

The role of the emitter on the diffusion current in $n^+ p$ -junctions

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On three different samples of crystalline p -silicon $n^+ p$ -junctions have been prepared by coating the surface with a phosphorous glass and a subsequent diffusion at 915°C for 30 min. From the measurement of the short circuit current density and the open circuit voltage under high illumination conditions the diffusion current of the solar cells has been determined as a function of the temperature between 77 K and 300 K. The contribution of the emitter and the base region to the diffusion current was examined. Under the assumption of Auger recombination governing the hole lifetime in the emitter the narrowing of the mobility bandgap due to the high density of states within the bandgap of the emitter was determined. A shrinkage as high as 0.18 eV was observed in the case of a 0.2 Ωcm sample of lower purity. For high purity 6 Ωcm silicon the reduction of the mobility bandgap was determined as 0.10 eV. A polycrystalline sample exhibits a shrinkage of 0.15 eV. The reduction of the mobility bandgap was found to determine the lower limit of the current losses due to carrier diffusion in our solar cells at current densities around $1 \times 10^{-7} \text{ Am}^{-2}$.

1. Introduction

At high illumination levels the internal current losses of commercial crystalline silicon solar cells are mainly due to the diffusion current across the pn -junction. The diffusion current is due to the gradient of electron and hole concentration across the pn -junction. The properties of the minority carriers on both sides of the space charge region determine the diffusion current. Silicon commonly used for solar cell manufacturing is Boron doped p -type in the resistivity range of 0.2 Ωcm to 10 Ωcm . The shallow emitter is achieved by phosphorous diffusion techniques. In order to prepare the $n^+ p$ -junction techniques have been developed which allow the formation of a large area planar pn -junction with a high throughput. A typical sequence is the screen printing of a paste containing phosphorous oxides onto

the silicon wafer and a subsequent high temperature treatment. The resulting emitter fulfills the requirements for a steep gradient of the phosphorous concentration at the location of the pn -junction plane as well as the necessity of a high phosphorous concentration at the metal-contact semiconductor interface. The steep gradient of the donor concentration ascertains a high potential barrier thus leading to possibly large values of the open circuit voltage. The high concentration of about $5 \times 10^{19} \text{ cm}^{-3}$ electrically active phosphorous donors at the surface avoids rectifying characteristics and a serious potential drop at the semiconductor-metal interface.

However the properties of the holes in the heavily doped emitter are governed by Auger recombination [1]. Purpose of this work was to investigate the influence of the emitter on the diffusion current.

2. Experimental

Three samples of crystalline p -type silicon have been used for our experiments. The first one with a resistivity of about 0.2 Ωcm was prepared by Siemens Munich by an unconventional way in order to reduce production costs. It suffers from a rather large amount of residual impurities and was characterized by means of deep level transient spectroscopy previously [2]. The second sample from Wacker Heliotronic (Burghausen) was polycrystalline in the resistivity range of 1 Ωcm to 5 Ωcm . The average resistivity of the 1 cm \times 1 cm substrates used for solar cell preparation was about 4 Ωcm . The last sample was Czochralsky pulled high purity silicon with a resistivity of about 6 Ωcm . The phosphorous diffusion was done by first coating the front side of our samples with a phosphorous glass. Then the diffusion was carried out in a furnace at 915°C for 30 min corresponding to the conditions of a single step diffusion from an unlimited source. Metallization of the 1 cm \times 1 cm to 2 cm \times 2 cm devices was done by the evaporation of aluminum at the backside and Ti/Pd/Ag grid structures at the front side. At the front surface silicon-monoxide was evaporat-

ed as an antireflection coating. The experimental set up used for the characterization of the solar cells consists of a fibre optic light source, an ammeter and a voltmeter and was computer controlled. The short circuit current, i_{sc} , and the open circuit voltage, V_{oc} , was recorded at different illumination intensities in the temperature range between 80 K and 300 K. The relation between i_{sc} and V_{oc} is given by the internal diode current losses as expressed by Eq. (1).

$$-i_{sc} = i_{diode} = i_0 \cdot \exp(qV_{oc}/nk_B T) - i_0 \quad (1)$$

i_{diode} ... diode loss current

n ... diode ideality factor

T ... temperature

k_B ... Boltzmann's constant.

The diode ideality factor, n , has a value of about 2 for the recombination current within the space charge region and a value of 1 in the case that the diffusion current is the dominant loss mechanism of the device.

