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Luminescence centers in silicon irradiated by femtosecond laser

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Photoluminescence in silicon grown by Czochralski technique and irradiated by femtosecond Ti:Sapphire laser with a wavelength 780 nm is studied. The formation of a wide band in area of $1.15-1.6\,\mu$m, narrow W, H, P- lines and the near-band-edge line is observed in the spectra. Influence of luminescence measurement temperature, wavelength and power of exciting laser on the spectra is investigated. An activation energy of temperature quenching of luminescence intensity and an excitation efficiency of W, H and P- lines are determined. With increasing excitation power, the integral intensity of the wide band increases but the integral intensity of the near-band-edge line decreases.

Keywords: silicon, femtosecond laser, point defects, activation energy of temperature quenching of luminescence, luminescence excitation efficiency.

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Introduction

Luminescence is an effective method for studying the nature and properties of defects formed during radiation exposure and subsequent thermal annealing [1,2]. These defects were formed from complexes or clusters of point defects formed from self-interstitial silicon atoms, vacancies, and impurity atoms (O, C, and elements of groups III and V of the Periodic table). The luminescence intensity of these centers decreased significantly (by several orders of magnitude) with the increase of temperature and therefore did not arouse interest for practical application. However, recently, low-temperature silicon LEDs have been used in a variety of fields, such as quantum optics, ultra-low temperature calculations, and neuromorphic computing [3,4]. LEDs with X- (wavelength 1193 nm), W- (1214 nm), G- (1280 nm), H- (1339 nm), C- (1571 nm), T- (1326 nm) and P- (1617 nm) centers are considered the most promising, since they are characterized by narrow and well-reproducible lines of optical emission and absorption lines [5–7]. Not all of the above-mentioned centers have a reliably determined structure, and the optical properties also need to be studied in more details. It should be noted that the study of the above-mentioned centers in silicon enriched with ^{30}Si makes it possible to reveal their new properties. Thus, in [8] the new data on width and fine structure of W-, C- and G-lines was obtained. Over the past 50 years, many technological methods have been developed to introduce these centers into silicon [2]. The method of ion implantation has become the most widespread, since it is used in fabrication of integrated circuits. However, the development of new technological methods for creating light-emitting structures continues. In particular, in paper [9] it was demonstrated that G- and W- centers may be formed using implantation of a focused (diameter 50 nm) ion beam with a nanometer accuracy. A combination of metal-assisted chemical etching (MACEtch) and implantation of carbon ions made it possible to form a system of nanopillars in the amount of one thousand pieces per square millimeter with luminescence of G-center [10]. The study of the possibility of luminescent centers formation using laser irradiation is of interest, since in most cases there's no more need for additional annealing, which is necessary after radiation exposure or ion implantation.

Currently, the effect of femtosecond laser pulses on monocrystalline silicon is widely used to create various kinds of functional micro- and nanoreliefs on its surface [11–13]. In particular, by femtosecond laser macrostructuring, it is possible to create anti-reflective reliefs on the silicon surface to increase the efficiency of solar cells and photodetectors [14–16], to control the hydrophobic/hydrophilic properties of the surface [17,18], to control cell adhesion [19]. Another potentially promising application of silicon laser processing is the possibility of forming optically active centers in the near-surface region. In paper [20], it was shown that treating the surface of monocrystalline silicon with a series of femtosecond laser pulses in SF6 followed by thermal annealing leads to the appearance of a wide band in the luminescence spectrum at low temperatures with its maximum at a wavelength of 1540 nm, which the authors interpreted as D1- dislocation-related luminescence line.

The formation of structural defects and luminescent centers in silicon irradiated with a femtosecond laser occurs as a result of intense thermomechanical action on the surface layers of the material [21,22]. Absorption of a laser pulse at a wavelength of 780 nm occurs due to single-photon and two-photon interband transitions, which leads to the generation of dense electron-hole plasma with a carrier concentration of $\sim 10^{21}$,cm^{-3}. Intense photoexcitation of a semiconductor leads to an increase in absorption by free charge carriers and their heating to temperatures $\sim 10^4$ K, while due to the short duration of exposure, the lattice remains practically cold on a femtosecond time scale. After the pulse ends on a picosecond time scale, hot carriers transfer energy to the lattice, which leads to an increase in its temperature. Due to the nonlinear nature of absorption, the depth of the laser exposure zone is significantly lower than the penetration depth of radiation in the linear absorption mode, which is 8 μm for a wavelength of 780 nm [23]. It is important that heating of the lattice occurs on a picosecond time scale almost isochorically (the material does not have time to expand), which leads to a strong increase in pressure in the surface layers. Evidence of pressure generation with values of several GPa and higher under femtosecond laser exposure is the fact that polymorphic modifications of silicon (high-pressure phases) were detected in the irradiated areas [24]. The possibility of using laser treatment with femtosecond pulses to create X-, W-, H-, C-, G-, T- and P-centers has not been studied. The purpose of this work is to study the luminescent centers formed in silicon during laser irradiation, as well as the effect of measurement temperature and excitation power on the parameters of these centers.

