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Electrical activity of extended defects in polycrystalline silicon

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Résumé. — On étend l'analyse de la relation entre microstructure du silicium polycristallin et longueur de diffusion des porteurs minoritaires en y incluant l'influence du carbone et de l'oxygène, deux impuretés dont on connaît l'effet sur l'activité électrique des dislocations et des joints de grain. On trouve qu'un terme de la forme $N_D \cdot (N_O - N_C)$, où N_D est la densité de dislocations et N_O , N_C les concentrations respectives d'oxygène et de carbone, rend bien compte de l'influence de ces deux impuretés sur la longueur de diffusion des porteurs minoritaires. Il en résulte que cette influence n'est que marginale et que la recombinaison aux joints de grain dépend presque exclusivement des dislocations.

Abstract. — The analysis of the dependence of the diffusion length of minority carriers on the microstructure in polycrystalline silicon has been extended by considering the influence of oxygen and carbon. These impurities are in fact known to have a definite effect on the electrical activity of dislocations and grain boundaries (GB). The results of this analysis show that a term of the type $N_D(N_O - N_C)$, where N_D is the dislocation density and N_O , N_C are the concentration of oxygen and carbon, respectively, well accounts for the influence of oxygen and carbon on the diffusion length of minority carriers. Oxygen and carbon, therefore, affect only marginally the recombination losses at GB in polycrystalline silicon, whose average diffusion length is determined almost exclusively by dislocations.

Polycrystalline semiconductors are unique examples of systems exhibiting electrical properties depending in a very complicated fashion on their intrinsic and extrinsic disorder (point defects, extended defects, impurities).

This is the reason why any attempt to feature their electrical behaviour in terms of zero order models, based on the absence of interactions between the single elements of the disorder, almost generally fails.

Dealing with the minority carriers properties, as an example, the use of the Mathiesen rule, which is generally written as

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} \quad (1)$$

— where τ_i is the recombination lifetime of a specific impurity or disorder element i — appears to be unpracticable, even when applied to well characterized systems.

Among the grounds for this failure, the strong temperature dependence of the recombination

properties of extended defects, arising from the onset of an impurity cloud (the Cottrell atmosphere) around them, is one of the key factors.

As a typical example, it is well known that in as grown polycrystalline silicon often grain boundaries (GB) appear to be almost electrically inactive [1-3] but turn to exhibit strong recombination properties as soon as impurity segregation on them (which could act as an effective dislocation or multiplication factor) is induced by means of suitable annealing cycles.

On these grounds, we proposed in a earlier paper [4] to account for the electrical activity of extended defects with a cross term of the type

$$k(L_{GB} N_D)$$

where L_{GB} is the density of grain boundaries per unit area and N_D is the dislocation density.

Here, as a mathematical artifice, the extended defects are considered distributed at random within the sample and electrically inactive unless in the case of intersection, albeit we know that the pinning of

dislocations at GB is of extrinsic origin. Accordingly, a relation of the type

$$L_n = L_n^0 [1 + k(L_{GB} N_D)]^{-1/2} \quad (2)$$

where L_n^0 is the diffusion length in the best single crystal of the same doping, taken equal to 200 μm , was used to fit the experimental dependence of the minority carriers diffusion length L_n on the microstructure of deep level impurity free polycrystalline silicon.

However, this first approximation has to be improved. First, it results only in fair agreement with the experimental results, as it is shown from the appreciable deviations from the constancy observed for the ratios

$$\frac{(L_n^0/L_n)^2 - 1}{L_{GB} N_D} \quad (3)$$

displayed in the last column of table I, which reports all the relevant data relative to the silicon samples considered. Secondly, it is well known that L_n depends mainly on the dislocation density, and varies with L_{GB} only to a lesser extent. Polycrystals with diffusion lengths approaching those of single crystals are in fact often found [5].

Thirdly, not the whole length of GB is electrically active, but only those parts of general GB's (excluding e.g. twin boundaries) which contain a large density of dislocations [4]. That is why equation (2), attributing recombination to active sites at the

intersection of GB's with dislocations is partly successful.

