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Characterization of «solar» multicrystalline silicon by local measurements

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Abstract. The features of local measurements of «solar» multicrystalline silicon (mc-Si) parameters are surveyed using examples of grain sizes, diffusion length of minority non-equilibrium charge carriers L_d and effective reflectivity of light R. It is revealed that the crystal grains in mc-Si have 4 groups of the reference sizes. The errors of the single local measurements of parameters are spotted. It is shown that the values of explored parameters are distributed under the normal law (the Gauss function). The algorithm to obtain the average values of mc-Si parameters with given precision is described. The used experimental procedures for the express non-destructive check of L_d and R in the mc-Si samples are briefly considered.

Keywords: multicrystalline silicon, solar cell, local measurements, errors, statistical distributions.

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1. Introduction

Coarse-grained multicrystalline silicon (mc-Si) is widely used now for manufacturing the solar energy photovoltaic converters – solar cells (SC) and modules. About 40 % of the crystalline silicon-based SC production is carried out using mc-Si grown as ingots by a method of a directional crystallization [1]. Mc-Si cost is lower than that of the monocrystalline silicon, and this fact is the strong stimulating factor for the works in this direction.

At development of the SC design and technologies the set of the characteristics both for initial silicon and material after particular technological operations is necessary to know. Mc-Si, contrary to monocrystalline one, is essentially non-uniform material, therefore its parameters cannot be correctly spotted from the single measurements in local areas of a chip. Such measurements are usually used in the basic procedures of the check specific (ρ) and surface resistance, diffusion length of minority non-equilibrium charge carriers (L_d), reflectivity R of Si and structures with anti-reflecting coatings. The fact of presence of ρ, L_d non-uniform planar distributions in mc-Si and their influence to the SC parameters is confirmed experimentally, in particular, in [2, 3].

It is known that characterization of non-uniform objects by measurements on their local sites, for deriving the parameter average values and determining error values, requires to use a large number of measurements and handling the obtained results by methods of a mathematical statistics.

In this paper parameters of a statistical distribution of grain sizes as well as L_d and R values in the samples of «solar» mc-Si are considered, and the algorithms of realization of local measurements of these parameters for deriving their values characterizing mean magnitudes with the desirable precision for concrete amount of measurements are described. The used experimental procedures are briefly surveyed.

2. Experiment

P-type boron doped mc-Si samples with a mean specific resistance of 1.4 Ohm·cm were investigated. Samples had the shape of wafers cut perpendicularly to the crystallization direction. Sample surfaces were not polished, and for removal of a dislocated layer were etched in a CP-type etchant by a depth of 5–10 μm.

The L_d parameter was measured by a method of spectral dependencies of a surface photo-voltage V_{ph}, for the first time described in [4]. The possible sources of errors marked in [5] were taken into account when calculating L_d from the data of measurements. In particular, the sample thickness should be not less, than 3 times more, than the inverse absorption constant α of a sounding light, and not less, than 2 times more than L_d value; thickness of the surface space charge region in a sample should be much less, than L_d. In the number of cases correct L_d measurements can be carried out at infringement of these requirements (see, for example [5, 6]).

A schematic view of experimental setup for V_{ph} measuring and design of a sample holder are given in Fig. 1. The set up allows to measure L_d value in any site of a sample of a diameter up to 300 mm and thickness up to 25 mm, and also on samples with non-parallel plate sides. Site localization of the V_{ph} measurements was given by the field electrode area (5×25 mm^2), and by the illumination area (that was varied from 4×15 mm^2 to 1×4 mm^2). Measurements were carried out at the arbitrary sites of the sample surface.

The dependence of V_{ph} amplitude on α in the fundamental absorption range for mono- and mc-Si can be described in most of cases by the next simplified formula

$$V_{ph} = V_{phm}\,\alpha L_d\,(1 + \alpha L_d)^{-1} \qquad (1)$$

where $V_{phm} = V_{ph}$ at the near-surface light absorption ($\alpha L_d >> 1$).

When processing the obtained experimental data, the V_{ph} signal should be normalized to the amount of absorbed light quanta for each wavelength. Relevant normalization function can be obtained using non-selective to light wavelength (bolometer, thermoelectric calorimeter) or gauged photo-detector.

