TEMPERATURE DEPENDENCE OF SOME PROPERTIES OF LOWER PURITY SILICON

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ABSTRACT

The temperature dependence of the absorption coefficient and the bandgap of lower purity crystalline silicon was determined between 80K and 400K. In order to evaluate the temperature dependence of the electron diffusion length in the base region of pn-junction solar cells which were prepared from lower purity silicon by phosphorus diffusion the photo current was recorded as a function of temperature under conditions of constant absorption and constant incident photon flux density. From the current voltage characteristic under different illumination conditions in the temperature range between 80K and 300K the current losses across the pn-junction were determined. From these results three mechanisms can be separated: (i) the diffusion current, (ii) the recombination current and (iii) a tunnel current becomes important below 170K. The temperature dependence of the intrinsic carrier concentration deduced from (i) and (ii) suggests that the high phosphorus concentration in the emitter causes a bandgap shrinkage of 0.18eV. The behavior of the minority carrier diffusion length is in accordance with the assumption of ionized impurity scattering as the dominant mechanism for the limitation of the diffusion length.

1. INTRODUCTION

The output of a pn-junction solar cell made from crystalline silicon can be predicted once the light induced photo current as well as the current losses across the pn-junction are known (1). The light induced photo current, i_{ph}, depends on the absorption coefficient in silicon and the minority carrier diffusion length. The current losses across the pn-junction are mainly determined by the preparation conditions. The aim of the present work was to determine the characteristic properties of free carriers in silicon of lower purity and the mechanisms governing the current losses across the pn-junction, which was prepared by a conventional phosphorus diffusion technique. Since the minority carrier diffusion length is very sensitive to electrically active deep impurity levels (2,3) the knowledge of the minority carrier diffusion length together with the mechanisms of the internal losses allows us to correlate electrically active impurity centers in our samples with the observed solar cell output.

2. EXPERIMENTAL

The materials we have used in our experiments are described by V.Schlosser and K.Wendl (2) together with a summary of electrically active point defects observed by means of DLT spectroscopy. The samples are crystalline p-Si which was purified merely by means of segregation during the crystal pulling processes. The resistivity ranges between 0.03 Ωcm and 0.3 Ωcm.

The following experiments were carried out on these samples: (i) The determination of the photon energy as a function of temperature between 80K and 400K which is necessary to maintain constant absorption in the sample. The absolute value of the absorption coefficient in the wavelength range between 800nm and 1100nm was determined at room temperature. The experimental setup and an anlysis of our results was previously published (4). This method allows us to evaluate the temperature dependence of the bandgap and as a consequence the temperature dependence of the intrinsic carrier concentration in our samples:

$$n_i^2 = 3.62\mathrm{x}10^{31}\ \mathrm{cm}^{-6}\mathrm{K}^{-3}\ T^3\ exp(-\varepsilon_g/k_B T) \qquad (1)$$

n_i ... intrinsic carrier concentration
ε_g ... bandgap
k_B ... Boltzmann Constant

n_i^2 is shown as solid line in fig.1.

