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J. Oualid, M. Bonfils, J.P. Crest, G. Mathian, H. Amzil, et al.. Photocurrent and diffusion lengths at the vicinity of grain boundaries (g.b.) in N and P-type polysilicon. Evaluation of the g.b. recombination velocity). *Revue de Physique Appliquée*, 1982, 17 (3), pp.119-124. 10.1051/rphysap:01982001703011900 . jpa-00244979

HAL Id: jpa-00244979

<https://hal.science/jpa-00244979>

Submitted on 1 Jan 1982

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Classification
Physics Abstracts
72.20I

Photocurrent and diffusion lengths at the vicinity of grain boundaries (g.b.) in N and P-type polysilicon. Evaluation of the g.b. recombination velocity (*)

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(Reçu le 28 septembre 1981, révisé le 16 novembre 1981, accepté le 23 novembre 1981)

Résumé. — Les photocourants, les longueurs de diffusion (L) et les vitesses de recombinaison aux joints de grains (s) ont été mesurés à l'aide d'un système de balayage optique sur des échantillons de silicium polycristallin de type N et P. Selon le type des grains, L varie entre 5 μm et 150 μm et s est supérieur à $10^4 \text{ cm} \cdot \text{s}^{-1}$. Les résultats concernant les mesures locales des longueurs de diffusion montrent qu'au voisinage des joints de grains s'exercent des fortes contraintes. Il semble que les potentiels de barrière aux joints de grains sont plus importants dans les échantillons de type N que dans ceux de type P pour expliquer la plus grande activité recombinaison des joints de grains dans le silicium polycristallin de type N que dans celui de type P.

Abstract. — Photocurrents, diffusion lengths (L) and g.b. recombination velocities (s) have been measured by optical scanning in N and P-type polysilicon. With type of grains, L is found to vary between 5 μm and 150 μm and s is always higher than $10^4 \text{ cm} \cdot \text{s}^{-1}$. The results on local measurements of diffusion lengths show that the vicinity of a g.b. is highly stressed. It seems that the g.b. potential barriers are higher in N-type than in P-type.

1. Introduction. — Polycrystalline semiconductors are increasingly employed in the fabrication of electronic or opto-electronic devices and photocells. The polycrystalline state is characterized by grain boundaries (g.b.) where many defects (interface states) are concentrated : intrinsic defects like dangling bonds, vacancies, dislocations or extrinsic defects like impurities or clusters [1].

These defects can trap the majority carriers. When ionized, they give a barrier height E_b^0 at the thermodynamic equilibrium and a space charge region in either side of the g.b. (Fig. 1).

Minority carriers drifted to the g.b. by the related electric field can recombine via the interface states [2].

In the vicinity of a g.b. the electronic properties of minority carriers such as lifetime τ , diffusion length L are affected, thus resulting in degradation of the luminescence in L.E.D. or LASER [3] and of the photocurrent in detectors or photocells [4]. This electrical activity near the g.b. is well characterized by a g.b. recombination velocity s [5].

Here, we report our local measurements of L and s using a focused scanned beam at different wavelengths (LBIC technique). These measurements have been performed on N and P-type Wacker cast polysilicon with density of impurities between 10^{15} cm^{-3} and 10^{16} cm^{-3} .

2. Experimental methods. — A schematic outline of the scanner is shown in figure 2. Light is provided by different sources :

- 0.633 μm and 1.15 μm He-Ne lasers which reveal respectively superficial and volumic defects,
- a monochromator with a step motor controlled by a microcomputer which allows the scanning of the wavelength between 0.45 μm and 1.15 μm .

A metallographic microscope is employed to obtain a light spot of 5 μm diameter. Samples are mounted on a stage driven by two step motors controlled by a microprocessor for X and Y displacements.

The diffusion length L is evaluated from the intersection of the straight line $Q^{-1} = f(\alpha^{-1})$ with the α^{-1} axis [6], where Q is the collection efficiency and α the optical absorption coefficient. The variation of α with the wavelength λ depends on the silicon samples,

(*) Communication présentée à l'ESSDERC, 1981.

