The Structure and Photoluminescence of Dislocations in Silicon[1]

L.I. Fedina[1], T.S. Shamirzaev[1], S.A. Song[2], A.K. Gutakoskii[1], A.L. Chuvilin[3], A.G. Cherkov[1], K.S. Zhuravlev[1], M.S. Seksenbuev[1], V.Yu. Yakovlev[4], A.V. Latyshev[1]

[1] Institute of Semiconductor Physics, Lavrentjev Avenue 13, Novosibirsk, 630090, Russia, Phone: +7383-309082, Fax: +73832 331080, E-mail: timur@thermo.isp.nsc.ru

[2] Samsung Advanced Institute of Technology, P.O.Box 111, Suwon, 440-600, Korea

[3] Technical University Ulm, 89069 Ulm, Germany

[4] Tomsk Polytechnic University, Tomsk, Russia.

Abstract – Influence of an atomic structure of a separated type of dislocations introduced in Si by ion implantation (Frank dislocations) followed with thermal annealing at T=900–1000°C or by a failure FZ-Si ingot growth (glide 60° dislocations) on photoluminescence (PL) has been studied in details. Investigations of a dislocation core structure and its transformation under excess of intrinsic point defects carried out by *in situ* electron irradiation in the high resolution electron microscope JEOL-4000EX operated at 400 keV at room temperature. Additionally, large areas (~1cm^2) of Si specimens containing the separated dislocation types were irradiated *ex situ* by pulse electron source with E=350°C to obtain PL-spectra. We conclude that the D2 line in PL spectra is unambiguously explained by an appearance of interstitial clusters near the dislocation core independently on the type of dislocation. The position of D1 line in PL-spectra does not depend on the type of dislocation and manifests itself the structure of dislocation core with dangling bonds number of which depends on Burgers vector of dislocations and reactions with point defects and impurities. D3 and D4 lines are never observed in Si specimens containing Frank dislocations because they can not be split.

1. Introduction

The electronic properties of dislocations have been studied for many years. This subject has gained particular interest in resent years as dislocation induced states increase the quantum efficiency of luminescence in silicon and light emission from silicon-based devices has recently attracted considerable attention [1, 2]. However, despite the vast amount of work done in the last tree decades, some aspects of the physics of radiative recombination of nonequilibrium carriers at dislocations are far from being totally understood. Major concerns arise from the unknown nature of the optically active centers and from the elusive role played by impurities and point defects in the recombination process. Here we present the detailed investigations of an atomic structure and photoluminescence of Czochralski (CZ) and float-zone (FZ) silicon samples containing a separated type of dislocations (Frank dislocation loops of interstitial type or glide 60°-dislocations). We will show that the dislocation-related luminescence in the range of D1-D2 bands does not depend on the dislocation type, but strongly correlates with an appearance of interstitial clusters in the core of dislocations.

2. Experimental part

Frank dislocation loops of interstitial type were introduced in CZ-Si substrates (produced by Wacker Company) by B^+ and O^+ ions implantation with the energy 30 and 150 keV and dose of 10^{15} and 10^{16} cm^{-2}, respectively, followed with high temperature (900–1000°C) annealing. Glide 60°-dislocations were introduced by a failure ingot growth of high purity FZ-Si. The atomic structure of dislocations was studied by means of high resolution transmission electron microscopy (HRTEM) at the JEOL-2010FX and JEM-4000EX operated at 200 and 400 keV, respectively. Structural atomic models including up to 4000 atoms which is necessary for HREM image simulation were optimized by fast force field calculation (MM+ force field optimization). Additionally, point defect clusters in the dislocation core were introduced by *in situ* electron irradiation at room temperature in the JEM-4000EX or by *ex situ* electron irradiation with a pulse source at 350 keV. In the last case an irradiated area was about 1 cm^2. The photoluminescence (PL) was excited by the Ar^+ laser (λ=488nm) and detected at temperature of 4.2 K by a liquid nitrogen cooled Ge p-i-n photodiode EI-L.