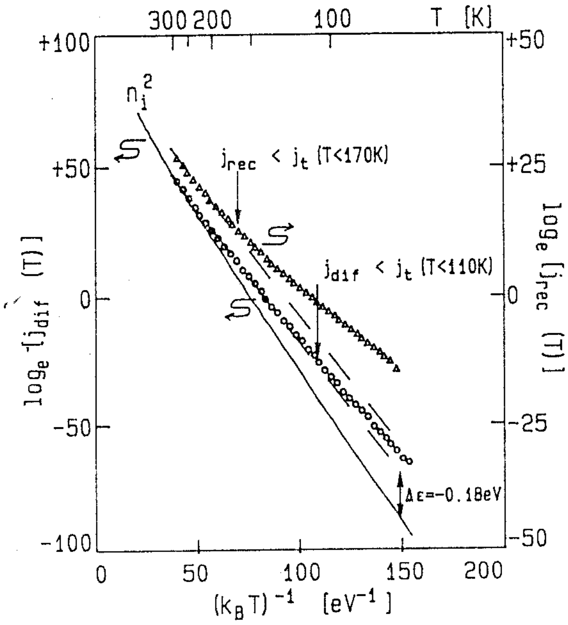

Fig.1: Semilogarithmic plot of the square of the intrinsic carrier concentration vrs. the reciprocal thermal energy: — ..calculated for the temperature dependence of the bandgap after ref.4, o ..derived from the diffusion current of a n^+p-solar cell and Δ..n_i derived from the recombination current of the same cell.Dashed lines show $n_i^{(2)}$ for a reduced gap.

Once the photon energy as a function of the temperature for the condition of constant absorption is known the photo current as a function of temperature was recorded in a second experiment (ii). In this experiment the photon flux density, N_{ph}, was kept constant. Since these experiments were carried out for values of α^{-1} around 50µm - α = absorption coefficient - which is two orders of magnitude larger than the depth of the pn-junction nearly the whole photo current is generated in the base region of the solar cell:

$$i_{ph} = \int_{x_j}^{d} dx\ N_{ph}\ \alpha exp(-\alpha x)\ exp(-(x-x_j)/L_n) \qquad (2)$$

x_j ... depth of pn-junction plane from surface
d ... thickness of the solar cell
L_n ... electron diffusion length

In fig.2 a typical result of the variation of the photo current with temperature under the conditions of constant absorption and constant photon flux density is shown. The inset displays the variation of the wavelength of the incident light necessary to obtain the required constant absorption. A consequence of keeping the absorption constant during the temperature variation is that changes in the photo current are exclusively due to changes in the electron diffusion length L_n in the base region. Another advantage of this computer assisted experiment is that the part of the sample used for the evaluation of the minority carrier diffusion length remains the same during the whole experiment. Thus errors introduced by inhomogeneities of L_n with depth are avoided. At room temperature the electron diffusion length was determined by the method described by Stokes (5).

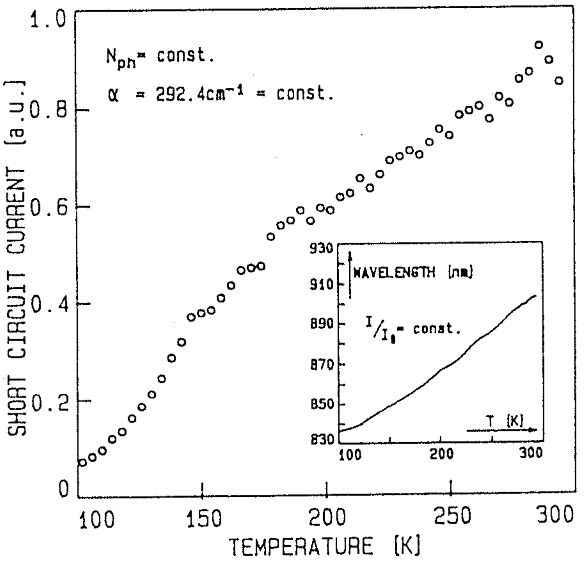

Fig.2: The temperature dependence of the light generated current of a n^+p-solar cell under conditions of: 1) constant absorption (The inset shows the variation of the wavelength of the incident light which is necessary to maintain constant absorption) and 2) constant photon flux density.

Between 80K and 300K the temperature dependence of L_n was derived from the experiment described above by solving equation 2 numerically. Following an approach of V. Schlosser (6) a plot of $(T/L_n)^2$ against T shows the temperature dependence of the capture cross section of the point defect which governs the minority carrier diffusion length. In fig.3 the results of a logarithmic plot of $(T/L_n)^2$ versus T is shown for two different samples of lower purity silicon. For temperatures below 150K a slope of -3.6 fits equally well for both samples. Above 180K a slope of -1.3 suits again for both results.