1. Experiment procedure

The initial sample was a single-crystal wafer of Si p- conductance type fabricated by Czochralski method (Cz–Si) in direction [100] with resistivity 20 Ω·cm (KDB-20). A femtosecond (fs) titanium-sapphire laser with a wavelength of 780 nm, a pulse duration of 100 fs, and a pulse repetition rate of 10 Hz was used for irradiation. The laser beam was featuring a Gaussian intensity profile and focused into a spot 150 μm in diameter at level e^{-1}. The wafer was irradiated in air under normal conditions by line-by-line scanning of an area with dimensions $3 \times 3\,\text{mm}^2$ at a speed of $\sim 100\,\mu$m/s (the distance between the scanning lines $\sim 100\,\mu$m). The energy in the pulse was $\sim 160-190\,\mu$J. The corresponding density of energy in the beam center was $\sim 0.95\,\text{J/cm}^2$. Luminescent centers were formed in a thin near-surface layer, since at high radiation power, the absorption coefficient in Si for the laser wavelength increases by several orders of magnitude [11].

Photoluminescence (PL) was excited by red (wavelength of 632 nm), green (532 nm) and violet (405 nm) light from continuous solid-state and semiconductor lasers with a power of up to 2–50 mW and was detected in the wavelength range of 1000–1650 nm at temperatures of 10–100 K using an automated monochromator MDR-23 and InGaAs-photodetector operating at room temperature. Correction for the optical path and detector sensitivity was performed using an Avalight-hal-cal calibration lamp with a known spectral distribution. The system resolution was 5 nm.

2. Experimental results and discussion

Characteristic PL spectra of samples after irradiation by laser measured at temperatures of 10–40 K, are illustrated in Fig. 1. In 1050–1200 nm area, luminescence lines associated with the boron dopant in the initial sample, and a high-intensity intrinsic luminescence line (1130 nm) [25], the so-called near-band-edge line (NBE), are detected. In the range of 1200–1650 nm we see formation of narrow lines with maxima at the wavelengths of 1213, 1340 and 1618 nm and a wide defect-related band. As the wavelengths increase, the intensity of the band decreases. This defect-related band was detected earlier after irradiation of silicon with fast particles [26] and ion implantation [2]. However, the nature of this band is still unclear [10]. The narrow lines belong to the known W-, H- and P-centers, respectively. W-line belongs to the center formed of three interstitial silicon atom (tri-interstitials) [27–29]. H- and P-lines belong to the complexes which incorporate oxygen atoms. They arise during irradiation and implantation, as well as after heat treatment of Cz–Si with a high oxygen concentration at temperatures 250 °C–600 °C and duration of 1–500 h [2,30,31]. The NBE line is usually not observed after irradiation or ion implantation, but may appear as a result of subsequent annealing.

Temperature dependences of PL intensities for H- and P-lines within the temperature range of 20–70 K are shown in Fig. 2. As can be seen from the figure, their intensity decreases with the increasing temperature. They are well described by the known formula [2]:

$$I(T) = I(0)[1 + A\exp(-E/kT)]^{-1}, \qquad (1)$$

where E — activation energy of luminescence quenching, A — coupling constant for this center. Activation energies

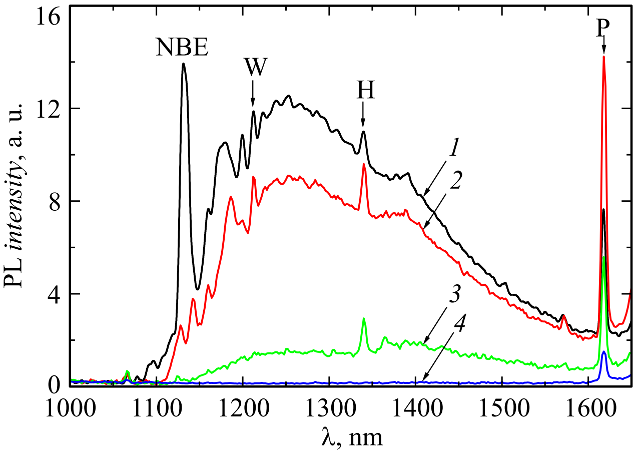

Figure 1. PL spectra of samples after laser irradiation at temperatures, K: *1* — 10, *2* — 20, *3* — 30 and *4* — 40. Power of green laser was 31 mW.