3. Results and Discussion

Fig. 1 presents the light microscope image of dislocated Fz-Si ingot in (110) cross-section after selective chemical etching bringing out dislocations introduced by stresses at crystal-melt interface. The density of dislocations varies locally from ~10^6 to ~10^8cm^{-2}. Fig. 2 a, b show the weak beam diffraction image of the dislocation taken along it (a) and HRTEM image taken end-on (b). Burgers contour outlined the dislocation core in HRTEM image clearly shows that it is the glide 60° dislocation. Both images demonstrate the absence of dislocation dissociation. However, PL-spectra in

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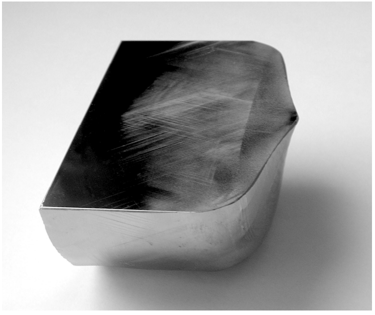

Fig. 1. Light microscope image of dislocated FZ-Si ingot etched in (110) cross-section by a selective chemical etchant.

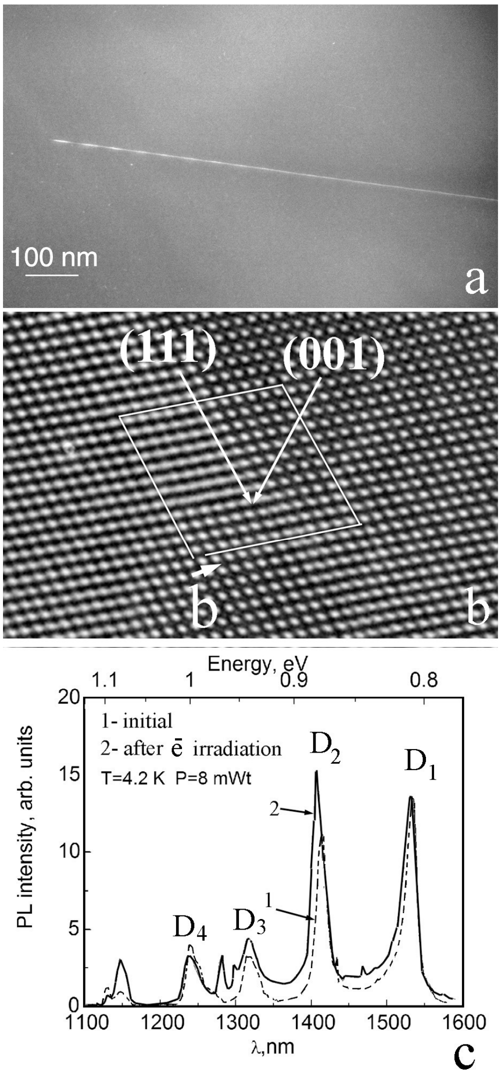

Fig. 2. Weak beam diffraction TEM image (a) and HRTEM image of glide 60^o-dislocation in FZ-Si with corresponded PL-spectra of specimen containing such dislocations before (c, line 1) and after (c, line 2) additional electron irradiation by electron gun at the dose $7x10^{16}$ electrons/cm^2

Fig. 2c demonstrates an appearance of all dislocation-related PL-bands: D1, D2, D3, and D4 two last of which are believed to correlate with the width of 60^o-dislocation dissociation into partial dislocations of Shockley type [3]. Small intensity of D3 and D4 bands suggests that some parts of dislocations can be indeed split. Additional *ex situ* electron irradiation of dislocated FZ-Si specimen by pulse source leads mainly to an increase of D2 line intensity in PL-spectrum (Fig. 2c, curve 2). *In situ* electron irradiation in the HRTEM shows that 60^o-dislocations strongly interact with intrinsic point defects and all known in Si types of metastable extended defects on {001}, {113} and {111} habit planes [4, 5, 6] consisting of self-interstitials are nucleated close to the cores (Fig. 3). Large strains existing around the dislocation core provide immediate (in 1–2 minutes)

