Opt Quant Electron (2017) 49:74
DOI 10.1007/s11082-017-0911-0

Mutual influence of Auger and non-radiative recombination processes under silicon femtosecond laser irradiation

Alexandra Shamova[1] · **Galina Shandybina**[1] ·
Evgeny Yakovlev[1] · **Alexandra Georgieva**[1]

Received: 9 October 2016 / Accepted: 17 January 2017 / Published online: 24 January 2017

Abstract The results of theoretical study of the contribution of recombination processes in additional heating of the surface of monocrystalline silicon during multipulse femtosecond laser processing are presented to discussion. The numerical evaluations are made in regimes of the laser radiation below the ablation threshold, when the microgeometry of the surface is formed due to the processes of self-organization. The influence of Auger recombination processes on the photoexcitation of the semiconductor during the pulse and relaxation after the pulse is studied in detail. It is shown that the additional heating of the surface due to non-radiative recombination is extremely small at pulse repetition rate 10 Hz–1 MHz. Mutual influence of recombination processes of both types is shown.

Keywords Recombination processes · Femtosecond laser pulses · Monocrystalline silicon

1 Introduction

In recent years, the focus is on studies of ultrafast processes in semiconductors occurring on the picosecond and femtosecond time scale (Willardson et al. 2000; Ruzicka 2012), that enhances perceptions of the semiconducting state of matter. As a result of this it becomes

---

This article is part of the Topical Collection on Fundamentals of Laser Assisted Micro- and Nanotechnologies.

Guest edited by Eugene Avrutin, Vadim Veiko, Tigran Vartanyan and Andrey Belikov.

✉ Alexandra Shamova
Sasha100111@yandex.ru

✉ Galina Shandybina
corchand@gmail.com

[1] University ITMO, 49 Kronverksky Pr., St. Petersburg, Russia 197101

possible to control the microgeometry of the surface and create materials with new physico-chemical properties.

Currently, one of the most interesting objects of research is the formation of micro- and nanostructures on the surface of semiconductors, particularly silicon, under the action of ultrashort laser pulses (Tan and Venkatakrishnan 2006; Harzic et al. 2005; Cerami et al. 2013). Formation of micro- and nanorelief on silicon surface improves the optical and electrical properties, which allows to extend the field of its application.

In the technology of femtosecond laser processing of semiconductors multipulse irradiation is widely used. The heat accumulation effects from pulse to pulse play important role in the final result of processing. In semiconductors recombination processes take part in the heating process.

For monocrystalline silicon two types of recombination, occurring in these conditions, are typical: Auger recombination and non-radiative recombination. Moreover, as previously shown in work (Guk et al. 2016), during irradiation of silicon by femtosecond laser pulses the contributions of recombination processes have different orientation. At pulse energy density below the threshold and pulse repetition rate 10–1000 Hz, due to non-radiative recombination additional heating of the lattice occurs, shifted in time relative to the heating by electron gas. Auger recombination decreases concentration of nonequilibrium carriers, without participating directly in the heating of the lattice, which results in the decrease of the contribution of non-radiative recombination in the heat of silicon surface for the next pulse.

In the paper the detailed study of the mutual influence of Auger recombination and non-radiative recombination in evaluating accumulative heating of silicon surface during multipulse femtosecond laser irradiation below the ablation threshold, based on model, that was presented earlier (Guk et al. 2016), is carried out.

2 The calculation of concentration and residual temperature of silicon surface taking into account recombination processes

The quantitative-analytical model of the photoexcitation and heating of silicon during multipulse femtosecond laser irradiation was presented earlier (Guk et al. 2015, 2016). The main points of the model are presented below.