Fig. 1. — Band structure near a grain boundary in N and P-type semiconductor.

i.e. whether they are stress relieved or not [7]. The relations $\alpha = f(\lambda)$ for stress relieved case are labelled by 1 and 2 other wise.

The g.b. recombination velocity s is evaluated by using a recent method given by J. D. Zook [8] which consists of measuring the area of the surface limited

by the g.b. photoelectric profile at a wavelength λ . This area defines the effective width $\bar{W}$ of a g.b. The variation of $\bar{W}$ (normalized by the diffusion length L_G in the adjacent grain) with λ (or α) is compared to the Zook's diagram, where the parameter is the normalized recombination velocity $S = sL_G/D$, D is the minority carrier diffusivity.

The samples of N-polysilicon Wacker have been studied after the realization of a Au-Si Schottky junction. A 150 Å film of gold is evaporated in a vacuum of 10^{-6} torr after a classical chemical treatment of the silicon surface. The contact is taken by means of silver point on a thicker (2 000 Å) layer of gold deposited in a corner of the Schottky diode. The ohmic contact is realized by means of a Nixel solution after a diffusion of 500 °C during 1 hour. In the case of P-type we used phosphorus diffused N⁺-P junctions obtained by a classical technology used for photocells [9]. The dopants of the N and P-type samples are phosphorus and boron respectively.

3. Experimental results. — 3.1 N-POLYSILICON. —

The g.b. present a very high activity which is shown in the photoelectric scanning (Fig. 3) performed with a white light spot. Attenuations greatest than 50 % can be observed in the g.b. The measurements of the diffusion lengths in the g.b. B and in the adjacent grains are illustrated by figure 4. Diffusion lengths in the grains varied between 5 μm and 15 μm. Those measured when the spot is in the position of the photocurrent minimum are smaller than the spot size. Also, they must be, certainly, over-estimated.

By integration of the g.b. profile shown in figure 5, we have measured the effective width $\bar{W}$ of the g.b. B for different wavelengths. The results have been reported on figure 6 and compared to the Zook's diagram calculated for $S = sL_G/D = \infty$. The dimensionless absorption coefficient A is defined by $A = \alpha L_G$.

The g.b. recombination velocity in N-polysilicon is

Fig. 2. — Schematic diagram of the optical scanning.

Fig. 3. — Photoelectric scanning of a Au-N polysilicon Schottky diode.

very high. S is always higher than 10. It is not possible to give a better precision when S is higher than 10. First, the results are highly dispersed following the grain boundary studied. For example, we have verified that the activity of twins is very low. We have no tried until now to correlate the values of S with the g.b. angle of desorientation or (and) with segregation of different defects near the g.b. Second, the Zook's curves for $S = 10$ and $S = \infty$ are very near and the dispersion of the results cannot allow a better determination for S as it is evident in figure 6.

By using the diffusion length L_G measured in the adjacent grains and taking the reported value of the minority carrier diffusivity $D \simeq 10 \text{ cm}^2/\text{s}$ in N-silicon,

Fig. 4. — $Q^{-1} = f(\alpha^{-1})$ graph in the g.b. B and in the adjacent grains shown in figure 3.

Fig. 5. — Photoelectric profiles at different wavelengths of a g.b. in N-type polysilicon.

Fig. 6. — Variation of the reduced effective width $\overline{W}/L_G$ of the g.b. B in N-type with the normalized absorption coefficient A . In full line the theoretical curve for $S = sL_G/D = \infty$ given of J. D. Zook [5].

the g.b. recombination velocities are higher than 10^5 cm/s. With such recombination velocities we must observe a quasi zero photocurrent in the g.b. This found to be not true in the present case because of the finite dimension of the spot and the small diffusion lengths in the grains. We can notice that the half-width of the g.b. photoelectric profiles is approximately $25\text{ }\mu\text{m}$. According to Zook's theory, it must be 2.5 time higher than the diffusion length L_G in the adjacent grains which is well verified.

