phys. stat. sol. (c) **4**, No. 8, 3095–3099 (2007) / **DOI** 10.1002/pssc.200675490

Influence of Cu contamination on dislocation related luminescence

E. A. Steinman and **A. N. Tereshchenko***

Institute of Solid State Physics, RAS, 142432 Chernogolovka, Moscow district, Russia

Received 17 September 2006, revised 22 March 2007, accepted 23 March 2007
Published online 1 June 2007

PACS 61.72.Hh, 66.30.Jt, 71.55.Cn, 78.55.Ap, 81.40.Tv

This work is devoted to investigation of Cu contamination on dislocation related luminescence (DRL) in Si. Cu is known to be a very fast diffuser with high solubility. Fz Si samples were plastically deformed at 950 °C up to dislocation density of about 10^7 cm^{-2}. Cu diffusion was performed by diffusion at 950 °C from a quartz ampoule contaminated with Cu. The presence and concentration of luminescent copper (Cu PL) centers was evaluated from the excitation dependence of the copper bound exciton no-phonon line (BE NP) line at 1.014eV, which was activated after annealing at 1100 °C and rapid quenching in the water. 10 minutes isochronous annealing of the samples in the temperature range 300–600 °C revealed quite a different behavior of D4 and D1/D2 lines. It was assumed that a strong decrease of D1/D2 line intensity in annealing interval 400–500 °C could be attributed to passivation of D1/D2 luminescence centers by Cu atoms.

1 Introduction The dislocation related luminescence (DRL) in Si used recently for the light emitting diode with external quantum efficiency of about 0.1% [1], was gradually enhanced by gettering of metallic impurities. On the other hand, it was reported that several transition metals could even activate DRL [2]. The passivation of dislocations by Cu contamination has been reported in Ref. [3] and quite the contrary an increase of recombination activity has been observed after contamination of dislocations with Ni [4]. This contradiction probably arises from a very complicated set of energetic levels introduced by dislocations into the forbidden gap and dependence of interaction of impurities with dislocations on the contamination level. The latter statement is supported by observation of dependence of dislocation recombination activity on the level of Cu contamination. For low level (~1 ppb) the EBIC contrast increased markedly at low temperatures, while for a Cu concentration of about 15 ppb the contrast was observed in the whole temperature range (80–300 K) [5]. In material with high Cu contamination (ppm range) the authors observed Cu precipitates along dislocations and dramatic increase of the contrast in the whole temperature range. The formation of copper precipitates in silicon greatly decreases carrier diffusion length [6].

The process of precipitation goes much faster in the presence of extended defects and at high Cu concentration even precipitate colonies have been observed [7]. The colonies are very effective recombination regions; an EBIC contrast as high as 93% has been reported for such colonies [8].

While the dramatic decrease of minority carrier life time at high Cu contamination is caused by formation of precipitate related defect band, less definitely we can presume an influence of Cu at low contamination level. At least four reproducible Cu related levels have been found in Si [9]. Their activity de-

* Corresponding author: e-mail: tan@issp.ac.ru, Fax: +7 496 524 97 01

pends on the level and type of doping. Taking into account a variety of dislocation related levels we can expect rather complicated behavior of Cu in the presence of dislocations. Part of dislocation related levels are radiative recombination centers while another part act as non-radiative centers. The efficiency of DRL therefore depends on competition between two sets of levels [10].
The objective of this work is investigation of influence of low level Cu contamination on DRL in Si.

2 Experimental The float zone grown (FZ) p-type silicon with B-doping 2.85×10^{15} cm^{-3} was used for experiments. Samples with dimensions 4x1x15 mm^3 with large face parallel to (111) plane and long edge along [110] direction were deformed by 3-point bending method at 950 °C in ceramic furnace in argon atmosphere. The dislocation density was varied in the range from 10^5 to 10^7 cm^{-2}, depending on distance from central point. The undeformed edges of the samples were used as reference samples.
Diffusion of copper was performed by heating at 950 °C during 1 h in a quartz ampoule contaminated with Cu. For activation of Cu luminescence centers samples were annealed at 1100 °C during 5 minutes and rapidly quenched in the deionized water. The postquenching isochronous annealing (10minutes) was performed in a quartz furnace with Ar flow in temperature range 300 °C–600 °C. Each step of thermal treatment was followed by photoluminescence (PL) measurements.
The samples were cleaned from Cu contamination by annealing in chlorine atmosphere at 1000 °C during 1 h. The dependence of the intensity of 1.014 eV line at temperature 4.2 K on the excitation power was used for evaluation of concentration of Cu luminescence centers [11, 12]. The excitation power was changed from 0.08 to 8 W/cm^2 using optical density filters.
The PL spectra were recorded using a conventional lock-in technique with a cooled Ge detector. PL was excited by GaAs laser with P_{exc} about 1W/cm^2 and λ = 920 nm. The area of laser spot was estimated to be about 1mm^2.