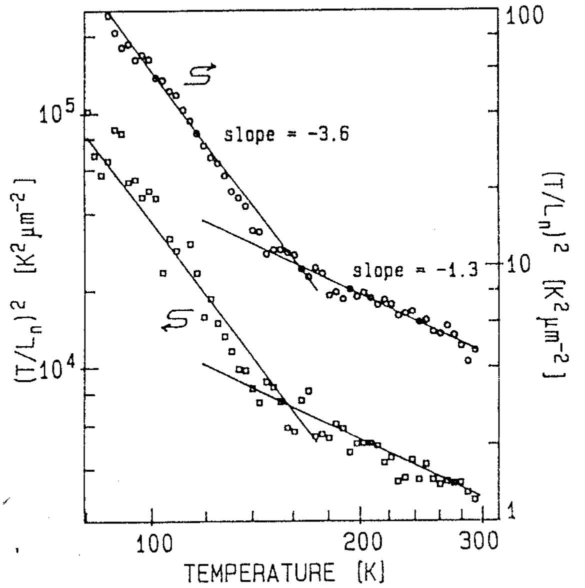

Fig.3: Logarithmic presentation of electron diffusion length L_n and temperature in order to evaluate the temperature dependence of the capture cross section of the point defect which governs L_n. ○ ..Sample of lower purity silicon prepared by conventional crystal pulling techniques, □ ..sample prepared by the heat exchanger method from metallurgical meltstock.

(iii) The last set of experiments uses the recorded values for the short circuit current, i_{sc}, and the open circuit voltage, V_{OC}, as a function of the temperature between 80K and 300K at two differnt illumination intensities. In addition a series of current-voltage curves were taken under forward bias condition at different illumination intensities and temperatures. In fig.4 three i-V curves are displayed: The result for room temperature is marked with squares and exhibits the typical characteristic expected for crystalline silicon solar cells with a pn-junction. Two regions can be seen once the curve is corrected for series resistance and shuntconductance. The first one is due to the recombination current which varies with $exp(qV/2k_BT)$ as long as the internal voltage across the pn-junction is below 0.4V. The second contribution varies with

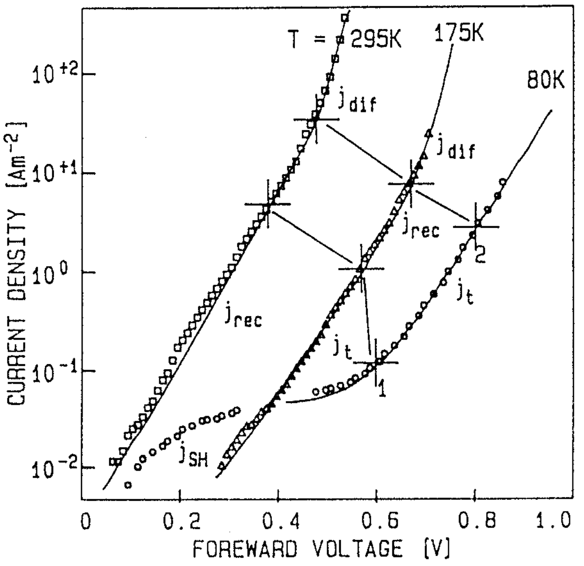

Fig.4: Current-voltage plot under forward bias conditions taken at different temperatures. j_{rec} indicates the region where the current is dominated by recombination, j_{dif} shows the diffusion current dominated region. Below 170K a tunnel current j_t superimposes both mechanisms. 1 indicates the recorded j_{sc} -V_{oc} (T) values at low incident light intensities and 2 at high intensities.