3.2 P-POLYSILICON. — The photoelectric line (Fig. 7) drawn with a $\lambda = 0.98\text{ }\mu\text{m}$ spot on a P-type polysilicon reveals some influential g.b. marked by the arrows. The photocurrent is normalized by its maximum value measured during the scanning.

For the $0.98\text{ }\mu\text{m}$ light, the depths of the minima at the g.b. are not sensitive to the spot size. The attenuation are nearly 50 %.

For comparison we have reported in figure 7 the measured values of the diffusion length by using the relation 2 of $\alpha = f(\lambda)$ corresponding to as-grown silicon. As expected, there is a good correlation between L and I_{ph} at the same point. It is well known that when $\alpha L < 1$, the photocurrent is a linear function of the diffusion length.

We can notice that the diffusion lengths are higher in P-type than in N-type silicon. We can point out the great difference between the photoelectric responses and the diffusion lengths of grains according to their crystallographic orientations.

Fig. 7. — Photoelectric line drawn with a $\lambda = 0.98\text{ }\mu\text{m}$ spot in a N^+P polysilicon junction. The dots give the diffusion lengths measured at the corresponding points.

In the figure 8, we compare a g.b. photoelectric profile at $\lambda = 0.98\text{ }\mu\text{m}$ and the variation of the diffusion length determined by using the relation 1 of $\alpha = f(\lambda)$ corresponding to stress-relieved silicon. We can observe the good correlation between the two profiles excepted at the photocurrent dip, marked by the arrow, which is certainly due to an optical defect.

We can note also that the attenuation of the diffusion length is weaker than the attenuation of the photocurrent. This apparent disagreement can be explained if the $\alpha = f(\lambda)$ relations 1 and 2 are employed in the grains and near the g.b. respectively. With this assumption the diffusion lengths would be $130\text{ }\mu\text{m}$ in the left adjacent grain (by using the relation 1) and $60\text{ }\mu\text{m}$

Fig. 8. — Comparison between a g.b. photoelectric profile at $\lambda = 0.98\text{ }\mu\text{m}$ and the variation of the diffusion length L in a N^+P polysilicon junction.

near the g.b. (by using the relation 2). The ratio of these two values is similar to the ratio of the corresponding photocurrents.

A further justification of the use of different $\alpha = f(\lambda)$ relations for grain and g.b. is given by figures 9a and 9b which show undoubtedly that the linearity

Fig. 9. — $Q^{-1} = f(\alpha^{-1})$ graphs for P-polysilicon obtained by using the $\alpha = f(\lambda)$ relations 1 and 2 adapted to the stress relieved case and to the as-grown case respectively : a) in a grain ; b) in a g.b.

Fig. 10. — Normalized photoelectric profiles of a same g.b. of a P-type polysilicon at different wavelengths.

of the graphs $Q^{-1} = f(\alpha^{-1})$ is better with the relation 1 in a grain and with the relation 2 near a g.b.

These observations confirm that in the vicinity of a g.b. high stresses can exist associated with dislocations which must contribute to the high density of traps and consequently to the degradation of the electronic properties.

In figure 11, we have superposed the normalized photoelectric profiles at different wavelengths of the same g.b.

We verify that the profiles broaden out and the attenuations at the g.b. increase with the wavelength. We have observed that the photoelectric profiles remain identical for all wavelengths higher than $1.05 \mu\text{m}$, because the attenuation depth of the light (α^{-1}) for $\lambda = 1.05 \mu\text{m}$ is nearly equal to the thickness of the sample.

