QUANTITATIVE DETERMINATION OF THE RECOMBINING ACTIVITIES OF 60° AND SCREW DISLOCATIONS IN FZ AND CZ SILICON**B. PICHAUD, F. MINARI and S. MARTINUZZI****Laboratoire de Physique Cristalline, U.R.A. 797 CNRS, Faculté des Sciences de St Jérôme, Av. Escadrille Normandie-Niemen, F-13397 Marseille Cedex 13, France***Laboratoire de Photoélectricité, Faculté des Sciences de St Jérôme, Av. Escadrille Normandie-Niemen, F-13397 Marseille Cedex 13, France*

Résumé: L'activité recombinante de dislocations vis et 60°, introduites de façon contrôlée dans le silicium FZ et CZ, a été caractérisée par les vitesses de recombinaison correspondantes tirées de mesures de longueurs de diffusion obtenues par la méthode SPV. Les résultats montrent que les dislocations 60° sont nettement plus actives que les vis, et que cette activité augmente avec la concentration en oxygène du matériau et avec la température de développement des dislocations.

Abstract: We have characterized quantitatively the recombining activities of 60° and screw dislocations by their recombination velocities. This parameter was derived from the diffusion length determined by using the SPV method. Dislocations were introduced in initially perfect FZ and CZ crystals, at different temperatures. The results show that 60° dislocations are much more active than screws, and that the activity increases markedly with oxygen content of the material and with the temperature at which dislocations were introduced.

I- INTRODUCTION

Process-induced dislocations are detrimental to microelectronic devices and solar cells. Since their occurrence can hardly be avoided, it is of major importance to know how strong their effects are on the final characteristics of the basic material. Information can be obtained by comparing the electrical properties of dislocation-free and dislocation-containing silicon, by means of photoluminescence, DLTS, EPR, EBIC etc... /1-2/. But these measurements are by no way characteristic of a given type of dislocation if the line orientations are randomly distributed, if the Burgers vectors are different, or if the dislocation density is high enough to cause overlapping of space charge cylinders. Moreover, the electrical properties can be strongly dependent on the oxygen content /3/ and on the temperature of dislocations generation (designed hereafter by T_D).

In the present work, we performed LBIC (light beam induced current) and SPV (surface photovoltage) measurements in well-defined conditions by controlling T_D and the character of dislocations. The oxygen content was varied using either FZ or CZ silicon. The starting material was initially dislocation-free, and different distributions of defects were introduced in limited regions by a local deformation procedure. Measurements were made on each sample both in dislocated and in perfect regions, the recombination strength of dislocations was determined as a function of their character, the temperature T_D and the oxygen content of the material.

II-EXPERIMENTAL

Rectangular samples $3 \times 0.5 \times 0.05 \text{ cm}^3$ were cut from 4" FZ (111) and (001) silicon wafers (oxygen concentration $< 10^{16} \text{ at.cm}^{-3}$) as well as from 4" CZ (001) wafers (oxygen concentration $\approx 5-7 \cdot 10^{17} \text{ at.cm}^{-3}$). All these wafers were boron-doped ($p = 10^{15} \text{ cm}^{-3}$) and optically polished on both faces. The samples length was always parallel to $\langle 110 \rangle$. The edges were chemically polished (CP4) in order to prevent undesired dislocations from running into the specimen during subsequent operations. Dislocation sources were nucleated by scratching the samples lengthwise with a diamond. Then dislocation half-loops were developed by cantilever bending of the samples along the transversal axis and heating under stress during 3h at $T_D = 700^\circ\text{C}$ or 30h at $T_D = 600^\circ\text{C}$ in a pure argon atmosphere /4/. Cooling was performed in the stressed state at a rate of 20°s^{-1} . The dislocations were characterized by X-ray transmission topography (XRT).

Elongated half-loops were obtained which were made of three segments parallel to the three $\langle 110 \rangle$ directions in the

Fig. 1 Dislocations developed from a diamond scratch by cantilever bending. a,b: sketch of the activated glide systems (a) in (111), (b) in (001) samples. c,d: X-Ray transmission topographs on the left side of the scratch (c) Reflection $\bar{1}11$, (d) $\bar{2}20$. e,f: optical micrographs of the corresponding etch-pit distributions.

glide plane: a long straight segment parallel to the surface and two short emerging segments.

In (111) samples, probably due to surface effects [5], among the four equivalent glide systems, two were predominant, namely $a/2[1\bar{1}0](11\bar{1})$ and $a/2[10\bar{1}](\bar{1}11)$ with their Burgers vectors parallel to the surface (Fig.1a). In this case, all the emerging segments were in 60° orientation and were homogeneously distributed across the surface (Fig.1c and e). In (001) samples, four glide systems were activated $a/2[101](\bar{1}\bar{1}1)$, $a/2[011](\bar{1}11)$, $a/2[0\bar{1}1](111)$ and $a/2[\bar{1}01](111)$, their traces on the surface were normal to the scratch and the four Burgers vectors were 45° away from the surface (Fig.1b). The emerging parts of the four types of half loops were either screw or 60° , mixed in equal proportions, they were homogeneously distributed (Fig.1d and f) as in the case of (111) orientation.

