy density of impacting laser radiation in the range 0.01 - 0.1 J/cm² have been measured. Analytical expressions were obtained. It is assumed, that they are also valid in the range 0.1 - 1.0 J/cm². With a further increase in the energy density, the dependence should acquire a more complex character due to the resulting optical breakdown.

1. Introduction

Laser radiation is widely applied in the technology of semiconductor materials [1, 2]. It is used for cutting, annealing, surface modification and for a number of other applications. However, in practical use, one has to deal with a change in the reflection coefficient of a semiconductor with an increase in the radiation power density. The phenomenon is caused by the fact that laser radiation, being absorbed in a crystal, transfers energy to electrons of the valence band, transferring them to the conduction band [3, 4]. This leads to the formation of a significant number of nonequilibrium electron-hole pairs, leading to an increase in the reflection coefficient. The phenomenon of the so-called plasma resonance in semiconductors is known, when at carrier concentration of $10^{20} - 10^{21}$ cm⁻³ the reflection coefficient can approach 95 - 98% [5].

For a number of technological processes, it is preferable to use ultraviolet (UV) radiation [6-8], in particular, a nanosecond pulsed Nd: YAG laser emitting at the third harmonic (wavelength $\lambda = 355$ nm) [9]. This is due to the high proportion of absorbed radiation.

UV radiation is used for the treatment of semiconductors in cases, where it is necessary to minimize the size of the irradiated area, which is proportional to the wavelength.

The refractive index of germanium was studied in [10-12]. At $\lambda = 355$ nm, the value of the refractive index ($n$) is slightly higher, than in the IR region: $n_{Ge} = 4.0746$ [10], 4.0238 [11], 4.1150 [12]. Reflection coefficient at $\lambda = 355$ nm is slightly higher in magnitude, than for the infrared region ($R \sim 0.36$). For silicon, according to [13] ($\lambda = 355$ nm), $R \sim 0.49$. However, these values were obtained for low-power radiation.
In [14-19] interesting results on the modification of the surface of single crystals of germanium and silicon under the action of frequency-pulse laser radiation ($\lambda = 355$ nm) of nanosecond duration were obtained. To analyse these results, it was necessary to know the values of the reflection coefficient of the impacting radiation. This article is devoted to obtaining these data.

2. Experimental technique

The optical scheme of measurements is shown in figure 1. The radiation source was, used in [6, 7, 10], a solid-state Nd: YAG laser, operating at the third harmonic ($\lambda = 355$ nm, pulse duration $\tau = 10$ ns, pulse energy (W) up to 8 mJ, pulse repetition rate (f) up to 100 Hz, laser beam diameter - 3 mm, divergence - 1-2 mrad).

![Figure 1. Scheme for measuring the reflection coefficient of germanium and silicon at $\lambda = 355$ nm: 1 - pulsed solid-state laser Opolette HR 2731 (OPOTEC Inc., USA); 2 - nonlinear crystal; 3 - light filter; 4 - translucent plate; 5 - radiation measuring device ILD - 2M (Experimental plant "Etalon", Volgograd); 6 - 6'-radiation measuring device NOVA II (Ophir Optronics Solutions Ltd., Israel); 7 - lens; 8 – the test sample.](image)

The measurements were carried out as follows. The laser emitted a series of 12 pulses with a frequency of 2 Hz, which was recorded by measuring devices in accordance with the scheme shown in figure 1. In the calculations, the average value of the energy density was selected from 12 pulses.

Before the start of measurements, mutual calibration of the ILD-2M and NOVA II measuring devices was carried out. For this, measuring device NOVA was placed in position 6, in front of the lens to record the radiation, directed on the sample. The radiation of laser 1, passing through nonlinear crystal 2, which converts laser radiation into the third harmonic ($\lambda = 355$ nm), and UV filter 3, was reflected by a quartz beam splitter 4 onto an ILD calorimetric laser energy measuring device ILD (6).

During the calibration, the coefficient $k_1$ was calculated, which was used to determine how the energy measured using NOVA and ILD, $E_{NOVA}$ и $E_{ILD}$, respectively, is related:

$$E_{NOVA} = E_{ILD} \cdot k_1.$$  \hspace{1cm} (1)