Since for V_{oc} the total current is zero there is no voltage drop due to the series resistance of the solar cell which may alter the $i_{sc}(V_{oc})$ -curve at high illumination intensities. In this case the right most term of (1) is negligible compared to the exponential term and has been neglected in our calculations. At room temperature for light intensities above 70 mWcm^{-2} the dependence of i_{sc} on V_{oc} is merely given by the diffusion current.

The contributions of the base of the solar cell and of the phosphorous doped emitter are given by (2)–(4) where j_0 equals i_0 divided by the area of the pn -junction [3]:

$$j_0 = j_{0 \text{ Base}} + j_{0 \text{ Emitter}} \quad (2)$$

$$j_{0 \text{ Emitter}} \simeq q \sqrt{D_p/\tau_p} (n_i^*{}^2/N_D^+) \quad (3)$$

$$j_{0 \text{ Base}} \simeq q(D_n/L_n)(n_i^*/N_A^-) \quad (4)$$

D_p, D_n ... diffusion coefficient of holes and electrons, respectively

τ_p ... lifetime of holes in the emitter

n_i^* ... intrinsic carrier concentration in the emitter

N_D^+ ... concentration of thermally ionized phosphor atoms

L_n ... diffusion length of electrons in the base

n_i ... intrinsic carrier concentration in the base

N_A^- ... concentration of thermally ionized acceptors in the base.

The difference in the intrinsic carrier concentration for the emitter and the base expressed in (3) and (4) takes into account that the high phosphorous concentration is leading to a high density of states near the band edges in the bandgap and causes a shrinkage of the mobility gap [4]. The dependence of the intrinsic carrier concentration in the base of the solar cell is mainly due to the temperature dependence of the bandgap:

$$n_i^2 = N_c \cdot N_v \exp(-\varepsilon_g/k_B T) \quad (5)$$

N_c, N_v ... effective density of states

Table 1. Properties of electrons in p -silicon materials which we have used in the experiments

Sample	# 1	# 2	# 3
ρ [Ωcm]	0.2	4.0	6.0
D_n [cm^2/s]	8.2	30	33
L_n [μm]	30	90	200

ε_g ... bandgap

$$N_c N_v = 3.62 \times 10^{31} \text{ cm}^{-6} \text{ K}^{-3} T^3 \quad (6)$$

Taking into account a shrinkage of the mobility gap in the case of the emitter expressed by $\Delta\varepsilon$ is leading to (7) for the determination of the intrinsic carrier concentration:

$$n_i^*{}^2 = 3.62 \times 10^{31} T^3 \exp(-(\varepsilon_g - \Delta\varepsilon)/k_B T) \quad (7)$$

Assuming that Auger recombination is dominating the minority carrier lifetime in the emitter will result in a value of $1.2 \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficient, D_p and 2 ns for the lifetime, τ_p [5].

The determination of the minority carrier diffusion length in the base of the solar cell, L_n , was derived from the measured short circuit current under monochromatic light conditions [6]. The results for our samples are summarized in Table 1. The determination of the electron lifetime was done on the unprocessed wafers by pulsed light experiments. The knowledge of both electron diffusion length and electron lifetime was used to calculate the electron diffusion coefficient in the base region:

$$D_n = \frac{L_n^2}{\tau_n} \quad (8)$$

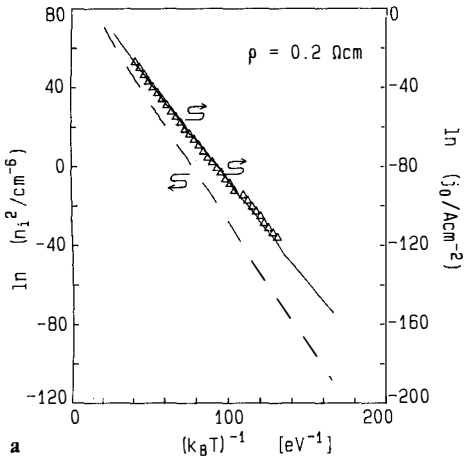
The temperature dependence of the bandgap in the temperature range between 77 K and 400 K was derived from the experimental determination of the absorption coefficient in the wavelength range from 800 nm to 1100 nm [7].

The only parameter for the calculation of the diffusion current which is left unknown is the magnitude of the shrinkage of the mobility gap, $\Delta\varepsilon$, in the highly doped emitter region. This parameter was varied in order to fit the calculated temperature dependence of the diffusion current to the measured data.

