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EFFECT OF HEATING SAMPLES DURING PULSED ELECTRON BEAM ANNEALING ON THE OPEN-CIRCUIT VOLTAGE OF SILICON SOLAR CELLS

A. Laugier, D. Barbier, M.S. Doghmane and G. Chemisky

Laboratoire de Physique de la Matière (LA 358), Institut National des Sciences Appliquées de Lyon, 20, avenue Albert Einstein, 69621 Villeurbanne Cedex, France

RÉSUMÉ

On a recherché les causes des faibles tensions en circuit ouvert associées au recuit pulsé électronique dans la réalisation des photopiles silicium implantées phosphore. Les défauts induits ont été analysés sur la base d'observations en microscopie électronique, en D.L.T.S. et d'étude de dégradation de diodes Schottky. On définit une méthode permettant d'améliorer notablement les valeurs de V_{oc} en associant des électrons de faible énergie cinétique moyenne (10 keV), des fluences faibles ($\leq 1 \text{ J/cm}^2$) sur cibles portées à 450°C. Des valeurs de V_{oc} comparables à celles obtenues par recuit thermique conventionnel sont observées.

ABSTRACT

Defects associated to pulsed electron beam annealing of P implanted Si solar cells lead to poor V_{oc} ($< 500 \text{ mV}$). Their nature is discussed on the basis of S.E.M. observations, D.L.T.S. study and degradation of electrical characteristics of Schottky barriers. An improved PEBA process is determined, characterized by a low mean energy electron beam (10 keV) associated to a starting temperature of 450°C and low fluences ($\leq 1 \text{ J/cm}^2$). Values of V_{oc} similar to conventional thermal annealing are obtained.

I. INTRODUCTION

Solar cells made by Pulsed Electron Beam Annealing (PEBA) of phosphorous implanted silicon are characterized by a very good short-circuit current and a rather poor open-circuit voltage $V_{oc}/1,2/$. As for laser annealing a significative improvement (typically 40 mV) is obtained with a post thermal treatment at $T \approx 400^\circ\text{C}$.

In this work effects of heating the samples during the pulse are investigated. In addition an optimization of the PEBA process is determined.

II. PEBA SOLAR CELLS

The starting material was phosphorous implanted (100) C.Z. boron doped silicon ($N_A = 10^{16} \text{ cm}^{-3}$). In order to give some basis for the PEBA treatment optimization, the results of two different solar cells processes are compared in this section.

n°1 : p^+ annealed with a 10 keV mean energy electron beam pulse /1,3/

n°2 : p^+ annealed with a higher mean electron energy (15 keV), leading to a more penetrating dose profile /2/.

Details about the PEBA process are also given in ref./2/. In both cases, the pulse duration was about 50 ns and fluences were in the range $0.8\text{--}1.2\text{ J/cm}^2$.

A computer simulation of PEBA induced thermal effects have been performed /4/ in order to investigate the particular features of the melting and freezing kinetics as a function of the substrate starting temperature.

For process n°1 at 20°C crystalline silicon is fully molten over 0.35 micron with only 1 J/cm^2 . For process n°2 with 1.2 J/cm^2 the enthalpy required for complete melting of crystalline silicon is not reached and an inhomogeneous physical state is obtained in the melting layer.

The amorphous front layer (0.2 micron) is fully molten while a "melt like" state is achieved in the underlying crystal up to 0.65 micron. So annealing at 1 J/cm^2 is more effective with process n°1 than with process n°2.

Moreover, the effect of heating silicon before PEBA consists essentially in an increase of the induced melting layer thickness for a given fluence and in a smaller thermal gradient in the solid leading to a longer freezing kinetic. With a 450°C starting temperature the same melting depths as at 20°C are obtained with only 0.85 J/cm^2 for the process n°1 and 1 J/cm^2 for the process n°2 respectively.

Excellent annealing is obtained with process n°1 at only 0.8 J/cm^2 and with process n°2 at 1.2 J/cm^2 . The junction depth is less than 200 nm with a N^+ layer dopant concentration higher than $10^{20}/\text{cm}^3$. Solar cells were realized with PEBA wafers according the following process.

Ti-Pd-Ag grid contacts were then evaporated and a 80 nm thick TiO_2 A.R. coating was deposited at 325°C . The transparency of the grid was 94.5 %. An aluminium layer was deposited on the back side of the wafers and annealed during 20 mn at 450°C . Assuming a uniform junction model the expected short circuit current I_{sc} and V_{oc} for our starting material are respectively 33 mA/cm^2 and 580 mV (AM1). The best experimental value obtained for I_{sc} was 32.4 mA/cm^2 . This value agrees with the theoretical one and with the spectral response shown on Fig.1 which is consistent with a base minority carrier diffusion length of 100 microns. So the overall process does not affect the starting material properties. Values of V_{oc} are plotted on table 1 and compared to values obtained with process n°1.