The reflection coefficient was measured in this way. The radiation of laser 1 was reflected by a quartz beam splitter 4 onto an ILD calorimetric laser measuring device (6), which controls the laser output energy. Then, the radiation was collected on the surface of a polished semiconductor sample by a quartz lens 7 with a focal length $f = 250$ mm into a spot with diameter varied from 1 mm$^2$ to 2 mm$^2$ by displacing the sample from the focal plane of the lens. As shown in the calculations performed in [6], during the time between pulses, the sample surface completely cooled down to room temperature. For each series, the arithmetic mean values of the pulse energy of the incident and reflected radiation were calculated. The energy of the radiation reflected from the radiation was recorded with a NOVA calorimetric detector located in the 6’ position. The reflection coefficient $R$ was measured according to the standard technique as the ratio of the radiation flux reflected from the sample to the incident one:
\[ R = \frac{F}{F_0} = \frac{E_{\text{NOVA}}}{E_{\text{IDL}} \cdot k_1} \cdot \tau, \]  

where: \( \tau \) - the transmittance of the lens, which is 0.9; \( F \) - the radiation flux reflected from the sample; \( F_0 \) - radiation flux incident on the sample; \( E_{\text{NOVA}} \) - energy of reflected pulsed radiation in mJ; \( E_{\text{IDL}} \cdot k_1 \) - the energy of the incident pulsed radiation in mJ.

For a given energy density, the indications of the \( E_{\text{NOVA}} \) and \( E_{\text{IDL}} \) measuring devices were measured, and the R value was determined from them. The laser pulse energy was changed in accordance with the laser control program.

3. Experimental results and discussion

The values of the specular reflection coefficients of polished samples of single crystals of germanium and silicon with a change in the energy density of the laser pulse (\( \lambda = 355 \text{ nm} \)) in the range 0.01 - 0.1 J/cm\(^2\) were obtained. As expected, the reflection increases with pulse energy density rising. In figure 2 and 3, the solid line shows the measured values of the reflection coefficients of germanium and silicon, and the dotted line shows the approximation results. It turned out to be impossible in this case to obtain experimental values of the specular reflection coefficients at an energy density of \( W \geq 0.1 \) J/cm\(^2\) due to the incipient degradation of the sample surface, accompanied by a noticeable increase in radiation scattering. These processes are described in detail in [14, 15].

Based on the experimental dependences (figure 2, single crystal of germanium, figure 3, single crystal of silicon), the analytical expressions were obtained, equation (3) and equation (4)

\[ R = 0.36 \cdot e^{0.174 W} \text{ (germanium)} \]  
\[ R = 0.49 \cdot e^{0.14 W} \text{ (silicon)} \]

**Figure 2.** Experimental dependence of the reflection coefficient of a germanium single crystal at a wavelength of \( \lambda = 355 \text{ nm} \) on the energy density of the impacting radiation of a Nd: YAG laser.

In figure 2 and 3, the dotted lines show the estimated reflection losses at a laser pulse energy density of 0.1 - 2 J/cm\(^2\), which we could not measure. We presume, that in the range of 0.1 - 1.0 J/cm\(^2\), this dependence will be quite valid, since the degradation of the surface occurs in a condensed state.

However, the need for extrapolation to the energy density range of 0.1–1 J/cm\(^2\) arose due to the fact that data on the reflection coefficient in the energy density range of 0.1–1 J/cm\(^2\) are necessary to understand surface processes, leading to an increase in radiation scattering on the surface at high energy density.
However, at 1.0 - 2.0 J/cm², a new factor arises, associated with optical breakdown and, associated with it, melting and evaporation of the material. In this case, the dependence apparently will become more complicated.

![Figure 3](image_url)

**Figure 3.** Experimental dependence of the reflection coefficient of a silicon single crystal at a wavelength of \( \lambda = 355 \) nm on the energy density of the impacting radiation of a Nd: YAG laser.

When impacted to a high-power short laser pulse, in addition to the generation of nonequilibrium carriers by absorbing photons, thermal generation of carriers also occurs due to heating of the surface layer. At the same time, intense diffusion of nonequilibrium carriers into the interior of the crystal occurs, as well as mutual annihilation of nonequilibrium donors and acceptors. However, reflection increases.

Experiments related with the impact of laser pulses on the surface of semiconductors and dielectrics showed, that the concentration of generated nonequilibrium carriers becomes so high, that the surface layer acquires the properties of a metal during the pulse. In [3] it is reported, that, when impacted to intense laser radiation, a semiconductor in its optical properties approaches metals - its reflection coefficient increases significantly. In this case, the reflection coefficient for germanium doubles at a power density \( q \sim 10^7 \) W/cm², and the absorption coefficient in this case reaches values of \( 10^4 - 10^5 \) cm⁻¹ [3].

Reflectivity is associated with a change in the number of non-equilibrium carriers - electrons, the generated concentration of which (\( \Delta n \)) can be determined from the ratio realized for quasi-stationary lighting conditions:

\[
\Delta n = \alpha \beta F_0
\]

where \( \alpha \) - is the absorption coefficient; \( \beta \) - coefficient showing the ratio of the generated carriers to the number of absorbed quanta; \( F_0 \) - the radiation flux incident on the sample.

The calculated concentration of generated carriers, taking into account the radiation parameters, can reach values of \( 10^{19} - 10^{22} \) cm⁻³ [3, 4].