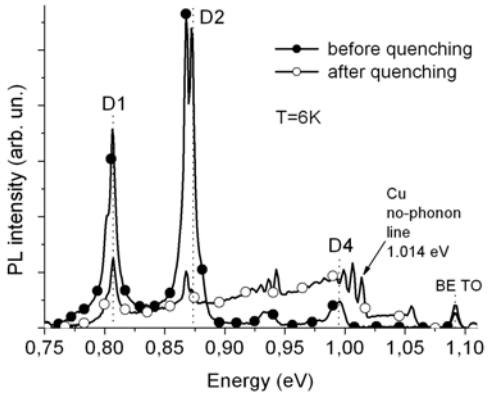

Fig. 1 The comparison of DRL spectrum of Cu contaminated Fz Si sample before and after rapid quenching from 1100 °C.

3 Results and discussion Due to the moderate level of Cu contamination the shape of DRL spectra did not change after diffusion. On the contrary the quenching of samples led to a considerable change of relative intensities of DRL lines. Figure 1 shows the DRL spectra of Cu contaminated sample before and after quenching. The intensive spectrum appears in the range 0.9–1.014 eV. The same spectrum was observed in a reference part of the sample. Moreover, a high-energy shoulder with the head line at 1.06 eV is also seen after quenching. The origin of this shoulder is unknown at the moment. The appearance of the copper bound exciton no-phonon line at 1.014 eV with its replicas after quenching is attribute of activation of luminescent copper (Cu PL) centers [11]. It is difficult to say whether the D4 line exist under Cu related spectrum or not, but the following results allow to suppose that its intensity is negligible in a quenched sample. It is clearly seen that a considerable decrease of D1 and D2 intensities is the result of quenching. It could not be explained by generation of some quenching defects, because the intensity of transverse-optical phonon replica of bound exciton (BE TO) is even higher after quenching.
The Cu related spectrum is very stable at room temperature. At least it does not change after storage for several months. Figure 2 shows the behavior of the whole spectrum after isochronous annealing of quenched sample in the temperature range 300–600 °C. Due to overlapping Cu related spectrum and D4 line after quenching we can not evaluate accurately the contribution of D4 line to the total intensity.

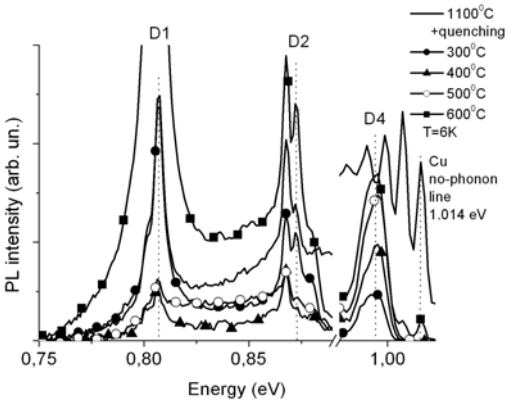

Fig. 2 The influence of isochronous annealing (10 minutes) on the spectral distribution of DRL intensity for Cu contaminated Fz Si sample after rapid quenching from 1100 °C.

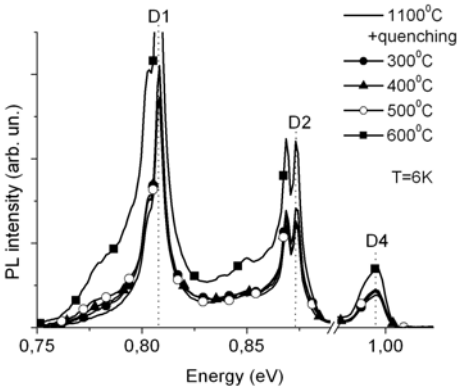

Fig. 3 The influence of isochronous annealing (10 minutes) on the spectral distribution of DRL intensity for the Fz Si sample after cleaning from Cu contamination and rapid quenching from 1100 °C.

Though it is seen from the shape of spectrum that this contribution is negligible. Almost complete quench of Cu related spectrum happens after 10 minutes of 300 °C annealing. It must be noted here that such an annealing is not enough for quench of Cu spectrum in reference part of the sample, where the annealing at 400 °C is required for complete quench. It implies that dislocations are the main sinks for Cu atoms.