Annealing	Thermal 850°C 15mn	450°C 10 mn PEBA (20°C)		PEBA 20°C		450°C 10 +PEBA (450°C)	
Process n°	Reference	1	2	1	2	1	2
V_{oc} (mV)	562	500	480	545	518	558	528

Table 1 - Open circuit voltage of P implanted Si versus PEBA process

Two important features appear. First the process n°1 gives the best value in all cases. Secondly PEBA at 450°C leads to 558 mV which is yet 20 mV below the theoretical value but is very similar to the reference. So a first conclusion is that an optimized PEBA process gives very good results compared to the conventional thermal process.

III. DISCUSSION

As other pulsed annealing technics PEBA induces defects in silicon. In a recent paper a thorough study of extended defect were performed by mean of electron microscopy /5/. Comparison made between conventional thermal annealing and PEBA have shown that the latter removes defects associated with thermal annealing. However observations has revealed the existence of dislocations and subgrain boundaries with a fluence increasing density. Polygonization seems to indicate that climb as well as glide are active in the dislocation mobility. Fig.2 shows the S.E.M. micrograph of a bevelled sample pulsed with 1.2 J/cm^2 at 20°C with the 15 keV mean energy electron beam pulse. One remarks first the array of dislocation emergence as previously described /5/. Secondly, the extent of the dislocated zone nearly

Fig. 1 - Spectral response of PEBA Si solar cell.

coincide with the melting zone thickness as calculated in sec.2. At 450°C no extended defects appear on samples treated up to 0.9 J/cm^2 . This can be related to the smaller thermal gradients and longer freezing kinetics in that case.

In the other hand quenched-in point defects are associated to pulsed annealing /6,7/. In a previous work /7/ deep level transient spectroscopy (DLTS) performed with Schottky diodes made on PEBA processed P-type virgin silicon revealed typical defects associated to PEBA depending on the irradiation characteristics.

In this work, we have performed DLTS study on p^+/n junction made as the above discussed solar cells (n^2 process). A typical spectrum is shown on Fig.3. Two discrete hole trap levels appear C_1 ($=0.22 \text{ eV}$) and C_3 ($=0.48 \text{ eV}$) for which the biasing conditions correspond to an analyzed surface layer thickness of about 0.6 micron. The capture cross sections are respectively 3.10^{-15} cm^2 and 10^{-14} cm^2 . The broad structure C_2 partially superimposed to the peak C_3 is likely to be due to a band of levels. The hole trap levels observed cannot be assigned to already known defect in Si.

Finally, in order to obtain informations about the effect of PEBA alone on the silicon surface degradation we have studied the electrical properties of Schottky barrier made

on virgin silicon after irradiation at 1.2 J/cm^2 with a 15 keV mean energy electron beam pulse. The results are shown on table 2. One can observe a strong degradation of the diodes after PEBA at 20°C . A post thermal treatment is not sufficient to completely recover the reference diode characteristics. An improvement is observed for the 450°C PEBA processed samples. However defects are always present as evidenced by the large value of the saturation current.

Fig. 2 - Scanning electron microscopy on bevelled sample of PEBA silicon. Dislocation emergence in whole the melting zone.

Fig. 3 - DLTS spectrum for Si p^+n diode.

	Sample Temperature	n	I_s (A/cm ²)	C (pF)	V_{Bn} (V)
PEBA	20°C	2.90	$3.35 \cdot 10^{-3}$	165.2	0.570
PEBA +450°C 30mn	20°C	1.96	$1.03 \cdot 10^{-3}$	124.2	0.600
PEBA	450°C	1.78	$4.51 \cdot 10^{-4}$	110.4	0.621
Reference		1.16	$6.60 \cdot 10^{-7}$	89.7	0.791

Table 2 - Evolution of Schottky barrier characteristics made on PEBA processed Si surface (1.2 J/cm^2) n : ideality factor ; I_s : saturation current ; C : capacitance at -1 V at 1 MHz ; V_{Bn} : barrier height.

IV. CONCLUSION

Patel et al /8/ have shown that dislocations could be annealed only at temperatures higher than 700°C. So the residual Schottky diode degradation and for the solar cells the value of V_{oc} after PEBA at 450°C could be related to dislocations. The poor value of V_{oc} after PEBA at 20°C could be related to a high concentration of quenched-in point defects.

The lower quenching rate induced by PEBA on silicon heated up to 450°C is likely to reduce the point defect generation mechanism and to improve the value of V_{oc} . An improved PEBA treatment of phosphorous implanted Si solar cells is determined by using a low mean energy electron beam (10 keV) associated to a sample temperature of 450°C. Then a fluence below 1 J/cm^2 is convenient and values of V_{oc} similar to conventional thermal annealing are obtained.

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