The different g.b. effective widths, suitably normalized, have been plotted on the Zook's diagrams as

Fig. 11. — Variation of the reduced effective width of the g.b. shown in figure 10 versus the wavelength.

shown in figure 10. We have distinguished the results measured on the left and on the right part of the g.b. profile and by using the $\alpha = f(\lambda)$ relations 1 and 2. We obtain the nearly same value for the g.b. recombination velocity $s = (1.5 \pm 0.5) \cdot 10^4 \text{ cm/s}$ (with $D \simeq 30 \text{ cm}^2/\text{s}$). This recombination velocity justifies very well the attenuation of the photocurrent at $\lambda = 1.05 \mu\text{m}$ observed at this g.b. The saturation effect observed in figure 10 is due to the finite thickness of the sample.

4. Discussion. — As it is expected we have obtained higher diffusion lengths in the grains of P-type polysilicon than in N-type.

The g. b. attenuations of the photocurrents due to the degradation of the diffusion lengths are less important in P-type than in N-type. This observation is confirmed by the g.b. recombination velocity measurements which are smaller in P-type than in N-type for approximatively the same doping.

Following the treatment of Card and Yang [10], we think that we can only accede, by our measurements, an effective g.b. recombination velocity given by

$$s = \frac{1}{2} s(0) \exp\left(\frac{E_B^0}{kT}\right) \quad (1)$$

where $s(0) = N_T \sigma v$ is the proper interfacial recombination velocity. N_T , σ are respectively defined as the density of active g.b. interface states and the minority carrier capture cross section. v is the thermal velocity of the minority carriers.

We can assume that $s(\sigma)$ is smaller than the recombination velocity of « clean » surfaces which lies between 10 and 10^2 cm.s^{-1} . Also, it is necessary, to justify the s values measured, to take into account like in (1), the effect of the electric field in the g.b. space charge region which drifts the minority carriers towards the g.b. We think also that $s(0)$ is nearly identical for N and P-type polysilicon. These two hypotheses lead to the conclusion that the g.b. barrier heights are higher in N-type than in P-type polysilicon. As the doping concentrations in N and P-type samples studied are nearly identical, we propose two additional assumptions to justify this conclusion. First, the neutral level which separates the acceptor and donor interface states at g.b. is nearer to the valence band than to the conduction band like for surfaces. Secondly, it is possible that in P-type, the boron segregates near the g.b. to dope them P^+ [11], which is sufficient to reduce the g.b. barrier height (when $N_G > 5 \times 10^{15} \text{ cm}^{-3}$) as shown in figure 12. This figure gives the g.b. barrier heights in silicon whatever the type because we have supposed that the neutral level is located at the middle of the band gap. The curves 1, 2, or 3 of the figure 12 are respectively related to a uniform, monoenergetic and exponential distribution of the g.b. interface states in the band gap in the case of a total density $N_T = 5 \times 10^{12} \text{ cm}^{-2}$ for each case. As it was expected,

Fig. 12. — Variation of the g.b. barrier height at the equilibrium versus doping density for three cases of interfacial state distribution ($N_T = 5 \times 10^{12} \text{ cm}^{-2}$). The variation of the difference E_F between the Fermi level and the intrinsic level has been drawn for comparison.

the monoenergetic case, when the g.b. trap level E_t is equal to the intrinsic level E_i , gives the higher barrier

heights. Evidently, these g.b. barrier heights increase with interface trap concentration.

5. Conclusions. — The optical scanning is a useful tool for characterizing the electronic properties in polycrystalline semiconductors, specially for semicrystalline materials for which the g.b. are perpendicular to the surfaces. This technique allows the local measurement of the photoelectric response at all wavelengths and of the diffusion lengths. The g.b. photoelectric profile permits an evaluation of the g.b. recombination velocity which gives the influence of grain boundaries on the minority carriers.

We have verified that in P-type polysilicon the recombination activity of grain boundaries is weaker than in N-type. Our results on local diffusion lengths can be explained by assuming that the vicinity of the g.b. is highly stressed.

Acknowledgments. — This work is supported by the COMES and the PIRDES/CNRS. The authors would like to thank M. D. Sarti (PHOTOWATT S.A. Paris) for P-type polysilicon photocells supplying.

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