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MINORITY CARRIER LIFETIME AND POTENTIAL BARRIER HEIGHT IN POLYCRYSTALLINE SILICON : EFFECTS OF LOW TEMPERATURE ANNEALINGS AND NEUTRON IRRADIATION⁺

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Résumé. - Les effets de recuits à température $T \leq 450^\circ\text{C}$, sous argon ou sous hydrogène, et d'irradiations par neutrons de 14 MeV sont comparés en terme de durée de vie volumique τ_v des porteurs minoritaires et de hauteur ϕ_B des zones de barrière de potentiel. Les mesures sont essentiellement réalisées par photocourant et photoconductivité transitoires, et par caractéristiques $I(V,T)$, dans des rubans RAD à gros grains (CZ, dopé B, 1 $\Omega\cdot\text{cm}$).

Les résultats montrent que les recuits, qu'ils soient réalisés sous argon ou sous hydrogène, affectent peu τ_v (~ 1 à $0,5 \mu\text{s}$). Il en est de même de ϕ_B (0,10 à 0,20 eV). Par contre, les effets des zones de barrière ϕ_B sur la conduction ne suivent le modèle de doubles barrières de Schottky que dans les échantillons non recuits sous hydrogène : en passivant les joints près de la surface, l'hydrogène rend les effets des zones de barrière restantes équivalents à ceux de zones électriquement isolantes.

La sensibilité du matériau aux irradiations s'avère également liée à la sensibilité des zones de barrière de potentiel :

- la dégradation de τ_v est équivalente à celle obtenue dans un monocristal ;
- les variations de ϕ_B entraînent une modification importante de la conduction pour des doses où la conductivité d'un monocristal n'est pas affectée.

Abstract. - The effects of annealing, at temperatures $\leq 450^\circ\text{C}$ under argon or hydrogen atmosphere, and of 14 MeV neutron irradiation on bulk lifetime τ_v of minority carriers and height ϕ_B of the potential barrier regions are compared. The measurements essentially involve transient photocurrent and photoconductivity responses, and $I(V,T)$ characteristics, of samples from large grain R.A.D. ribbons (CZ silicon, boron doped, 1 $\Omega\cdot\text{cm}$).

The results show that the low temperature annealing with argon or hydrogen scarcely modifies both the τ_v (1 to $0,5 \mu\text{s}$) and ϕ_B ($\sim 0,10$ to $0,20$ eV) values. But the effects of the regions with potential barriers ϕ_B on the material conductivity only agree with the double-Schottky barrier model when the samples have not been annealed under hydrogen : by passivating grain boundaries near the sample surface, hydrogen makes the effects of the remaining barrier regions analogous to the effects of insulating zones.

Following neutron irradiation the behaviour of the electrical properties of the material is again strongly related to the behaviour of the potential barrier regions :

- the degradation of τ_v appears comparable to the degradation observed in single-crystalline samples ;
- the variations of ϕ_B are responsible for the change in sample conduction which is observed at the low irradiation doses where single-crystal conductivity is not affected.

⁺ work performed under collaboration with P.I.R.S.E.N.

Grain boundaries are known to change the conduction properties of polycrystalline materials : as these boundaries are surrounded by potential barriers of height ϕ_B , material conduction is then regulated by the potential barrier regions, i.e., by the effects of the barriers on the material free carriers. It is thus of major interest to know what changes in the potential barrier appear due to the treatments (thermal annealing, particle irradiation,...) the material has been subjected to, and to correlate these changes with those induced in the charge transport properties of the sample, especially conductivity and free carrier lifetime.

The cases of low temperature annealings ($T \leq 450^\circ\text{C}$) and of room temperature irradiation by 14 MeV neutrons up to flux of $10^{13} \text{ n.cm}^{-2}$ are investigated in the present paper. The low temperature annealings allow to anneal the material point defects (vacancy-impurity complexes, interstitials.../1/) and, in the presence of hydrogen, to saturate the dangling bonds in the grain boundary regions /2/. On the other hand, irradiation by particles such as 14 MeV neutrons is a way for introducing vacancy-type complexes V^2 , $V-I$... : the effects of defect introduction in polycrystalline material and in single-crystalline material may be compared.

The work has been performed on single-layered polycrystalline silicon with large grains of $\geq 100 \times 300 \mu\text{m}^2$, 60-80 μm thick, elaborated for photovoltaic purpose from CZ boron doped 1 Ωcm silicon, on carbon substrate, by the R.A.D. technique/3/. A dozen of samples issued from a same technological process have been used in the study.