$exp(qV/k_BT)$ which is valid for the diffusion current. Thus for high illumination intensities V_{OC} is determined by the diffusion current and for low intensities -$V_{OC}<0.4V$- by the recombination current. As light source for a high illumination intensity the beam of a HeNe-Laser -λ=632nm- was coupled into a glass fibre and directed onto the surface of the solar cell. The illuminated area was approximately 0.07 cm^2. At room temperature this illumination produces an $i_{sc} \approx 2mAcm^{-2}$ and a V_{OC} of more than 0.45V. Referring to fig.4 this is the region where the current losses are due to the diffusion current. Hence the relation between i_{sc} and V_{OC} can be written as follows:

$$i_{sc} = i_{01}exp(qV_{OC}/k_BT)-i_{01} \qquad (3)$$

For a lower light intensity a light emitting diode with a center wavelength of 912nm was used with the same fibre optic setup. At room temperature a V_{OC} of about 0.35V was obtained. Again reffering to fig.4 we find that this set of i_{sc}, V_{OC} - data is in a range where the current is dominated by the recombination current. The relation between i_{sc} and V_{OC} is given by:

$$i_{sc} = i_{02}exp(qV_{OC}/2k_BT)-i_{02} \qquad (4)$$

The results for $i_{sc}(T)$ and $V_{oc}(T)$ are shown in fig.5.

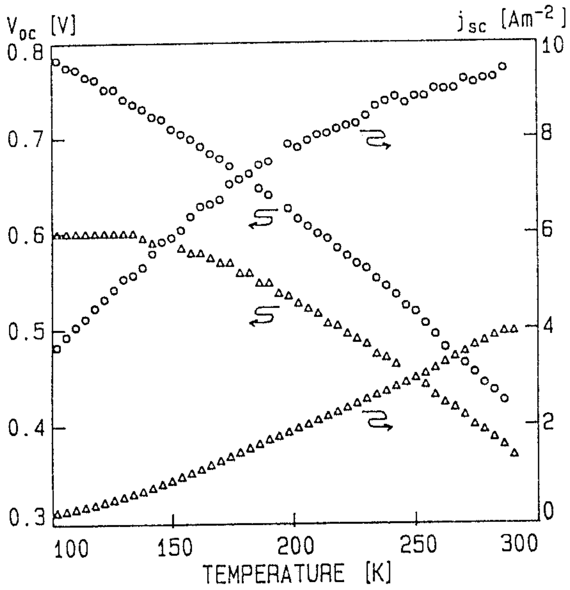

Fig.5: The temperature dependence of the short circuit current density j_{sc} and the open circuit voltage V_{oc} for two different light intensities: o ..incident light from a HeNe - laser (wavelength = 632nm), ▵ ..light source is IR - LED (wavelength = 912nm).

3. RESULTS

For highly doped emitters i_{01} is entirely determined by the shallow diffused region of the pn-junction (7). Hence i_{01} can be expressed by:

$$i_{01} \approx q(D_p/\tau_p)^{1/2}\, n_i^2/n_n \qquad (5)$$

D_p ... diffusion coefficient of holes
τ_p ... lifetime of holes
n_n ... concentration of electrons

A plot of i_{01} versus temperature thus should display the temperature dependence of n_i^2 as long as there is no significant freeze out of the ionized phosphorus donors - $n_n \simeq N_D^+$ -. Neglection of the 2nd term of the right part of eq.3 leads to:

$$ln(i_{01}) \approx ln i_{sc} - (qV_{oc}/k_BT) \qquad (6)$$

A plot of the above relation is given in fig.1 marked with circles and corresponding to the left scale. As low as 110K the difference in the slope of n_i^2 and the slope of eq.6 remains constant at 0.18eV ± 0.02eV. At lower temperatures the difference increases to 0.28eV. Referring to fig.4 the reason for the discrepancy at low temperatures can be explained by the fact that at these temperatures the whole i-V characteristic obeys merely one exponential law which is neither due to the diffusion current nor due to the recombination current. The curve taken at 175K marked with triangles in fig.4 exhibit three different exponential contributions corresponding to (i) the diffusion current at high forward voltages, (ii) the recombination current at around 0.6V and (iii) below 0.5V a contribution which is nearly independent of the temperature. At 80K the third current voltage plot in fig.4 marked with circles merely show this third exponential contribution up to 0.9V which is given by:

$$i \approx i_{03} exp(C_t V) \qquad (7)$$

At 175K C_t equals 16.5V^{-1} at 80K C_t=18.3V^{-1}. This temperature independence is a strong indication that a tunnel mechamism is responsible for this current loss.