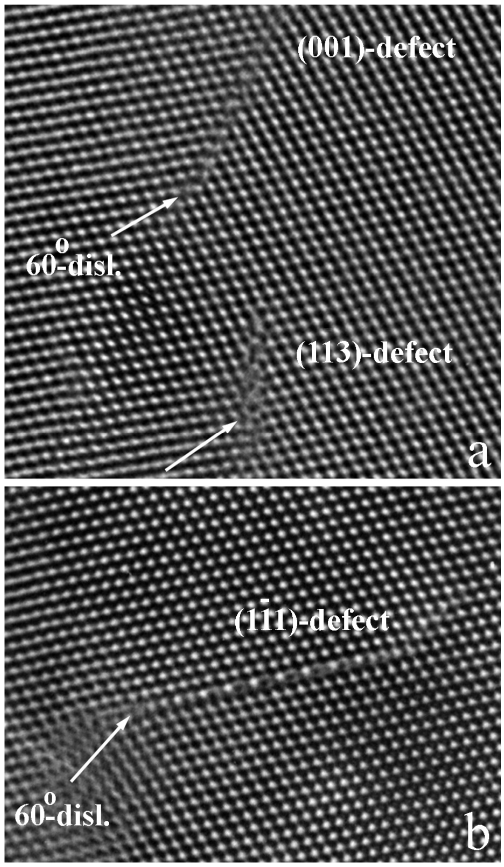

Fig. 3. (a, b) HRTEM images of interstitial clusters in the shape of (001)-, (113)– and (111)-defect induced in the cores of 60^o dislocations by in situ electron irradiation in the JEOL-4000EX operated at 400 keV at room temperature. Time of irradiation is 1–2 minutes. Dose rate of irradiation is $\sim 10^{20}$ electrons/cm^2sec. Cores of 60^o-dislocation are shown by arrows.

nucleation of point defect clusters during investigation of dislocated specimens in the JEOL-4000EX operated at 400 keV which is greatly higher than the threshold energy of 200 keV for Frenkel pair formation in Si. Plurality of cluster types nucleated close to the core reflects the fact that several habit planes come to the end in the core of glide 60^o-dislocation, two of which are (001) and (-111) planes clearly seen in Fig. 1b. Interaction of self-interstitials with one of extra-plane in the dislocation core predetermines the type of extended defects. Fig. 4a, b, c show the magnified experimental HRTEM image of {001}-defect joined to the core of 60^o-dislocation (a) and a defect model superimposed with the image (b) and simulated image (c). For image simulation we used the model in Fig. 4b optimized by Mm+ force field. Small discrepancy observed between experimental and simulated images are due to the fact that the real cluster structure is far from equilibrium at room temperature [7]. The lack of 60^o-dislocation dissociation creates numerous dangling bonds in the core. It is interesting to note that interstitials joined to the core are not bonded with core atoms having dangling bonds, but create a proper succession of double five- and single eight-membered rings on (001) plane in the shape of (2x1) reconstructed structure. Few reconstruction defects shown in Fig. 4b may also induce dangling bonds. This type of cluster consisting of four-fold coordinated self-interstitials (I_4) was earlier assumed to form in the core of 90^o partial dislocation (in the case of dissociated 60^o-dislocation) [8]. From first-principles calculations it was shown that

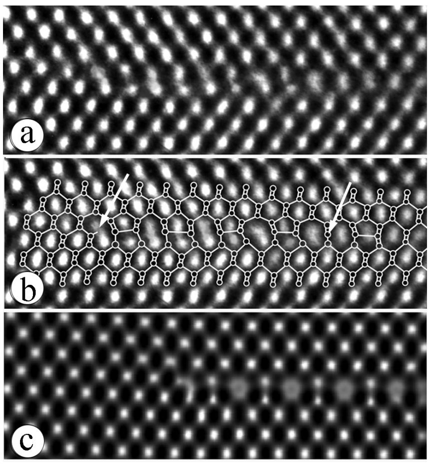

Fig. 4. Magnified experimental (a) and simulated (c) HRTEM images of (001)-defect joined to the core of 60^o-dislocation and the model used for simulation (b). Parameters of simulation: defocus value- (-40nm), thickness of crystal – (6.2 nm). Arrows in (b) show dangling bonds in the core and within reconstruction.