The annealing behaviour of D4 and D1/D2 lines is quite different. While the D1 intensity does not change after 300 °C annealing, the D4 line has intensity, which could not be hidden under Cu spectrum. The further annealing leads to gradual growth of D4 line intensity. On the contrary, the D1/D2 line intensities decrease after 400 °C and 500°C annealing. The noticeable growth of their intensity starts after annealing at temperature ≥ 600 °C.

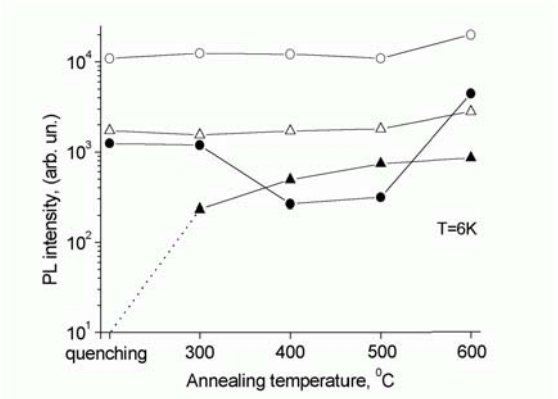

Fig. 4 The comparison of behavior of D1 and D4 line intensities during isochronous annealing (10 minutes) after rapid quenching for Cu contaminated and clean from Cu samples: -●- D1 and -▲- D4, Cu contaminated; -○- D1 and -Δ- D4, after Cl gettering.

Figure 3 shows the result of same quenching and annealing procedure with the sample, which has been cleaned from Cu contamination by a gettering in Cl atmosphere. No Cu related spectrum was observed after quenching. This fact indicates that Cu concentration decreases after Cl gettering. The main difference in annealing dependence of D1/D2 line intensities is the absence of intermediate decrease of their amplitudes.

Figure 4 shows a comparison between annealing behavior of D1 and D4 lines in clean and Cu contaminated samples.

From the absence of Cu related spectrum in as doped sample it follows that the level of Cu contamination is not very high in our case. We made an attempt to evaluate the upper limit of Cu concentration. Figure 5 shows the dependence of the 1.014 eV line on the excitation power. Taking into account a large penetration depth of GaAs laser radiation, the level of excitation is not very high in our case.

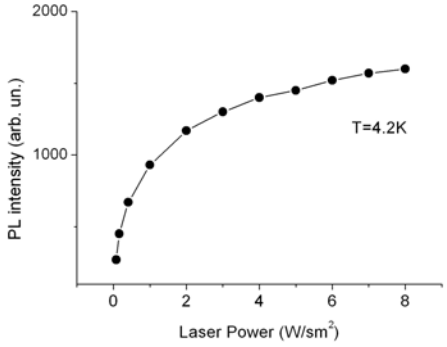

Fig. 5 Dependence of the copper bound exciton no-phonon line at 1.014 eV on the excitation power.

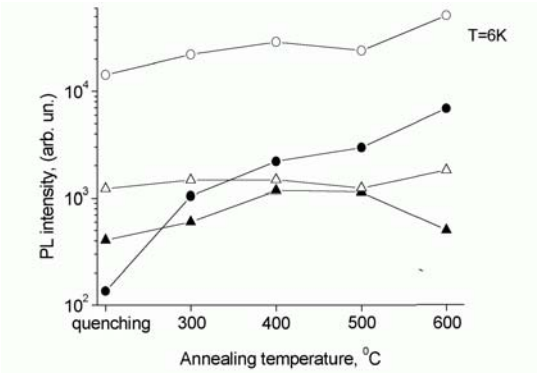

Fig. 6 Dependence of intensity BE TO after rapid quenching on isochronous annealing (10 minutes) for Cu contaminated sample and for sample after Cl gettering: -●- reference part and -▲- dislocation part, Cu contaminated -○- reference part and -Δ- dislocation part, after Cl gettering.

On the other hand, due to the fact that nonradiative recombination path usually dominates in Si samples, the concentration of free excitons must be proportional to the excitation power. The rapid saturation of Cu PL implies a low concentration of Cu related PL centers. Comparing our results with Ref. [12] we can roughly estimate the upper limit of concentration of Cu PL centers as 10^{10} cm^{-3}.