Semi-transparent $4 \times 4 \text{ mm}^2$ diodes were processed by evaporating a thin Al layer (5-10 nm) after cleaning in 10% HF. These diodes covered dislocated and undislocated regions of the deformed samples. The ohmic contact was achieved by liquid Ga-In alloy smeared over the back surface.

Each diode was scanned, in a direction parallel to the scratch and far from it, by a light beam, either mono (940 nm) or polychromatic focused in a $10 \mu\text{m}$ diameter spot on the surface and modulated by a chopper at a frequency of 400 Hz. The photocurrent was recorded by a synchronous detector. The distance between successive scanning lines was $10 \mu\text{m}$. In addition to these usual LBIC measurements the local minority carriers diffusion length L_n was determined using the SPV method [6]: for this, the beam could be stopped anywhere along a scanning line and the wavelength could be continuously tuned between 800 and 1100 nm. Owing to the spot size the photoresponse of a diode at a given point concerned several dislocations, therefore it was a mean value.

After these measurements, the Al layer was removed and the local dislocation densities were deduced from etch pits counts (Sirtl or Secco etchant) taking into account the angle between the free surface and the emerging segments.

III- RESULTS

All the samples FZ and CZ had the same initial diffusion length L_n^0 150 μ m. Furthermore we verified that, after the different thermal treatments, the diffusion length was unchanged in undischarged zones.

Figure 2 shows a typical example of our experimental results concerning dislocations developed at $T_D = 700^\circ\text{C}$ in (001) FZ samples. We give the photocurrent evolution, the dislocation density as a function of the position across the diode and some values of the local diffusion length L_n measured at particular points along the first scanning line. This diode exhibits regions containing different dislocation densities, although in each region the dislocations are rather uniformly distributed. A very close correlation between photocurrent intensity, dislocation density and local diffusion length is evidenced.

Fig. 2 LBIC scan and corresponding etch-pits density (EPD) in a diode processed on a FZ (001) sample $T_D = 700^\circ\text{C}$. Photocurrent in arbitrary units. Some values of the local diffusion length L_n are given.

Since the general features of the LBIC scans in the different experimental situations (orientation, T_D , oxygen content) are similar to those in figure 2, we do not give the corresponding diagrams but Table 1 displays the values of local diffusion lengths for a fixed dislocation density $5 \cdot 10^5 < \rho < 10^6 \text{ cm}^{-2}$. One can remark that:

- (i)- the recombining activity is stronger for dislocations developed at higher temperature.
- (ii)- this activity is more pronounced in (111) samples as compared to (001).
- (iii)- the activity is stronger in CZ than in FZ silicon.

These results establish a close correlation between dislocation density, minority carrier diffusion length and photocurrent intensity. However, in order to quantify this relation it was essential to verify if each emerging dislocation had a

Table 1 Values of L_n for different experimental conditions and for a fixed dislocation density $\rho \sim 7 \cdot 10^5 \text{ cm}^{-2}$.

Orientation	Nucleation temperature	T_D	Nature of Si	Local diff. length L_n (μ m)
(111)	700°C		FZ	30
(001)	700°C		FZ	40
(001)	600°C		FZ	60
(001)	700°C		CZ	15

recombining activity or not. Electron beam induced current (EBIC) experiments performed on FZ (001) samples confirmed a one to one correspondence between etch pits and electrical images of emerging dislocations (figure 3a and b) but a numerical analysis of these images showed that dislocations could be classified in two separate families with respect to their electrical activity (figure 3c). This fact is probably due to the presence, in (001) orientation, of both 60° and screw emerging segments. In figure 3c the ratio 50/50 between these emerging segments is not verified because of the limited area of the images 3a and 3b. Nevertheless, in LBIC measurements, involving larger areas, this ratio is usually obtained.