Eventually, the relative amounts of oxygen and carbon dissolved in silicon have been found to have an important influence on the diffusion length [6-9].

The main purpose of this paper is to include, in the formal description of structure sensitive recombination in deep level impurity free silicon the influence of oxygen and carbon impurities.

In order to do so, we consider that :

i) in dislocation free single crystal silicon grown by the Czochralski technique, carbon and oxygen impurities, albeit being by themselves electrically inactive, induce a severe degradation, under specific circumstances, of the electrical properties. This is caused by the nucleation and precipitation of polynuclear complexes and precipitates during the thermal treatments of the material [3, 9] as well as by the interaction of oxygen and carbon with doping elements [10] ;

ii) the electrical activity of dislocations in polycrystals is strongly dependent on the oxygen content N_O [6], while it is only the dislocation density which increases with the carbon content N_C [6, 9] ;

iii) oxygen and carbon segregate at GB's, possibly creating a variety of strain field compensation effects, and then, a variety of dislocation generating conditions [11]. Direct evidence that oxygen can activate a previously inactive GB has been established [1, 12] ;

Table I. — *Microstructural, chemical and physical properties of the polycrystalline silicon samples examined.*

Sample	N_O ppma	N_C ppma	L_{GB} cm	N_D cm	L_n um	$N_O-N_C [(L_n^0/L_n)^2-1]/L_{GB} N_D$ ppma	$N_O-N_C [(L_n^0/L_n)^2-1]/L_{GB} N_D$ cm
221/12	13.50 ± 2.00	7.60 ± 0.90	10.5	1.5 E4	52.22 ± 10.66	5.90	8.70 E-5
221/29	10.35 ± 0.05	7.10 ± 0.50	8.7	2.3 E4	97.00 ± 19.00	3.25	1.60 E-5
221/50	4.70 ± 1.40	6.25 ± 0.15	9.2	2.3 E4	174.18 ± 76.8	-1.55	1.51 E-6
221/71	0.65 ± 0.05	6.80 ± 0.20	12.3	9.1 E4	164.50 ± 25.7	-6.15	4.34 E-5
227/12	14.90 ± 0.50	5.85 ± 0.15	23.7	1.5 E4	44.23 ± 8.47	9.05	5.46 E-5
227/30	8.25 ± 0.25	5.85 ± 0.15	17.9	2.4 E4	134.29 ± 10.8	2.67	2.83 E-6
227/50	3.95 ± 0.05	7.50 ± 0.30	14.0	5.4 E4	85.70 ± 16.28	-3.55	5.86 E-6
234/12	7.25 ± 0.05	5.80 ± 0.20	26.8	1.7 E4	82.06 ± 26.3	1.45	1.09 E-5
234/29	7.10 ± 0.90	7.15 ± 0.15	25.1	3.6 E4	93.57 ± 19.9	0.05	3.95 E-6
234/50	4.50 ± 0.60	8.15 ± 0.30	28.1	4.5 E4	74.03 ± 19.34	-3.65	4.84 E-6
234/68	2.60 ± 0.60	9.00 ± 0.30	30.4	2.7 E5	51.70 ± 14.23	-6.40	1.78 E-6
236/29	3.50 ± 0.30	7.10 ± 0.60	16.5	1.8 E4	169.91 ± 22.90	-3.60	1.33 E-6
238/29	8.15 ± 1.00	5.25 ± 0.60	17.8	1.3 E4	103.09 ± 18.70	2.90	1.20 E-5
238/50	4.60 ± 0.20	6.45 ± 0.40	17.5	2.4 E4	113.88 ± 27.28	-1.85	4.96 E-6
238/72	2.15 ± 0.25	8.50 ± 0.50	14.4	5.2 E4	91.09 ± 32.03	-6.35	4.89 E-6
240/29	4.35 ± 0.25	4.70 ± 0.30	29.0	2.4 E4	68.21 ± 24.33	-0.35	7.34 E-6
240/50	3.05 ± 0.25	5.50 ± 0.50	24.0	9.4 E4	72.62 ± 9.16	-2.45	2.92 E-6
247/29	7.75 ± 0.90	4.35 ± 0.50	26.6	2.4 E4	152.73 ± 48.4	3.40	1.12 E-6