Under the assumption of local quasi-equilibrium the spatiotemporal dynamics of the concentration of nonequilibrium carriers $n(z, t)$ (z-axis is directed into the material) during the pulse action is calculated, which is determined by two-photon absorption of light quanta, diffusion of the carriers, by the flows of external photoemission and thermoemission and Auger recombination. The model is supplemented with the equation describing the luminous flux density distribution inside the semiconductor for the domed temporal laser pulse shape. The temperature of electron gas and the temperature of the lattice during laser irradiation are calculated using equations of two-temperature model, taking into account the changes of heat capacity of electron gas. After irradiation the maximum temperature T_{max}, to which due to electron–phonon coupling the silicon surface is heated before the beginning of cooling, is calculated. At stage of cooling the change of the temperature of silicon surface due to thermal conductivity before the next pulse at pulse repetition rate f is calculated. The additional heating of the lattice that occurs during the time between pulses due to the non-radiative recombination T_{rec} is calculated by the condition that the heat source can be considered as surface, with time-dependent heat flux.

To simplify the analysis of the contribution of recombination processes in the total heating of silicon surface it is invited to evaluate the residual heating of the surface per N femtosecond pulses using following equations:

$$\Delta T(z = 0, t = N/f) = \Delta T_1 + \Delta T_2 \tag{1}$$

$$\Delta T_1 = \frac{T_{\max}}{\alpha\sqrt{\pi a/f}} \sum_{i=1}^{N} \frac{1}{\sqrt{i}} \tag{2}$$

$$\Delta T_2 = T_{rec} \sum_{i=1}^{N} \frac{1}{\sqrt{i}} = E_g \frac{\sqrt{a} n_r l_e}{\sqrt{\pi} t_{rec} \lambda_i} \int\limits_{o}^{t} \frac{\exp(-u/t_{rec})}{\sqrt{t-u}} du \sum_{i=1}^{N} \frac{1}{\sqrt{i}} \tag{3}$$

where $t = 1/f$, $a = 0.86$ cm^2 s^{-1}—silicon thermal conductivity, $\alpha = 7.5 \times 10^4$ cm^{-1}—absorption coefficient, corresponding to the absorption coefficient in the moment of time, when surface temperature reaches its maximum (T_{max}), it is calculated as the reciprocal to the depth in the above-stated moment, at which temperature decreases e times, t_{rec}—non-radiative recombination coefficient, $l_e = 10^{-6}$ cm—electron mean free path, n_r—initial concentration of exited electrons, involved in non-radiative recombination, $\lambda_i = 0.2$ - J cm^{-1} K^{-1}—thermal conductivity of the lattice, $E_g = 1$ eV—band-gap energy of silicon.

The expression (1) describes the total residual heating of the surface for (N + 1) pulse at pulse repetition rate f; the expression (2) determines the residual heat, caused by the heat exchange between electron gas and the lattice (Yakovlev et al. 2013); the expression (3) determines the residual heat, caused by non-radiative recombination (Veiko et al. 2008).

For the calculations the experimental data is used (Martsinovsky et al. 2009; Zhu et al. 2005), corresponding to the characteristic regimes of low-frequency microstructuring of silicon surface: energy density of a single pulse $Q = 0.4$ J cm^{-2}; wavelength $\lambda = 1250$ nm, pulse repetition rate $f = 10$–1000 Hz; pulse duration $\tau = 80$ fs; pulse number $N = 1$–1200.

3 Results and discussion

The Auger recombination coefficient is a quantitative characteristic of the Auger recombination rate (Hawley M.J. 1993). It should be noted that the values of the Auger recombination coefficient β_3 in the literature differ by an order of magnitude under identical irradiation conditions. Currently, there are no methods for direct measurement of this parameter. As a rule, the resulting parameter strongly depends on the experimental conditions and the model. Therefore in the calculations three most common in the literature (Beck and Conradt 1973; Li et al. 1997; Gerlach et al. 1972; Ashitkov et al. 2004; Hopkins et al. 2010) values of Auger recombination coefficient $\beta_3 = 1 \times 10^{-31}$ cm^6 s^{-1}, $\beta_3 = 4 \times 10^{-31}$ cm^6 s^{-1}, $\beta_3 = 1 \times 10^{-30}$ cm^6 s^{-1} are used.

As previously shown in work (Guk et al. 2016), during the femtosecond laser pulse action, the account of contribution of Auger recombination leads to decrease in the concentration of nonequilibrium carriers by 10–20%, depending on the value of Auger recombination coefficient. Calculations show, that after the pulse due to Auger recombination the concentration of nonequilibrium carriers for the first 10 ps decreases by 30–50% depending on the value of Auger recombination coefficient, which affects heat capacity of electron gas, and, correspondingly, affects the heat transferred to the lattice.