1. ELECTRICAL PROPERTIES : MEASUREMENTS AND BEHAVIOUR

The electrical properties dealt with are the concern of the charge transport allong the pulling axis of the polycrystalline ribbon.

Two measurement techniques are involved :

- I(V) characteristics versus measurement temperature /4/ ;
- electrical responses to transient excitation by 1.06 μm laser pulse of 40 ns duration : (i) decay of the photoconductivity responses $\Delta V(t)$ /5/, (ii) ways of decay of the diffusion photocurrent $i_D(t)$ associated to the free minority carriers /6,7/.

Following the analysis given in a previous paper /8/, the effect of the grain boundary regions on the I(V) characteristic of such a material may be schematized using two current components (figure 1) :

$$(1) \quad I = I_1 + I_2$$

The component I_1 is the electrical current crossing a double barrier of Schottkydiode with area S. This component is given, under low perturbation conditions, by :

$$(2) \quad I_1 = S J_s \operatorname{sh} \left(\frac{qV_A}{2mkT} \right)$$

where m is the ideality factor of the Schottky barrier, V_A the applied voltage across the double barrier of Schottky and J_s the density of the saturation current.

The component I_2 is the electrical current through the possible discontinuities of the boundary represented by the shunt resistance R_{sh} :

$$(3) \quad I_2 = V_A / R_{sh}$$

where V_A corresponds to (cf. figure 1) :

$$(4) \quad V_A = \frac{V}{N} - IR_s$$

if V is the voltage applied across the N modulus "grain-grain boundary" of the sample. Using the thermionic emission-diffusion theory /9/, the current density J_s may be written as follows :

$$(5) \quad J_s = A^{**} T^2 \exp. \left(- \frac{E_{Fj}}{kT} \right)$$

E_{Fj} is the Fermi level inside the boundary region such as

$$(6) \quad E_{Fj} = \phi_{Bo} + (E_{Fv} - E_v)$$

ϕ_{Bo} being the grain boundary potential barrier height and E_{Fv} the Fermi level inside the grain. In (5), A^{**} is the effective Richardson constant :

$$(7) \quad A^{**} = \frac{f_T f_{pr} A^*}{1 + f_T f_{pr} v_R / v_D}$$

if we note by A^* the Richardson constant, f_T the tunneling carrier probability, f_{pr} the overall probability of the carrier backdiffusion, v_R the effective recombination velocity of the carriers entering into the barrier region and v_D the velocity of these carriers inside this region (usually $v_D \gg v_R$). For large enough values of V so that $V_A \gg mkT/q$, the general expression of the current thus obey the relation :

$$(8) \quad I = \frac{V_A}{R_{sh}} + \frac{S f_T f_{pr} T^2 A^*}{1 + \frac{f_T f_{pr} v_R}{v_D}} \exp \left(- \frac{\phi_{B0} + E_{Fv} - E_v}{kT} \right) \exp \left(\frac{qV_A}{2mkT} \right)$$

The plot of $\log I$ versus V leads to J_s at given temperature T . Measurements at various temperatures allow to study the variation of $\log (J_s/T^2)$ versus $1/T$ (figure 2) and we obtain a value ϕ_{B0} of the potential barriers which is an averaged value for the potential barriers inside the sample.

The values of ϕ_{B0} obtained in the as-grown samples are given in Table 1.

$I(V)$	ϕ_{B0} (eV)	$\tau_V (i_p)$ (μs)	$\tau (\Delta V_\sigma)$ (μs)
I_1	0.15 (0.12 - 0.18)	0.7 - 0.8	(τ_σ) 15-30

Table 1 : $I(V)$ behaviour, barrier height ϕ_B , bulk minority carrier lifetime τ_V and time constant τ_σ at the decay beginning of the photoconductivity response ΔV_σ in the as-grown polycrystalline samples.

At the lowest temperatures (cf. figure 2), the increase in $\log (J_s/T^2)$ may be explained by carrier tunneling through the boundaries /9,10/ due to the increased effect of f_T -see (7)- when T decreases /9/.

Transient diffusion photocurrent $i_D(t)$ is due to the excess minority carriers (electrons in our case) created in the sample by uniform bulk photoexcitation and collected by diffusion.

With thin samples, this method allows to study both τ_V (bulk carrier lifetime) at the decay beginning, and τ_a (due to surface recombination, $\tau_a \propto \mu_n^{-1/2}$) at the end of the decay/6/(figure 3).