Fig. 3 recombining activity of emerging dislocations(a) etch-pits. (b) EBIC image of the same area. (c) Histogram of the recombining activities of emerging points, measured by their EBIC signal

IV- INTERPRETATION: RECOMBINATION VELOCITY ASSOCIATED WITH DISLOCATIONS

These experimental results may be expressed in a more relevant way by a parameter characterizing the recombining activity due to dislocations: the so-called recombination velocity S_d associated with dislocations. This parameter may be deduced using the model proposed by El Ghitani and Martinuzzi /7/ for the recombining activity of a homogeneous distribution of emerging dislocations. These authors determined the excess minority carriers distribution due to an electrical or a light excitation, using the Green function method /8/. This allows the expression of the photocurrent to be deduced and an effective diffusion length L_{eff} to be obtained /9/ as a function of dislocation density ρ . The curves $L_{eff} = f(\rho)$ can be drawn for a given L_n^0 (here $L_n^0 = 150\mu m$) and for S_d as a parameter. Figure 4 shows three of these curves computed for $S_d = 5 \cdot 10^2$, 10^3 and $2 \cdot 10^3 \text{ cm s}^{-1}$ in the (001) case. Our experimental points deduced from figure 2 fit reasonably with such a curve which would correspond to $S_d = 8 \cdot 10^2 \text{ cm s}^{-1}$. This agreement confirms the validity of the model which can be used for a direct computation of S_d in the different experimental situations.

In FZ silicon we found $S_d^{(001)} = 8 \cdot 10^2 \text{ cm s}^{-1}$ and $S_d^{(111)} = 1.5 \cdot 10^3 \text{ cm s}^{-1}$ respectively for (001) and (111) orientations. As it was already pointed out, in (111) orientation, the emerging segments are all of 60° character so that the corresponding recombination velocity may be unambiguously ascribed to this type of dislocation: $S_d^{60^\circ} = 1.5 \cdot 10^3 \text{ cm s}^{-1}$. In (001) orientation, the emerging segments are screws and 60° in equal proportions, so the corresponding velocity is $S_d^{(001)} = 1/2 (S_d^{screw} + S_d^{60^\circ})$. The contribution of 60° 's being known, the recombination velocity of screws can be evaluated as $S_d^{screw} \approx 10^2 \text{ cm s}^{-1}$ quite lower than that of 60° 's. This result is consistent with the two families of recombining activity evidenced by EBIC (Fig. 3c). Accounting for the poor activity of screw segments we neglected their contribution, i.e. in (001) orientation, $S_d^{60^\circ}$ has been directly determined by dividing by two the measured dislocation density. The corresponding $S_d^{60^\circ}$ values are given in Table 2. As shown in this table, for different distributions of dislocations developed at $T_D = 700^\circ\text{C}$ and 600°C in (001) FZ samples, one obtains $S_d^{60^\circ} = 1.5 \cdot 10^3 \text{ cm s}^{-1}$ and $S_d^{60^\circ} = 3 \cdot 10^2 \text{ cm s}^{-1}$ respectively: the recombination velocity is very sensitive to temperature T_D .

Comparison between FZ and CZ (001) samples ($T_D = 700^\circ\text{C}$) shows a very strong dependence of $S_d^{60^\circ}$ with the oxygen content: the recombination velocity increases from $S_d^{60^\circ} = 1.5 \cdot 10^3 \text{ cm s}^{-1}$ in FZ samples (oxygen concentration $< 10^{16} \text{ at.cm}^{-3}$) to $S_d^{60^\circ} = 5 \cdot 10^4 \text{ cm s}^{-1}$ in CZ (oxygen concentration $\approx 5 \cdot 7 \cdot 10^{17} \text{ at.cm}^{-3}$).

Fig. 4 Comparison between our experimental determinations of the local diffusion length (full symbols), and theoretical curves $L_{\text{eff}} = f(\rho) / 6 / \text{FZ (001)}$ sample same diode as in figure 2.

Table 2: $S_d^{60^\circ}$ in different experimental situations

T_D	Nature of Si	$S_d^{60^\circ}$ (cm/s)
700°C	FZ	$1.5 \pm 0.3 \cdot 10^3$
600°C	FZ	$3 \pm 1 \cdot 10^2$
700°C	CZ	$5 \pm 3 \cdot 10^4$

The high values of $S_d^{60^\circ}$ observed in CZ silicon may be compared to those measured by El Ghitani and Martinuzzi /10/ in polycrystalline oxygen-rich silicon for solar cells. They found $5 \cdot 10^3 \text{ cm s}^{-1} < S_d < 10^5 \text{ cm s}^{-1}$. In this case the dispersion of the S_d values is probably related to the fact that the dislocations were developed at very high temperature at the beginning of the rapid cooling of the ingots and then are not of well-defined character as in our experiments. Nevertheless these values are not very different from ours.

A high recombining activity of dislocations in oxygen-rich silicon was also evidenced by Pizzini et al. /3/ using LBIC measurements on stress-induced dislocations, but their results cannot be directly compared with ours because of the higher temperature they used and also because these results are not converted in terms of recombination velocity.