the I_4 defect causes deep levels to appear in the band gap and optical transitions between these levels may account for the luminescent bands relating to plastically deformed Si. Other first-principal calculations predict electrical activity of reconstruction defects [9] and even of four-fold coordinated interstitial configurations including five- eight-membered rings [10]. Such conclusions are in agreement with our results in general, however, there is a strong doubt concerning the possibility of I_4 cluster formation in the core of 90^o-partial dislocation due to heavy distortion of the dislocation core and introducing additional elastic strains in this case. On the contrary, our results show that cluster formation provides the relaxation of core strains. Because of small Burgers vector of the extended {100}-defect (a/4<100>, see in [4]) a summary displacement vector of a defect complex including the 60^o-dislocation and {100} defect becomes progressively smaller: a/2<110>-1/4<100> = a/4<121>. This will lead to a decrease of elastic energy in the area of defect complex. We will see below that a similar decrease of the displacement vector is observed in the case of {111}-defect formation close to the Frank dislocation core. Detailed description of the formation mechanisms of {111}- and {113}-defects can be found in [6, 7, 11]. Apart the strong increase of D2 line observed at 0.875eV, the PL-spectrum of 60^o- dislocations after *ex situ* electron irradiation is characterized by an appearance of small peak between D3-D4 bands and a small increase of TO-replica of silicon exciton PL (see Fig. 2c). The peak between D3-D4 bands is due to formation of {113} defects not bonded with dislocations which are known to induce a proper PL-line at 0.97eV (1.28 μm) [12].

Fig. 5a, b, c, d, present the bright field diffraction (a, b) and HRTEM images (c, d) of Frank dislocations introduced by B^+ (a, c) and O^+ implantation (b, d) and thermal annealing with corresponded PL-spectra (e). One can see that the atomic structure of dislocation cores is different for B^+ and O^+ implantation. The core is close bonded in the first case (Fig. 5c), while the core is very complicated in the second case (Fig. 5d). Furthermore, a high density of oxygen precipitates (~10^{11} cm^{-2}) is observed in Si implanted with O^+ and annealed at T=900^{o}C (image not shown). We should also note that the HRTEM image in Fig. 5c has been obtained by using the JEOL4000EX operated at 400 keV, which immediately introduce small cluster in the core, whereas the one shown in Fig. 5d is obtained in JEOL2010FX at 200 keV, at which clusters in the core are never induced. Formation of extended {111} defect in the Frank dislocation core under electron irradiation at 400 keV is presented in Fig. 6 a. From the model superimposed with experimental HRTEM image (Fig. 6b) a clear atomic structure of both the {111} defect and the dislocation core can be deduced because the formation of {111} defect provides the relaxation of the dislocation core: a/3<111>- a/5<111> = a/8<111> [6]. Simulated image of {111} defect fits perfectly the experimental one (Fig. 6d, inserted in the frame). According to the different core structure PL-spectra of Frank dislocations induced by B^+ implantation have no dislocation-related PL- bands, while strong D1 and D2 bands arise in Si specimen implanted with O^+ ions (see Fig. 5e). We assume that unlike boron a segregation of oxygen in the dislocation core leads to the growth of oxygen precipitates which strongly disturb the core structure and prevent an insertion of interstitials in the plane of dislocation loop. The PL-intensities of the TO exciton and D1, D2 lines increase with the increasing of annealing temperature (Fig. 5, curve 1). Clear splitting of D1 band observed between 0.812 and 0.830eV in PL-spectrum of Si specimen annealed at T=900°C is related with the high density of oxygen precipitates. No D3 and D4 bands are observed in samples with Frank dislocations even if they provide luminescence because they can not be split.