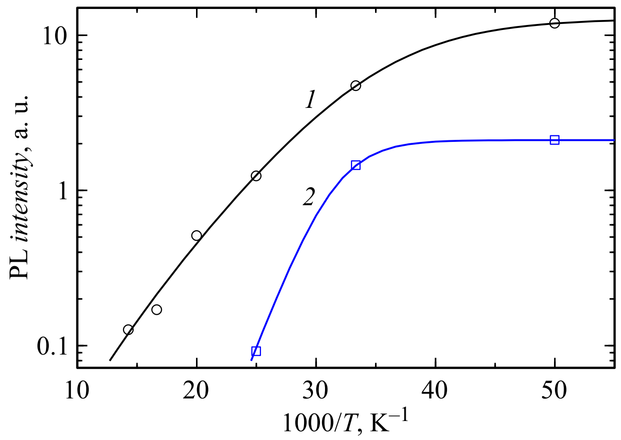

Figure 2. Temperature dependencies of PL intensities for P- (*1*) and H- (*2*) lines.

of PL intensities quenching are equal $E_H = 34.9$ meV and $E_P = 12.8$ meV. As a rule, quenching is caused by multiphonon nonradiative recombination.

In [30] for the sample obtained by implantation of erbium and oxygen ions, the quenching energy of the H-center was 19 meV. The almost twofold difference observed is probably due to a different defective system of structural defects, which can slightly alter the structure of the luminescent H-center, and the system of centers of nonradiative luminescence. The activation energy of PL quenching obtained in this work for P-center is very close to the values of the quenching energy determined in [2] (14.7 meV), and [30] (11 meV).

Figure 3 shows the PL spectra measured at 10 K and different powers of exciting light (photon flux density, F) with the wavelength of 532 nm. For W-, H-, and P-lines, an increase in pumping power does not change their position, but increases the intensity of PL. In contrast to these centers, an increase in pumping power leads to a declined intensity of NBE-line (compare Fig. 3, *b* and *c*).

The dependencies of intensities of the point defects lines on photon flux density are shown in Fig. 4. They are described by the well-known formula [32]:

$$PL(F) = PL_{\max}\sigma\tau F/(\sigma\tau F + 1), \qquad (2)$$

where $PL_{\max}$ — maximum PL intensity, σ — photon capture cross-section at the center and τ — lifetime of the center in the excited state. The higher the excitation efficiency, the lower then pumping power at which luminescence intensity is saturated. The approximation of the experimental dependences by the above formula gives the values for H-center (1240 nm) $(\sigma\tau)_H = 4.8 \cdot 10^{-19}$ cm^2·s, for P-center (1678 nm) $(\sigma\tau)_P = 10 \cdot 10^{-19}$ cm^2·s, and for W-center (1214 nm) $(\sigma\tau)_W = 1 \cdot 10^{-19}$ cm^2·s. As far as we know, the excitation efficiency of luminescent W-, H-, and P-centers has not been studied before.