The transient photoconductivity response $\Delta V_\sigma(t)$ is measured under constant polarization current. It leads to the variation in conductivity $\Delta \sigma(t)$ induced by the excess electrons and holes created in the sample. Thus the $\Delta V_\sigma(t)$ response takes into account the density-mobility product, $p(t)\mu_p(t)$, $n(t)\mu_n(t)$, for these carriers. In the case of a polycrystalline (P type) material, because of the charge conduction mechanism involved, two components have to be distinguished in a photoconductivity response /5/ : one is related to the decrease in the potential barrier height $\Delta \phi_B$ induced by the excess minority (electron) carriers which have been trapped inside the potential barrier regions ; the other one comes from the free excess carriers $\Delta n, \rho(t)$ (where $\Delta n(t) < \Delta \rho(t)$) produced inside the grains. Depending on the mechanism which dominates the charge carrier transport in the polycrystalline sample, behaviours of a signal may be summarized as follows :

- When charge conduction is dominated by carrier transport through the potential barrier regions (i.e., $I(V)$ ruled by I_1 component in (1)), photoconductivity decay τ_σ is controlled by the variation in the majority carrier mobility $\mu_p(t)$ and the return to equilibrium of the potential barrier variation $\Delta \phi_B(t)$ because trapped minority carriers are emitted over the $\phi_{B0} - \Delta \phi_B(t)$ barrier. Because the photoconductivity measurements are performed under low polarization conditions, expression of the majority carrier mobility can be deduced from expression (8) written for $V_A \ll 2mkT/q$. It gives :

$$(9) \quad \mu_p(t) = \mu_{p0} \exp(-\Delta\phi_B(t)/kT)$$

with

$$(10) \quad \mu_{p0} = \frac{A \pi \pi_T}{2 k m N_V} \exp(-\phi_{B0}/kT)$$

and

$$p(t) = N_V \exp\left(-\frac{E_{FV} - E_V}{kT}\right) = p_0 + \Delta p(t)$$

- On the contrary, when charge conduction is defined by ohmic process i.e., $I(V)$ given by the I_2 component in (1), photoconductivity decay is controlled by the recombination τ_V of the excess electrons and holes $\Delta n, p(t)$. End of the response may then show a tail, due to the contribution of trapped minority carriers.

II. RESULTS

Thermal annealing with hydrogen or argon

The electrical properties obtained with samples annealed for periods of 5 minutes under hydrogen ($T = 450^\circ\text{C}$) or argon ($T \leq 400^\circ\text{C}$) are summarized in Table 2.

	$I(V)$	$\phi_{B0}(\text{eV})$	$\tau_V (\mu s)$	$\tau (\Delta V_G) (\mu s)$
H_2 anneal	$\sim I_2$	-	0.8 - 1.0	(τ_V) 1.0
A_r anneal	I_1	0.18	0.5	(τ_G) 20

Table 2 : Parameters of the charge carrier transport in the polycrystalline samples following thermal annealing with hydrogen or argon at $T_r = 450$ or 400°C (annealing duration at T_r is five minutes)

These properties are deduced from the characteristics $I(V, T)$ and the transient photoresponses $\Delta V_G(t)$, $\Delta\phi(t)$ at room temperature as previously described in Section I. By comparison with the electrical properties of the as-grown samples (Cf. Table 1), the first result to note is the effect of the annealing with argon. Both the $I(V, T)$ characteristics and the photoconductivity responses $\Delta V_G(t)$ stay then dominated by the component associated with carrier transport through a double Schottky barrier. Moreover, an increase of the corresponding potential barrier height ϕ_{B0} clearly appears. On the contrary, following anneal at 400°C , the free carrier lifetime τ_V is little modified (figure 5a). But the minority carrier mobility $\mu_n \propto \tau_G^{-1}$ should be increased by a factor 2 (figure 5b) : this well agrees with the opposite effects that a potential barrier has on the majority and minority carrier mobilities. Effect of thermal annealing with hydrogen is strongly different since carrier conduction with ohmic character then becomes dominant in the $I(V)$ characteristics (see I_2 in (1)). Simultaneously, the appearance of a strong component from free carriers $\Delta n, p(t)$ is observed in the photoconductivity responses.

Neutron irradiation effects

The variations which have been measured versus neutron flux are illustrated in the figures 4b, 5 and 6 for, respectively : (i) ϕ_{B0} , τ_V and $\tau_G \propto \mu_n^{-1}$, in the cases of an as-grown sample and of a sample previously annealed up to 400°C with argon, and (ii) for τ_V in the case of P-type monocrystalline and polycrystalline samples irradiated simultaneously.