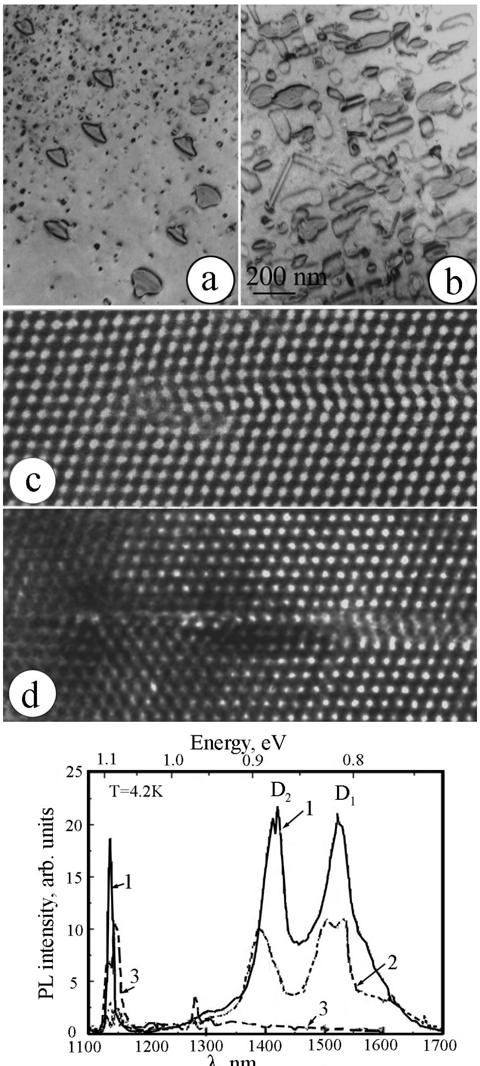

Fig. 5. Bright field (a, b) and HRTEM images (c, d) of Frank dislocations introduced by B+ (a, c) and O+ (b, d) implantation followed by annealing at T=1000°C. (e) PL- spectra of Si implanted by O+ (1, 2) and B+ ions (3) and annealed at T=900 (2) and 1000°C (1, 3).

Finally we conclude that the D2 line in PL spectra of silicon samples is unambiguously explained by interstitial cluster formation near the dislocation core independently on the type of dislocation. We assume that D1 line manifest itself the structure of a dislocation core with broken bonds number of which depends on Burgers vector of dislocation and reactions with point defects and impurities.

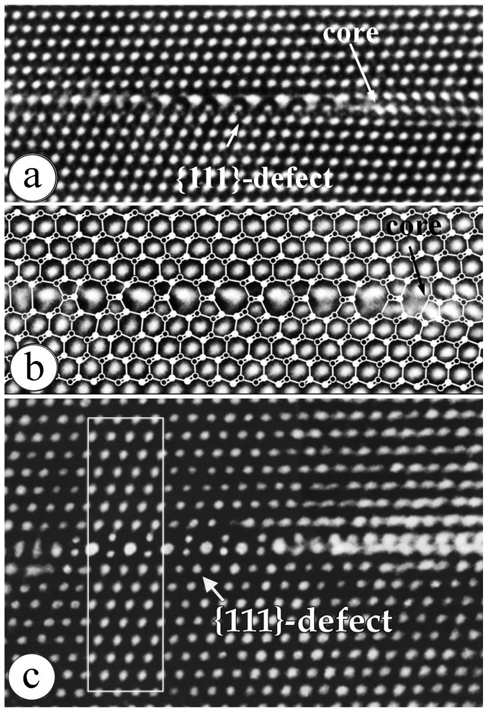

Fig. 6. HRTEM image of {111} defect induced in the Frank dislocation core in 1–2 minutes of electron irradiation in the JEOL-4000EX (a) with the defect model (b). (c)- [110]-aligned defect image in comparison with the simulated one (inserted in frame). (c). Dose rate of irradiation is ~10^{20} electrons/cm^{2}sec.

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