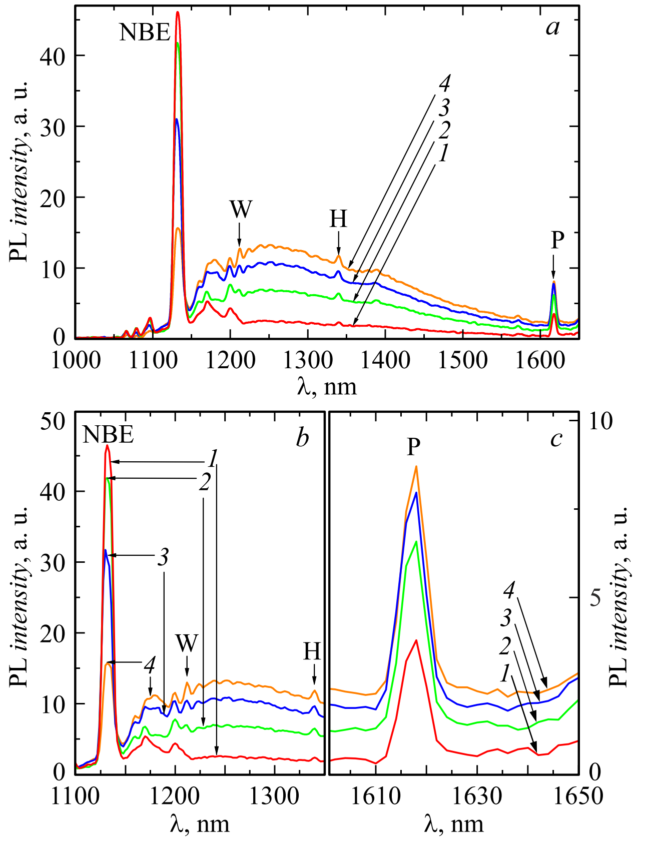

Figure 3. PL spectra of samples after laser irradiation at excitation power of green laser, mW: *1* — 6, *2* — 9, *3* — 19 and *4* — 35, measured at a temperature of 10 K within the ranges of the wavelengths, nm: *a* — 1000–1650, *b* — 1100–1350, *c* — 1600–1650 (*c* — the scale along the luminescence intensity axis has been reduced by 5 times).

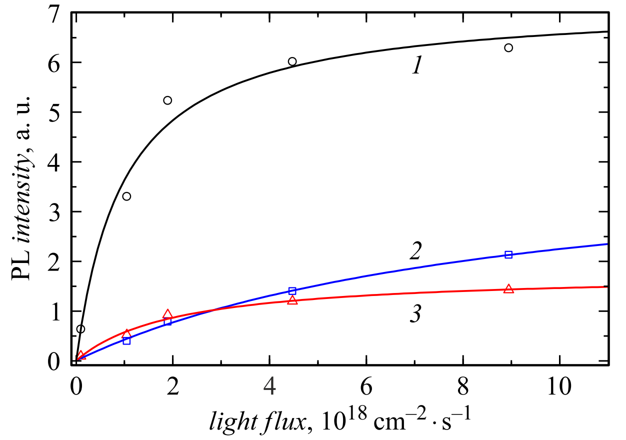

Figure 4. Dependences of PL intensities for: *1* — P-, *2* — W-, *3* — H-lines versus the photon flux density at a temperature of 10 K.

Increase of the pumping power leads to an increase in the intensity of PL of the defect-related band (Fig. 3, *a*). At that, the shape of the spectrum is not changing. This means that the structure of the luminescent centers in this band does not change, but the concentration of excited centers increases. The dependence of the integral intensity of the defect-related band on the pumping power is shown in Fig. 5. It is important to note that this integral dependence also tends to saturate, as do the centers of point defects studied above.

An increase in pumping power is accompanied by a decrease in the integral intensity of PL NBE line (Fig. 3, *b*). This contradicts the available experimental data for samples in which the light-emitting layer was created during the annealing of silicon implanted with ions Er [30,33], Si [34,35], O [36,37], P [34], liquid-phase recrystallization of the amorphous layer formed during laser irradiation of [38], and splicing of silicon wafers (the so-called bonding process) [34]. At that the luminescent centers of Er^{3+}ions [30,33], $\{113\}$ defects [36] and dislocation luminescence [30,34–37] were located in the near-surface layer formed during the process of thermal annealing of the defective layer. Often, after annealing, a line of NBE luminescence appeared in the luminescence spectra. It has been shown that this line occurs deeper than the disturbed layer. As a rule, with an increase in the intensity of the exciting light or the pumping current, its intensity increases and may even exceed the intensity of the formed luminescent centers as the concentration of excited centers rises [30]. It is reasonable to assume that in our experiment, the centers responsible for PL of W-, H-, P-lines and the defect-related band were formed in the near-surface layer modified by laser irradiation, and the near-band-edge luminescence (NBE-center) is excited in the region located behind a defective layer. To test our assumption, the photoluminescence spectra were measured when it was excited by different lasers (Fig. 6).