**4. Conclusion**

The dependences of the reflection coefficients at a wavelength of \( \lambda = 355 \) nm for germanium and silicon single crystals on the energy density of the acting laser radiation in the range 0.01 - 0.1 J/cm² have been measured. Analytical expressions were obtained. It is assumed, that they are also valid in
the range $0.1 - 1.0 \text{ J/cm}^2$. With a further increase in the energy density, the dependence should acquire a more complex character, due to the resulting optical breakdown.

Acknowledgments
This work was carried out using the resources of the Center for Collective Use of Tver State University as part of the state assignment for scientific activity (No 0057-2019-0005 and No 0817-2020-0007).

References
[1] Claeyts L, Simoen E 2007 Germanium–Based Technologies: From Materials to Devices (Berlin: Elsevier) 480 p doi: 10.1016/S1569-7021(07)70279-1
[2] Zimmermann H 2018 Silicon Optoelectronic Integrated Circuits (Springer Series in Advanced Microelectronics Book 13) (Switzerland: Springer Nature) 441 p
[3] Libenson M N, Yakovlev E B, Shandybina G D 2008 Interaction Of Laser Radiation with Matter (power optics) Lecture notes edited by V. P. Veiko Part I. Absorption of laser radiation in matter. (Saint-Petersburg: ITMO) 141 p. [In Russian]
[4] Dyukin R V, Martinsinovskii G A, Shandybina G D and Yakovlev E B 2011 J. Opt. Technol. 78(2) 88 doi: 10.1364/JOT.78.000088
[5] Zhukov N D, Shishkin M I and Rokakh A G 2018 Tech. Phys. Lett. 44 362 doi: 10.1134/S1063785018040284
[6] Crouch C H, Carey J E, Warrender J M, Aziz M J, Mazur E and Génin F Y 2004 Appl. Phys. Lett. 84(11) 1850 doi: 10.1063/1.1667004
[7] Harzic R Le, Dörr D, Sauer D, Neumeier M, Epple M, Zimmermann H and Stracke F 2011 Phys. Procedia 12(2) 29 doi: 10.1016/j.phpro.2011.03.102
[8] Pedraza A J, Fowlkes J D and Lowndes D H 1999 Appl. Phys. Lett. 74. 2322 doi: 10.1063/1.123838.
[9] Shelygina S N, Akimov A A, Burov N V, Shaimadieva D S, Karri Rao 2019 Photonics 13(3) 252 doi: 10.22184/FRos.2019.13.3.252
[10] Nunley T N, Fernando N S, Samarasingha N, Moya J M, Nelson C M, Medina A A and Zollner S 2016 J. Vac. Sci. Technol. 34(6) 061205, doi: 10.1116/1.4963075
[11] Aspnes D E and Studna A A 1983 Phys. Rev. B 27(2) 985 doi: 10.1103/PhysRevB.27.985
[12] Jellison G E Jr. 1992 Opt. Mat. 1(3) 151 doi: 10.1016/0925-3467(92)90022-F
[13] Green M A 2008 Sol. Energ. Mat. Sol. Cells 92 1305 doi: 10.1016/j.solmat.2008.06.009
[14] Malinskii T V, Mikolutskii S I, Rogalin V E, Khomich Yu V, Yamschikov V A, Kaplunov I A and Ivanova A I 2020 Tech. Phys. Lett. 46 831 doi: 10.1134/S0040674420080234
[15] Zhelezov V Yu, Malinskii T V, Mikolutskii S I, Rogalin V E, Filin S A, Khomich Yu V, Yamschikov V A, Kaplunov I A and Ivanova A I 2020 Izvestiya Vysshikh Uchebnykh Zavedenii. Materialy Elektronoi Tekhniki = Materials of Electronics Engineering. 23(3):203-212 doi: 10.17073/1609-3577-2020-3-203-212 [In Russian]
[16] Malinskii T V, Mikolutskii S I, Rogalin V E, Khomich Yu V, Yamschikov V A, Kaplunov I A and Ivanova A I 2020 Physical and chemical aspects of the study of clusters, nanostructures and nanomaterials 12 628 doi: 10.26456/pcasenn/2020.12.628 [In Russian]
[17] Khomich Yu V, Malinskii T V, Mikolutskii S I, Rogalin V E, Yamschikov V A, Kaplunov I A and Ivanova A I 2020 J. Phys. Conf. Ser. 1697 012254 doi: 10.1088/1742-6596/1697/1/012254
[18] Makin V S and Makin R S 2013 Opt. Spectrosc. 115(4) 591 doi: 10.1134/S0030000X13070102.
[19] Mikolutskii S I, Khasaya R R, Khomich Yu V, Yamschikov V A 2018 J. Phys.: Conf. Ser. 987 012007 doi: 10.1088/1742-6596/987/1/012007