V- DISCUSSION: ORIGIN OF THE RECOMBINING ACTIVITY OF DISLOCATIONS

A. Intrinsic activity (FZ silicon)

In FZ silicon, quite different recombination velocities may be attributed to 60° and screw emerging segments (Table 2). Since these dislocations are dissociated, the difference in S_d may be due to the difference in the nature of their partials: two 30° for the screw, one 30° and one 90° for the 60° . Therefore it may be inferred that the 30° has a poor recombining activity whereas the major part of the effect is due to the 90° partial. The partial dislocation cores are probably reconstructed and only very few sites are active: about 1% at 700°C /11/. That approximately corresponds to the density of double kinks (DK) which can be extrapolated from the value (0.1%) given by Louchet at 600°C /12/ using a DK formation energy of 2eV. Since the ratio of DK densities at 600°C and 700°C is close to the ratio of the corresponding recombination velocities, the DK and their associated dangling bonds or solitons might be considered as the main recombining sites along dislocations. The higher recombining activity of the 90° partial as compared to the 30° would be due to a higher DK density consistent with a higher mobility as shown by Wessel and Alexander /13/. The enhancement of the donor character of dislocations between 600°C and 700°C /14-15/ could be invoked to explain part of the corresponding increase of S_d . But, as measurements of carrier density reveal some effect only for $\rho > 10^7 \text{ cm}^{-2}$ while the difference between $S_d^{600^\circ\text{C}}$ and $S_d^{700^\circ\text{C}}$ is effective down to $\rho = 10^3 \text{ cm}^{-2}$, this contribution may be neglected.

B. Effect of oxygen content: comparison between FZ and CZ silicon

The very large difference between the values of $S_d^{60^\circ}$ measured in FZ and CZ materials for the same T_D (700°C) may obviously be ascribed to the difference in oxygen concentration. In CZ silicon the last being markedly above the solubility limit, SiO_2 or more generally SiO_x precipitation might occur. However even if precipitation is favoured in dislocated zones, it occurs also in perfect regions where small interstitial loops are frequently observed, which are its visible consequence /16/. As we did not measure any significant variation of the local diffusion length after our thermal treatments in dislocation-free zones, direct effects of precipitation such as interface states generation, metallic impurities gettering... may be neglected.

It remains indirect effects resulting from the association of dislocations with point defects and/or precipitates.

(i)- Self-interstitials produced by accommodation between silicon and oxide precipitate lattices or by thermal donor generation might be attracted by dislocations, producing jogs along the lines. These jogs provide supplementary dangling bonds or related solitons. This hypothesis is supported by the fact that in CZ samples, in the vicinity of dislocations, due to the gettering of self-interstitials, we never observed any condensation loops.

(ii)- Oxide precipitates act as obstacles to dislocation motion /17/. This is confirmed by the complex shapes of dislocations in CZ crystals (Fig 5) as compared with the straight lines parallel to $\langle 110 \rangle$ in FZ (Fig 1d). It results both in a global increase of dislocation density and in an increase of the kink density along the lines. This leads to a greater number of dangling bonds or solitons increasing the recombination velocity S_d . Jogs due to self-interstitials condensation might also play

the role of obstacles to dislocation motion and, up to now, nothing allows us to separate these two possible effects.

Finally, in CZ crystals, part of the recombination rate increase after deformation could also be associated with electrical activity of complexes left behind dislocations during their movement in glide planes /18/.

Fig. 5 X-Ray topograph of dislocations developed at 700°C in a CZ (001) crystal. Compare with the straight lines in Fig.1 relative to FZ (001) at the same temperature.

VI- CONCLUSION

In (001) and (111) FZ and CZ silicon we introduced well-controlled distributions of dislocations. On diodes containing these dislocations, we performed photoelectric measurements using SVP and LBIC methods. Using the model by El Ghitani et al. /8/ we got a close correlation between photocurrent, local diffusion length and dislocation density. The recombination velocity S_d associated with dislocations was derived as a function of the experimental parameters. We showed that:

- (i)- 60° dislocations exhibit a higher recombining activity than screws
- (ii)- The recombination velocity increases with the temperature T_D at which dislocations were developed
- (iii)- S_d increases with the oxygen content of the starting material.

The two first points were interpreted by considering that the recombining activity is mainly due to geometrical defects distributed along the dislocations cores: double kinks or their associated dangling bonds or solitons. Thus the 90° partial would recombine more strongly than the 30° partial, which probably exhibits a lower DK density. It results a corresponding difference in the recombining activities of 60° and screw (perfect) dislocations. In the same way, the effect of T_D might be interpreted in terms of DK density along the lines, at least for dislocation densities lower than 10^7 cm^{-2} .

Concerning the increase of S_d with the oxygen content, although direct effects of precipitation cannot be ruled out, we consider precipitation and/or jogs condensation as providing obstacles to dislocations motion, yielding a strong increase in geometrical defects density along the lines. A modification of electrical properties of active slip planes may also be invoked.

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