In case of a violet laser, there is practically no near-band-edge luminescence, the ratio of the integral intensity of NBE-line to the integral intensity of the defect-related luminescence (R) tends to zero, since almost all the light from the laser is absorbed in the defect-related layer. The penetration depth of green light in silicon is greater than violet, and it penetrates already into the layer undisturbed by laser irradiation, causing the appearance of near-band-edge luminescence and increasing. Red light penetrates even deeper, and the proportion of penetrating laser radiation (PL inducing NBE) is a large part of the total radiation compared to green light, and, accordingly, increases R. In these experiments, as a rule, the intensity of the near-band-edge luminescence is directly proportional to the intensity of the excitation. This indicates that the degree of disruption of the defective structure does not cause a change in the absorption coefficient of the exciting light with an increase in its intensity. As mentioned above, when silicon is irradiated with a femtosecond laser, more significant deviations of the defect-related structure may occur. In particular, the light absorption coefficient may increase as it approaches the surface. As a result, as the intensity of the exciting light increases, the efficiency of its absorption in the disturbed layer rises and most of it goes to excite W-, H-, P-lines and a wide band, and a decrease in the proportion of transmitted light, which induces the near-band-edge luminescence, is accompanied by its lower intensity (Fig. 5).

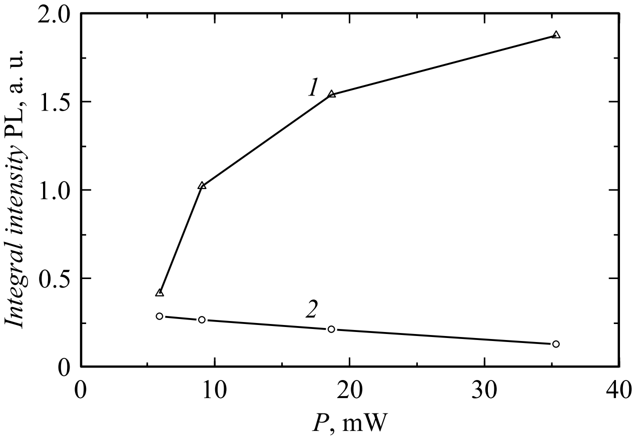

Figure 5. PL integral intensity versus excitation power of green laser for the defect-related band (*1*) and NBE-line (*2*). The measurement temperature is 10 K.

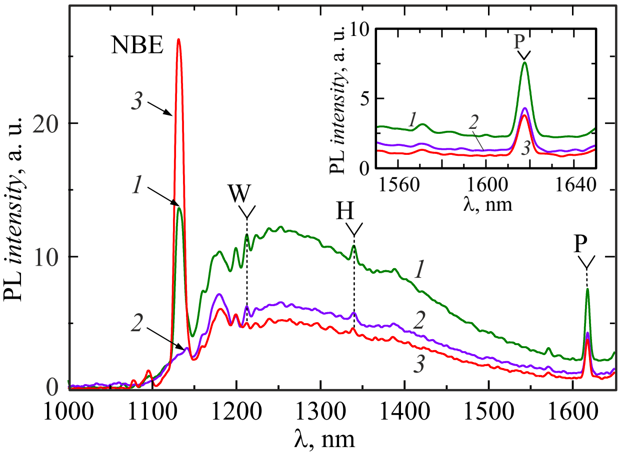

Figure 6. PL spectra when excited by different lasers at a temperature of 10 K. Excitation light wavelength of λ, nm (laser power, mW): *1* — 532 (35), *2* — 405 (46) and *3* — 632 (30).

Conclusion

PL was studied in silicon grown by Czochralski method and irradiated with a femtosecond titanium-sapphire laser with a wavelength of 780 nm. In PL spectra of the irradiated samples, a wide band in the region of $1.15-1.6\,\mu$m, narrow W-, H-, and P-lines, as well as the near-band-edge luminescence line are formed. The effect of the measurement temperature, pumping power, and wavelength of the exciting laser on these spectra is investigated. An increase in the measurement temperature leads to a decrease in the intensity of PL of H- and P-lines with quenching energies of 34.9 and 12.8 meV for H- and P-lines, respectively. For the H-line, the energy value depends on the sample fabrication conditions, whereas for the P-line, it does not depend on the technology used. The luminescence intensities of the W-, H-, and P-lines, as well as the integral intensity of the defect-related band rise with increasing excitation power. The efficiencies of PL excitation were determined for the first time for W-, P- and H-centers: $1 \cdot 10^{-19}$, $10 \cdot 10^{-19}$ and $4.8 \cdot 10^{-19}\,\text{cm}^2\cdot\text{s}$ respectively. It has been established that the luminescence centers of the narrow lines and the defect-related band are located in the near-surface layer modified by laser irradiation.

Conflict of interest

The authors declare that they have no conflict of interest.

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