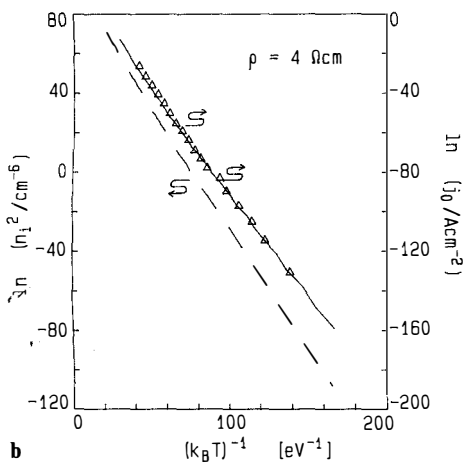
3. Results

In Figs. 1a through 1c the measured temperature dependence of the diffusion current is presented by triangles in an Arrhenius plot. The solid lines represent the calculated temperature dependence for the best agreement between experimental and calculated data achieved by a variation of $\Delta\varepsilon$.

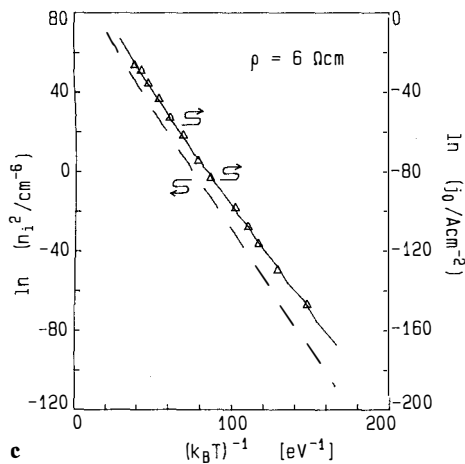
For comparison reasons the temperature dependence of n_i^2 is given by a dashed line which will represent the temperature dependence of the diffusion current in the absence of a shrinkage of the mobility gap. In the case of the solar cell made from 0.2 Ωcm lower purity silicon



a



b



c

Fig. 1. a Arrhenius plot of the diffusion current density for a sample of lower purity silicon. Triangles show experimentally obtained values from short circuit current vs. open circuit voltage measurements. The line represents calculated data for a shrinkage of the mobility gap of 0.18 eV. Dashed line indicates the temperature dependence of n_i^2 . b Same as a but for a sample of polycrystalline silicon. The gap shrinkage used for the calculation is 0.15 eV. c Same as a but for high purity silicon. The gap shrinkage used for the calculation is 0.10 eV

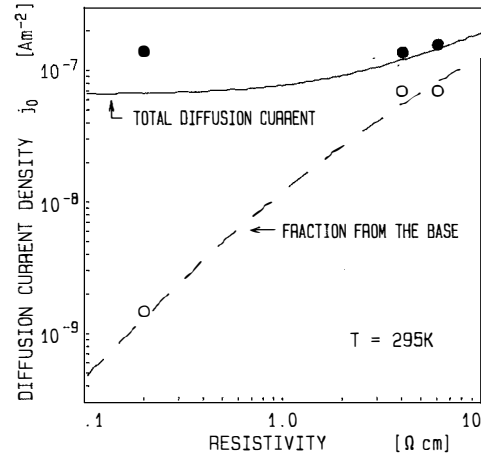


Fig. 2. Measured (circles) and calculated dependence of the diffusion current density on the resistivity of *p*-silicon. Dashed line and open circles represent the contribution from the base of the *pn*-junction. Full line and full circles represent the total current density. The contribution of the emitter is calculated for a mobility gap-narrowing of 0.18 eV

a decrease of the mobility gap of 0.18 eV describes the experimentally determined behavior of the diffusion current. The solar cell made from polycrystalline silicon exhibits a temperature dependence of the diffusion current which will suggest a gap shrinkage of 0.15 eV. The smallest influence on the mobility gap of the highly doped emitter has been observed for the cell made from high purity silicon. The value of 0.10 eV is in good accordance with previously published values [1]. However it is still responsible for an increase of the total diffusion current from the base and the emitter by a factor of three. For a temperature of 295 K the dependence of the part of the diffusion current arising from the base of a solar cell as a function of the resistivity of the starting material is shown in Fig. 2. The line represents a calculated dependence derived from published values for L_n and D_n [4]. The circles show our present results. Assuming a constant narrowing of the mobility band gap of 0.18 eV as well as values for D_p and τ_p valid for Auger recombination is leading to the upper curve in Fig. 2 representing the total diffusion current density.