It should be noted that approximation of time-independent heat capacity of electron gas is used in cases when the concentration of nonequilibrium carriers is changed slightly. At value of Auger recombination coefficient $\beta_3 = 1 \times 10^{-31}$ cm^6 s^{-1} the concentration of nonequilibrium carriers after the first pulse action remains practically unchanged and the highest maximum surface temperature is reached. The influence of Auger recombination on the maximum surface temperature slightly, so T_{max} can be considered constant and equal to 1200 K (without taking into account the initial temperature).

To evaluate the heating of the surface due to non-radiative recombination, it is necessary to estimate the value of concentration of nonequilibrium carriers, involved in non-radiative recombination n_r. We equate the rates of non-radiative recombination and Auger recombination $n(z, t)/t_{rec} = \beta_3 n^3(z, t)$. For the values of the coefficients of Auger recombination $\beta_3 = 1 \times 10^{-31}$ cm^6 s^{-1}, and non-radiative recombination $t_{rec} = 10^{-6}$ s, the corresponding concentration of nonequilibrium carriers can be evaluated $n(z, t) = n_r = 3.2 \times 10^{18}$ cm^{-3}.

The dynamics of concentration of nonequilibrium carriers $n(z, t)$ on the surface after the single pulse action represented on Fig. 1. From the graph, knowing the value of n_r, one can define the time, at which the rates of non-radiative recombination and Auger recombination are equal. It is approximately 150 ns. It can be considered, that exactly in this moment of time there is an additional heat source—recombining electrons.

The dependence of the concentration of nonequilibrium carriers n_r on the value of Auger recombination coefficient represented on Fig. 2. As can be seen in Fig. 2, with the increase of value of Auger recombination coefficient by an order of magnitude the concentration of nonequilibrium carriers, involved in non-radiative recombination, decreases 3 times, which results in the increase of the time, through which an additional heat source, caused by non-radiative recombination, turns on from 130 to 200 ns.

To evaluate the contribution of non-radiative recombination in the heat of silicon surface, let us consider (Fig. 3) the dependences of residual temperature of silicon surface on the pulse number. Figure 3a represents the change of the first term of Eq. (1), where the heat source is the heat exchange between electron gas and the lattice. Figure 3b represents the change of second term of Eq. (1), where the heat source is non-radiative recombination.

The comparison of Fig. 3a with b allows us to evaluate the contribution of recombination heating. It is approximately 0.18% of the total residual temperature of silicon surface.

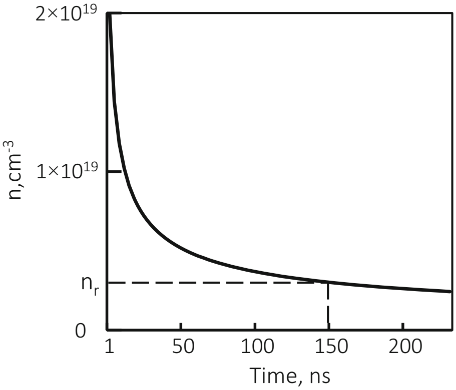


Fig. 1 The dynamics of concentration of nonequilibrium carriers $n(z, t)$ on the surface after the single pulse action. $Q = 0.4$ J cm^{-2}