The origin of the recombination current is within the space charge region of the pn-junction. The current voltage behavior described by eq.4. i_{02} can be expressed as (8):

$$i_{02} = q(W/2\tau_{depl})n_i \qquad (8)$$

W ... depletion layer width
τ_{depl} ... lifetime of electron and holes

Thus the slope in a plot of i_{02} versus $(k_BT)^{-1}$ should yield $n_i(T)$ in contrast to n_i^2 derived for the diffusion current. Following the argumentation given for the diffusion current a plot of the function:

$$ln(i_{02}) \approx ln i_{sc} - (qV_{oc}/2k_BT) \qquad (9)$$

is shown in fig.1 - marked with triangles and using the right scale -. Down to 170K the slope equals the one derived from the diffusion current indicating that the bandgap in the heavenly doped n^+-emitter of the solar cell is 0.18eV smaller than the one in the bulk material derived from absorption measurements. Below 170K the recombination current is superimposed by the tunnel current. Hence eq.9 is no longer valid. As a result the displayed relation exhibits a rather large deviation from the dependence at temperatures above

Table I: Properties of the n^+p-junction of a solar cell made from lower purity silicon.

Temperature [K]	n_i^2 ε_g-0.18eV [m^{-3}]	Diffusion Current calc. 1)		Recombination Current	Depl.layer 2)	Rec.time	Tunnel Current 3)		Electron diffusion-length in the bulk [µm]
		j_0 [Am^{-2}]	exp.	j_0 [Am^{-2}]	[µm]	[µsec]	I_0 [A]	C_t [V^{-1}]	
295	$8.5x10^{28}$	$7.0x10^{-8}$	$1.4x10^{-7}$	$2.1x10^{-3}$	0.097	1.1	--	--	29.7
175	$2.8x10^{16}$	$4.3x10^{-20}$	$4.3x10^{-20}$	$5.7x10^{-10}$	0.134	3.1	$5.5x10^{-10}$	16.5	13.0
80	$5x10^{-20}$	--	--	--	--	--	$8.0x10^{-12}$	18.3	0.4

1) Assuming the diffusion current is dominated by the highly doped emitter [7]:

$$j_0 = q\sqrt{\frac{D_p}{\tau_p}}\,\frac{n_i^2}{N_D^+} \qquad D_p = 1.3\ cm^2sec^{-1},\ \tau_p = 2x10^{-9}sec \quad [9].$$

2) Numerical solution of the Poisson equation for the phosphor concentration profile in the emitter.

3) Due to the uncertainity of the total area of the tunnel current the values are not normalized.

170K which are displayed in fig.1 by dashed lines.

Since a simple evaluation of the diffusion or built-in voltage V_{bi} and the depletion layer width from capacitance measurements as a function of the reverse biased pn-junction failed the depletion layer width W was numerically calculated. The phosphorus doping profile necessary to solve the Poisson equation was deduced from the diffusion temperature and time. The calculated depletion layer width W was used to characterize τ_{depl} given in eq.8. For three temperatures 295K, 175K, and 80K, respectively, the results obtained from our measurements are summarized in table I.