Considering different annealing behavior of D4 and D1/D2 lines let us remember that they originate from different parts of dislocations. While D1 and D2 centers are related to point defects on dislocation lines, the D4 line occurs due to recombination at straight segments of 60° dislocations [13–16]. Therefore an extended wave function of D4 center would be less disturbed by interaction with isolated Cu atom than localized function of deep point defect. At low temperature annealing Cu atoms diffuse to dislocations and interact with dislocation related defects. The sharp decrease of D1/D2 lines at 400 °C and 500 °C means that corresponding centers are passivated due to this interaction [3]. On the contrary, the intensity of BE TO line increases in this temperature interval (Fig. 6), confirming the passivation of alternative recombination channels. The increase of annealing temperature leads to increase of local Cu concentration near dislocations and accelerates the precipitation process due to diffusion along dislocations. The collecting of Cu atoms in precipitates at some sites on dislocations acts as a cleaning procedure for the rest of dislocation length. Indeed, the intensity of D1/D2 lines grows and the intensity of BE TO line decreases. Besides a selective influence on different dislocation related centers the Cu contamination decreases the efficiency of radiative recombination independently on the annealing temperature. Comparing the dependence of intensity on the heat treatment (Figs. 4 and 6) for dislocation related and excitonic lines we see that in pure material corresponding intensities are substantially higher. It is worth to note, that the influence of quenching on the excitonic line intensity is higher in reference part than in dislocated part of same sample. It implies that some amount of Cu atoms is gathered by dislocations even after rapid quench.

4 Conclusion We have carried out the comparative measurements of intensity dependence of DRL and excitonic lines in Cu contaminated and pure Si samples. The dependence of D1/D2 intensities in Cu contaminated samples due to isochronous annealing in the temperature range 300–600 °C revealed the unusual decrease in intensity in the temperature interval 400–500 °C, which was attributed to passivation of corresponding centers by Cu. The further increase of D1/D2 intensities at higher annealing temperature has been interpreted as redistribution of captured Cu atoms along dislocations with creation of small number of larger Cu precipitates with partial restoration of D1/D2 centers. It implies that the binding energy of Cu atoms to D1/D2 centers is low enough to allow a back injection of captured atoms at temperature ≥600 °C. The mechanism of this passivation is not understood yet.

Acknowledgements This work was partially supported by Russian Academy of Sciences under Programs "New materials and structures" and "Influence of atomic-crystal and electronic structure on the properties of condensed matter". The Russian Foundation for Basic Research (RFBR) is thanked for financial support under grant 06-02 16195.

References

[1] V. Kveder, M. Badylevich, W. Schröter, M. Seibt, E. Steinman, and A. Izotov, Appl. Phys. Lett. **84**, 2106 (2004).
[2] V. Higgs, C. E. Norman, E. C. Lightowlers, and P. Kightley, Mater. Res. Soc. Symp. Proc. **163**, 57 (1992).
[3] Jae-Gwang Lee and S. Roy Morrison, J. Appl. Phys. **64**, 6679 (1988).
[4] V. Kveder, M. Kittler, and W. Schröter, Phys. Rev. B **63**, 115208 (2001).
[5] M. Kittler, C. Ulhaq-Bouillet, and V. Higgs, J. Appl. Phys. **78**, 4573 (1995).
[6] R. Sachdeva, A. A. Istratov, and E. R. Weber, Appl. Phys. Lett. **79**, 2937 (2001).
[7] L. Fiermans and J. Vennik, phys. stat. sol. **12**, 277 (1965).
[8] A. Correia, D. Ballutaud, A. Boutry-Forveille, and J. L. Marice, J. Appl. Phys. **78**, 6543 (1995).
[9] A. A. Istratov and E. R. Weber, Appl. Phys. A **66**, 123 (1998).
[10] V. V. Kveder, E. A. Steinman, S. A. Shevchenko, and H. G. Grimmeiss, Phys. Rev. B **51**(16), 10520 (1995).
[11] J. Weber, H. Bauch, and R. Sauer, Phys. Rev. B **25**, 7688 (1982).
[12] H. B. Erzgräber and K. Schmalz, J. Appl. Phys. **78**, 4066 (1995).
[13] R. Sauer, J. Weber, J. Stolz, E. R. Weber, K. H. Küsters, and H. Alexander, Appl. Phys. A **36,** 1 (1985).
[14] R. Sauer, C. Kisielowski-Kemmerich, and H. Alexander, Phys. Rev. Lett. **57**, 1472 (1986).
[15] Yu. A. Ossipyan, A. I. Kolyubakin, S. A. Shevchenko, and E. A. Steinman, Sov. Phys. Solid State **26**(3), 407 (1984).
[16] A. N. Izotov and E. A. Steinman, Sov. Phys. Solid State **28**(4), 567 (1986).