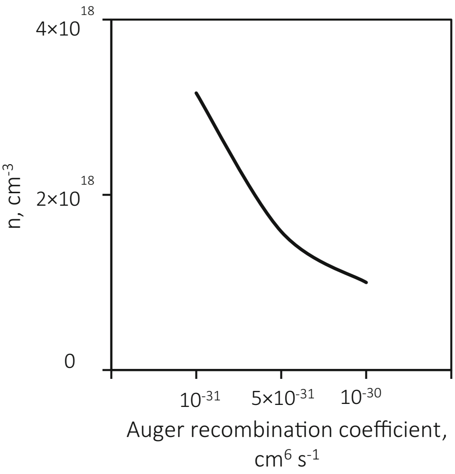
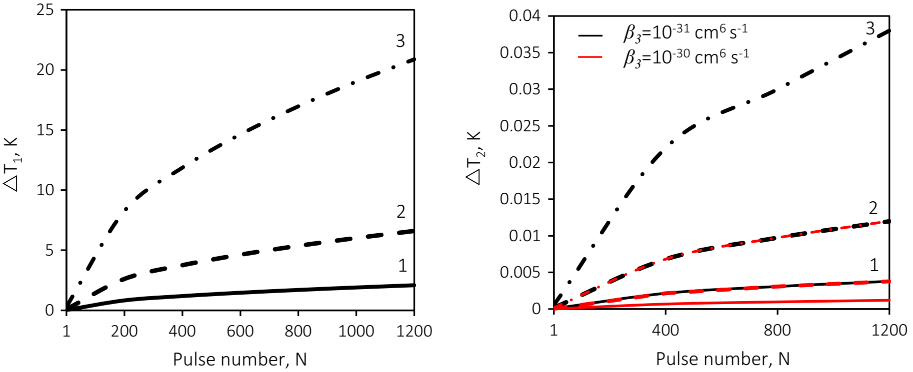


Fig. 2 The dependence of the concentration of nonequilibrium carriers n_r on the value of Auger recombination coefficient. $Q = 0.4$ J cm^{-2}



(a) **(b)**

Fig. 3 The dependence of residual temperature of silicon surface on the pulse number. *Curve* 1 at pulse repetition rate 10 Hz, *curve* 2 100 Hz, *curve* 3 1 kHz. **a** First term of Eq. (1), **b** second term of Eq. (1)

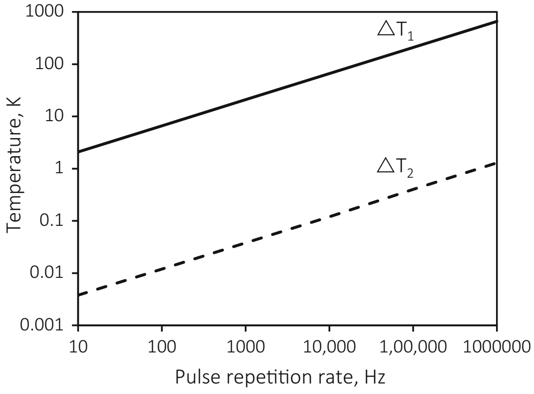


Fig. 4 The comparison of residual temperature without contribution of non-radiative recombination (ΔT_1) with the heat due to non-radiative recombination (ΔT_2). $Q = 0.4$ J cm^{-2}, $N = 1200$

During multipulse irradiation the residual temperature of silicon surface changes with the increase of pulse repetition rate. At Fig. 4 the dependence of residual temperature of silicon surface, irradiated by 1200 laser pulses with energy density $Q = 0.4$ J cm^{-2}, on pulse repetition rate is shown. As can be seen in Fig. 4, with the increase of pulse repetition rate by two orders of magnitude the residual temperature increases by an order of magnitude. The contribution of additional heating due to non-radiative recombination is small, at pulse repetition rate of 1 MHz and value of Auger recombination coefficient $\beta_3 = 1 \times 10^{-31}$ cm^6 s^{-1} is 1.3 K.

4 Conclusion

Thus, despite the fact that two types of recombination separated in time, they can have opposite effect on the accumulation of the heat of silicon surface. Auger recombination does not give an additional contribution in the heat of the crystal lattice. However, its high rate can noticeably reduce the concentration of nonequilibrium carriers after the laser pulse action, which results in the decrease of the contribution of non-radiative recombination. Decisive importance in assessing the role of Auger recombination belongs accuracy knowledge of its coefficient. Due to non-radiative recombination there is an additional heating of the lattice leads to the increase of surface temperature of silicon in nanosecond time range.

During multipulse irradiation the residual temperature of silicon surface changes with the increase of pulse repetition rate. It is shown that with the increase of pulse repetition rate by two orders of magnitude the residual temperature increases by an order of magnitude.