4. DISCUSSION

In order to verify the assumption of a bandgap shrinkage of 0.18eV in the highly doped emitter ni^2 was calculated. Taking published values of the diffusion coefficient for holes in n^+-Si (9) $D_p \approx 1.3\ cm^2sec^{-1}$ and the lifetime of holes $\tau_p \approx 2x10^{-9}$ sec the diffusion current density was calculated using eq.5. Substituting the majority carrier concentration n_n by the ionized donor concentration $N_d^+ \approx 5x10^{19}cm^{-3}$ a fair agreement is obtained between the calculated and the experimental values of the diffusion current evaluated from the i-V curve displayed in fig.4. The equality of the experimental and the calculated values at 175K is rather occasionally since n_n was roughly approximated by 50 per cent of the ionized donor concentration at room temperature. Taking into account the uncertainity of the values of n_n, D_p and τ_p the assumption of a bandgap shrinkage of 0.18eV describes the diffusion current sufficiently well. The bandgap shrinkage of 0.18eV is further confirmed by published values for a total concentration of phosphor of more than $4x10^{20}cm^{-3}$ (9). This high phosphor concentration usually occurs during the diffusion from an unlimited source and is in accordance with our cell preparation.

Using the calculated values for the depletion layer width τ_{depl} was calculated from the recombination current density according to eq.8. It shall be noted that this parameter includes the simplification that the lifetime of holes and electrons within the depletion region is equal. However a value of τ_{depl} = 1.1µsec at room temperature corresponds pretty well with the electron diffusion length of 29.7µm in the bulk. The increase of τ_{depl} with decreasing temperature appears to be contraticionary to the decrease of L_n. Assuming that $\tau_{depl} \approx \tau_n$ in the bulk τ_{depl} and L_n are related by the diffusion coefficient which is proportional to the mobility, μ_n, of electrons in the bulk. Since impurity scattering is the mechanism which governs L_n the mobility should increase as $T^{3/2}$. This temperature dependence of D_n is sufficient to explain the opposite dependence of τ_n and L_n on the temperature.

The origin of the observed tunnel current can not be deduced from our experiments. Two possible explainations are given: (i) The tunnel current occurs in the Schottky barrier between the phosphorus doped emitter and the front metallisation. In this case the barrier is only located under the metal covered area which is less than 10 per cent of the total front surface. As a consequence our solar cells can no longer be regarded as a device where the space charge region is a layer perpendicular to the current flow. Therefore the simple integration over x given in eq.2 used for the calculation of $L_{n(T)}$ is no longer applicable. (ii) The second explanation takes into account that our solar cells shall rather be treated as heterojunction devices with two different bandgaps. The tunnel current then may result from a discontinuity of valence- and conductionband on each side of the pn-junction. Although the influence of this tunnel current on solar cell operation appears to be negligible it may be important for the correct interpretation of measurements made on these devices. As mentioned above the first explanation for the tunnel current must be taken into account for the interpretation of $L_n(T)$ determination which was used to find the temperature dependence of the capture cross section of the dominating impurity. Two different slopes were derived from fig.3. Above 180K the slope is -1.3 and can be interpreted as the variation of the capture cross section of a neutral deep level with temperature (3). The second slope of -3.6 for temperatures below 150K can not be interpreted by means of a temperature variation of the capture cross section of an ionized impurity as long as it is uncertain whether eq.2 is still valid for the evaluation of L_n or not. Since both samples show the same dependence it can be concluded that the same kind of defect is responsible for the limitation of minority carrier diffusion length in both samples as deduced from the results of DLTS measurements on the same kind of materials (2).

5. CONCLUSIONS

Solar cell parameters -i_{sc} and V_{oc}- have been used to evaluated pn-junction characteristics and minority carrier diffusion length in silicon of lower purity. A bandgap shrinkage of 0.18eV in the phosphorus doped emitter was found to be essentially responsible for the magnitude of the current losses across the pn-junction for temperatures between 170K and 300K. The electron diffusion length is limited by the same kind of defect in two samples which have been prepared by different methods from different sources of metallurgical grade silicon.

6. REFERENCES

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