For low resistivity material – $< 1 \Omega\text{cm}$ – the total diffusion current is nearly exclusively due to the emitter. Above $1 \Omega\text{cm}$ the fraction of the diffusion current coming from the base rapidly increases. However the emitter still contributes a significant fraction to the total diffusion current.

4. Discussion

Although the agreement of the experimentally obtained values of the diffusion current density measured at room temperature on the solar cell of lower purity silicon differs by a factor of two compared to the calculation the temperature dependence between calculated and measured data is equally well for all three samples, thus suggesting that the assumptions of (i) Auger recombina-

tion of holes in the emitter as well as a mobility gap shrinkage of between 0.10 eV and 0.18 eV are justified.

For the calculated curves shown in Figs. 1a through 1c the temperature variation of both D_n and L_n have been neglected since the exponential variation of the intrinsic carrier concentration with temperature is the dominant effect whereas the variation of both the minority carrier diffusion length as well as the diffusion coefficient is merely given by a power law of the temperature [6]. For the solar cell device made from lower purity 0.2 Ωcm silicon a calculation including the temperature dependence of D_n and L_n was made for comparison. It turns out that the differences between both calculations, with and without taking into account the temperature dependence of D_n and L_n are too small to be seen in a plot like that one given in Fig. 1a. Except for the sample of polycrystalline silicon the values of the diffusion current contributed by the base region are in fair agreement with the calculated curve of Fig. 2. In the case of polycrystalline silicon it shall be noted that average values of L_n and D_n have been used which may vary significantly near grain boundaries. For all three samples the measured total diffusion current density at room temperature is well above the calculated ones. A mere explanation of that fact by assuming an error in the determination of the area of the pn -junction plane appears to be unlikely. However the assumption that surface recombination contributes an additional current to the experimentally observed $i_{sc}(V_{oc})$ data pairs can explain the difference between the experimentally observed values and the calculated ones. Rather surprisingly it turns out that under equal conditions of the formation of the highly doped emitter the shrinkage of the mobility gap depends strongly on the properties of the starting material. In the case of the sample prepared from lower purity silicon – 0.2 Ωcm – the large shrinkage of 0.18 eV may be due to the fact that the starting material is partly compensated and contains quite a few impurities. The difference of 0.05 eV between the solar cell made from polycrystalline silicon compared to that one made from high purity silicon can not be explained by the differences of the background concentration which is similar in both cases. It is potentially due to the presence of grain boundaries

which influences (i) the process of phosphorous diffusion during cell manufacturing and (ii) the effective density of states near the edges of the valence and conduction band at grain boundaries, thus obscuring the effect of the undisturbed region within the grains.

6. Conclusions

The attempt to prepare the pn -junction of a crystalline silicon solar cell by means of a low cost, high throughput phosphorous diffusion process was leading to a current loss mechanism of the solar cell due to the diffusion current which is mainly governed by (i) a significant mobility gap shrinkage and (ii) hole recombination due to Auger processes in the highly doped emitter. For our samples the contribution to the total diffusion current coming from the base is small compared to the part of the diffusion current caused by the emitter thus leading us to the conclusion that the lower limit of the diffusion current density is in the range of $5 \times 10^{-8} \text{ Am}^{-2}$ to $1 \times 10^{-7} \text{ Am}^{-2}$ for pn -junctions made by a simple planar phosphorous diffusion technique on p -silicon in the resistivity range between 0.1 Ωcm and 10 Ωcm regardless of the purity of the starting material.

References

1. Fossum, J.B., Shibib, M.A., Lindholm, F.A.: IEEE Trans. Electron Devices **ED-26**, 1294 (1979)
2. Schlosser, V., Wendl, K.: Proceedings of the 8th European Photovoltaic Solar Energy Conference. pp. 1249. Dordrecht: Kluwer Academic Publishers 1988
3. Sze, S.M.: Semiconductor devices. p. 91. New York: John Wiley & Sons 1985
4. Tada, H.Y., Carter, Jr., B.R., Anspangh, B.E., Downing, R.G.: Solar cell radiation handbook. p. B-7. Pasadena: Jet Propulsion Laboratory 1982
5. Landolt-Börnstein: Numerical data and functional relationships in science and technology (New Series). Vol. 22, Subvol. a, p. 272. Berlin, Heidelberg, New York: Springer 1987
6. Schlosser, V.: Proceedings of the 9th European Photovoltaic Solar Energy Conference. p. 394. Dordrecht: Kluwer Academic Publishers 1989
7. Schlosser, V.: Mater. Sci. Forum **38-41**, 1313 (1988)