The increase in the heating due to non-radiative recombination is from 3.8×10^{-3} to 1.3 K in the range of pulse repetition rates from 10 Hz to 1 MHz per 1200 pulses with energy density of a single pulse 0.4 J cm^{-2}, which is less than 1% in the total growth of residual temperature of the surface.

Acknowledgements The authors are grateful to I.V. Guk for useful discussions. This work was supported by Grant 14-29-07227 from the Russian Foundation for Basic Research and by Grant 14-12-00351 from the Russian Science Foundation.

References

Ashitkov, S.I., Ovchinnikov, A.V., Agranat, M.B.: Recombination of an electron-hole plasma in silicon under the action of femtosecond laser pulses. JETP Lett. **79**, 529–531 (2004)

Beck, J.D., Conradt, R.: Auger-recombination in Si. Solid State Commun. **13**, 93–95 (1973)

Cerami, L., Mazur, L.E., Nolte, S., Schaffer, C.B.: Femtosecond laser Micromachining. Ultrafast Nonlinear Optics, Chapter 12. Springer, New York (2013)

Gerlach, W., Schlangenotto, H., Maeder, H.: On the radiative recombination rate in silicon. Phys. Status Solidi A **13**, 277–283 (1972)

Guk, I., Shandybina, G., Yakovlev, E.: Infuence of accumulation effects on heating of silicon surface by femtosecond laser pulses. Appl. Surf. Sci. **335**, 851–855 (2015)

Guk, I.V., Shandybina, G.D., Yakovlev, E.B., Shamova, A.A.: Role of recombination processes during multipulse femtosecond microstructuring of silicon surface. Opt. Quantum Electron. **48**, 1–10 (2016)

Harzic, R., Schuck, H., Sauer, D., Anhut, T., Riemann, I., König, K.: Sub-100 nm nanostructuring of silicon by ultrashort laser pulses. Opt. Express **13**, 6651–6656 (2005)

Hawley M.J.: High pressure studies of strained layer semiconductor' lasers. Ph.D. thesis, University of Surrey, (1993) Hopkins, P.E., Barnat, E.V., Cruz-Campa, J.L., Grubbs, R.K., Okandan, M., Nielson, G.N.: Excitation rate dependence of Auger recombination in silicon. J. Appl. Phys. **107**, 1–6 (2010)

Li, C.-M., Sjodin, T., Dai, H.-L.: Photoexcited carrier diffusion near a Si(111) surface: non-negligible consequence of carrier-carrier scattering. Phys. Rev. **B 56**, 15252–15255 (1997)

Martsinovsky, G.A., Shandybina, G.D., Dement'eva, Y.S., Dyukin, R.V., Zabotnov, S.V., Golovan', L.A., Kashkarov, P.K.: Generation of surface electromagnetic waves in semiconductors under the action of femtosecond laser pulses. Semiconductors **43**, 1298–1304 (2009)

Ruzicka, B.A.: Ultrafast optical studies of electronic dynamics in semiconductors. Ph.D. thesis, University of Kansas (2012)

Tan, B., Venkatakrishnan, K.: A femtosecond laser-induced periodical surface structure on crystalline silicon. J. Micromech. Microeng. **16**, 1–6 (2006)

Veiko, V.P., Libenson, M.N., Chervyakov, G.G., Yakovlev, E.B.: Vzaimodeistvie Lazernogo Izlucheniya s Veshchestvom [Interaction of Laser Radiation with Matter]. Fizmatlit, Moscow (2008)

Willardson, R.K., Weber, E.R., Tsen, K.T.: Ultrafast Physical Processes in Semiconductors. Elsevier, Amsterdam (2000)

Yakovlev, E.B., Sergaeva, O.N., Svirina, V.V., Yarchuk, M.V.: Modeling of thin Cr film oxidation under the action of ultrashort laser pulses. SPIE 9065, 906509-1-906509-6 (2013)

Zhu, J., Li, W., Zhao, M., Yin, G., Chen, X., Chen, D., Zhao, L.: Silicon microstructuring using ultrashort laser pulses. Lasers in Material Processing and Manufacturing II. Proc. SPIE, **5629**, 276–283 (2005)