General behaviour of the results obtained with the polycrystalline samples shows that the degradation rate of the minority carrier lifetime stays analogous to the degradation rate measured in monocrystalline materials of comparable resistivity.

But, due to variations in the values of ϕ_B , notable change in carrier conductivity may appear in the polycrystalline materials when they are irradiated by neutron fluxes at which the conductivity of monocrystalline samples is not affected (see results at $D = 10^{12} \text{ n.cm}^{-2}$, for instance).*

Furthermore, it is to notice that, under irradiation an as-grown sample shows a

higher degradation rate of ρ_v and a lower modification of conduction than a sample previously annealed up to 400°C with argon.

SUMMARY

There are the potential barrier zones which are sensitive to the constraints ; and, thus, they rule the electrical behaviour of a large grain polycrystal. Indeed, the conductivity variations are always associated to the potential barriers zones after the annealing under hydrogen or argon atmosphere.

It is the same for the neutron irradiations in the low flux range : they affect not only the carrier lifetime (as in monocrystalline sample case), but also the sample electrical conductivity due to the impact of the irradiation on the potential barrier heights.

BIBLIOGRAPHY

- 1 CORBETT, J.W., BOURGOIN, J.C., CHENG, L.J., CORELLI, J.C., LEE, Y.H., MOONEY, P.M. and WEIGEL, C., *Inst. Phys. Conf. Ser.*, **31** (1977) 1
- 2 GINLEY, D.S. and HAALANG, D.M., *Appl. Phys. Lett.*, **39** (1981) 271
- 3 BELOUET, C. BELIN, C., SCHNEIDER, J., PAULIN, J., 3è P.V. Solar En. Conf., Cannes (1980)
- 4 TARNG, M.L., *J. Appl. Phys.*, **49** (1978) 4089
- 5 ROUX, M. and BIELLE-DASPET, D., *Rev. Phys. Appl.*, **16** (1981) 497
- 6 BIELLE-DASPET, D. and GASSET, G., *Solid. State Electron.*, **21** (1978) 1219
- 7 BIELLE-DASPET, D., JOHAN, A. and ESPIOUSSAS, F., *Rev. Phys. Appl.*, **15** (1980) 945
- 8 JOHAN, A. AYERZA, J. BIELLE-DASPET, D. ROCHER, A. and FONTAINE, C., 2è P.V. Solar En. Conf., Berlin (1979)
- 9 See for instance SZE, S.M., *Physics of semiconductors devices*, (J. Wiley and Son N.Y.), 1970, pp. 382-390
- 10 SEAGER, C.H. and PIKE, G.E., *Appl. Phys. Lett.*, **40** (1982) 471

Figure 1 Equivalent electrical schema of a "grain-grain boundary" modulus in a polycrystalline material

* Simultaneously, the DLTS spectra also differ from the response of single-crystalline specimen : the dominant energy levels are located at $E_v + 0.40$ and 0.16 eV in the single-crystalline and polycrystalline materials, respectively, after irradiation.

Figure 2 The $\text{Log}(J_s/T^2)$ for $V \gg \frac{kT}{q}$, plotted versus the reverse temperature $1/T$ for both samples G98-1 and G98-2 at two irradiation fluxes $D = 10^{12} \text{ n.cm}^{-2}$ and $D = 10^{13} \text{ n.cm}^{-2}$

Figure 3 Shape of a diffusion photocurrent response created by brief penetrating excitation of duration $\delta/6$

Figure 4 Conductivity $\langle J \rangle$ (+, -) and potential barrier heights Φ_B (•, •) plotted versus the annealing temperature T_r and the irradiation dose D .
 $\langle \sigma \rangle$ is deduced from the I/V ratio measured under low values of the polarisation-cf. (1) to (3) - Unannealed and argon-annealed samples G98-1 and G98-2. Annealing duration at T_r is five minutes.

Figure 5 Evolution of (a) τ_v , bulk carrier lifetime, and (b) τ_G , lifetime due to surface recombination, versus annealing temperature T_r , and irradiation dose D .

Figure 6 Degradation rate $(1/\tau_{vo} - 1/\tau(p))$ versus irradiation dose D for polycrystalline samples G98-1 and G98-2 (G98-2 sample which is annealed at 400°C before irradiation) and 1.2 cm and 10.2 cm monocrystalline samples.