iv) quite generally, the electrical activity can vary along GB. Point ii) could suggest to introduce in equation (2) a term of the type $k'' N_O N_D$. However, we found [6] that the dominant chemical parameter determining L_n is $(N_O - N_C)$ rather than N_O alone, and we explained this fact by the already established stability of C-O complexes in silicon [13-14].

It seems thus reasonable to implement equation (2) with a term of the type $k'' \times N_D \times f(N_O - N_C)$, where

$$f(N_O - N_C) = N_O - N_C \quad \text{if } N_O \geq N_C$$

and

$$f(N_O - N_C) = 0 \quad \text{if } N_O < N_C.$$

Under such conditions equation (2) could be reformulated as :

$$L_n = L_n^0 [1 + k' (L_{GB} N_D) + k'' f(N_O - N_C) N_D]^{-1/2} \quad (4)$$

and used to verify whether a better fit of the experimental data reported in table I could be obtained.

It should be mentioned here that the second term of equation (2) and (4) is already (even not explicitly) dependent on the oxygen and carbon concentration for what concerns the dislocation density (*vide supra*).

The effectiveness of the term $k'' N_D f(N_O - N_C)$ could now be appreciated from a closest inspection of table I, where one could remark first that the ratio (3) is actually constant when $N_O < N_C$ and takes a mean value of $(3.92 \pm 2.01) \times 10^{-6}$, which well fits with its value (3.95×10^{-6}) when $(N_O - N_C)$ is close to zero (sample 234/29). For all the other samples, the linear dependence of the ratio (3) on the oxygen excess, expected from equation (4) is instead clearly observed, as it is shown in figure 1.

It must be mentioned here that the relatively large dispersion of the experimental values displayed in figure 1 comes from the intrinsic inhomogeneity of the samples we examined and on the inhomogeneity of the recombination activity along the individual defects, regardless of the technique used for the determination of the average diffusion length. In our case it was determined using the standard SPV

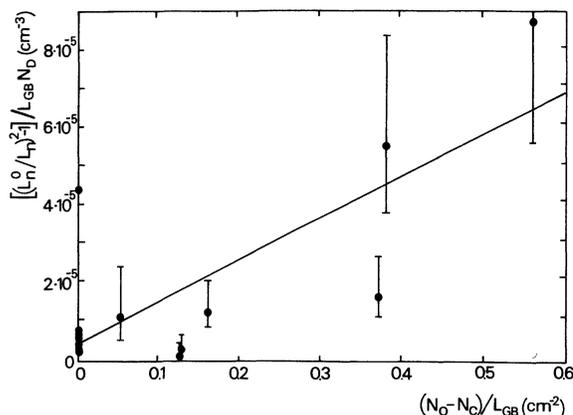


Fig. 1. — Dependence of the reduced diffusion length on the oxygen excess.

method on nine different positions of a $25 \times 25 \text{ mm}^2$ slice, with a light beam of 1 mm^2 , comparable in size with the smallest grains of the sample and averaging the value with the method of the weighted averages, using the individual correlation coefficients as the weight factor and the standard deviations of the average diffusion length as an estimate of the experimental incertitude.

In conclusion, the fact that equation (4) accounts for the experimental values in the whole range of oxygen and carbon impurity concentration is an illustration :

- i) of the secondary role of structural reconstruction of extended defects [15] with respect to their « chemical » reconstruction, originated from the segregation of oxygen, carbon and other impurities ;
- ii) of the role of the Cottrell atmosphere surrounding the extended defects on their electrical activity, which is only marginally influenced by residual dangling bonds, in good agreement with earlier anticipations [1, 11].

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