To be convinced of a correctness when determining L_d, this parameter was also measured on samples made of monocrystalline Si by a method of kinetic dependencies of photoconductivity relaxation and method of coordinate dependencies of photocurrent at point Schottky contact and scanning light probe along the sample surface. The results obtained by all three methods coincided.

Parameter R was determined at the wavelength of GaAs light-emitting diode radiation (920...935 nm) with application of opto-pair with the unclosed optical channel. Tested area was about 20 mm^2. In the case of mc-Si, having rough surface, R represents an effective parameter including both reflection and light scattering on inhomogeneities of a sample surface. The simplified block-scheme of the setup for the R parameter measuring and construction of the optoelectronic cell are represented in Fig. 2. The R parameter has been measured at arbitrary sites of the sample surface by scanning the 3D-coordinated table with a sample.

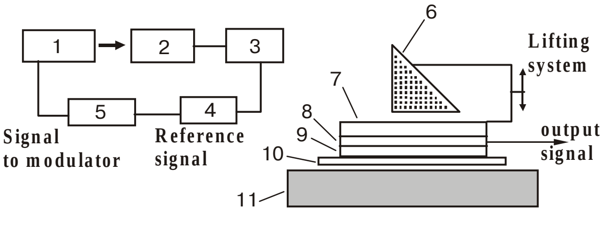

Fig. 1. The simplified scheme of the setup for a surface photovoltage measurements and design of a sample holder. 1 – source of modulated monochromatic light with a tunable wavelength, 2 – sample in a holder, 3 – pre-amplifier with a high input impedance, 4 – lock-in amplifier, 5 – generator, 6 – prism, 7 – glass plate, 8 – ITO layer, 9 – TiO$_2$ layer, 10 – sample, 11 – 3D-coordinated and angle-adjusted table.

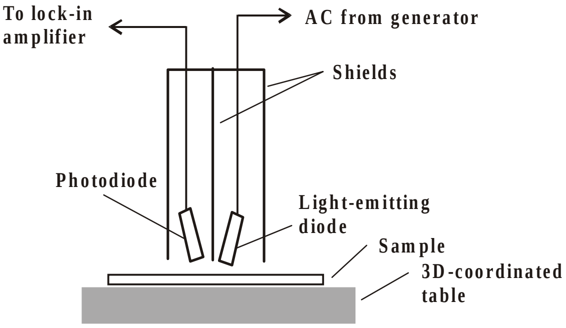

Fig. 2. The scheme of the setup for reflection measurements.

As our experiments have shown, depending on the test geometry (distance of the optoelectronic cell from the sample surface, the angle of its inclination), and on the character of Si surface roughness, the light intensity, registered by the photodiode, may be both some higher and some lower than for the sample with polished surface.

Distribution of grains by sizes on the sample surface was investigated by optical microscopy.

3. Results and discussion

In Fig. 3a, the histogram of typical distribution of grains by the mean size d, constructed by results of 100 measurements on arbitrary sites of a sample surface is given. It is obvious that one can separate 4 groups of grains: small (d_{m1} = 0.15 mm), medium (d_{m2} = 2.9 mm), large (d_{m3} = 8.2 mm), and extra large (d_{m4} = 15 mm). The distributions of the first three groups of grains are approximated by the sum of three Gauss functions Y_i (curve in Fig. 3a):

$$Y_i = [1 / \sigma_i\,(\sqrt{2}\,\pi)]\,\exp\,[-(x - x_{m\,i})^2 / 2\sigma_i^{\,2}] \qquad (2)$$

where i = 1, 2, 3.

It is reasonable to believe that the given distribution does not reflect the fact, that exactly large and extra large grains, though their concentration is small, occupy the main area on a sample surface and, thus, mainly determine its characteristics, see Fig. 3b. On the other hand, the concentration of small grains determines basically the area of inter-grain boundaries, the part from which can have recombination and electrical activity and, thus, influence on solar cell parameters [2].

The histogram of distribution of the L_d parameter values for a mc-Si sample obtained by 100 measurements on arbitrary sites of a surface (points) is given in Fig. 4a.

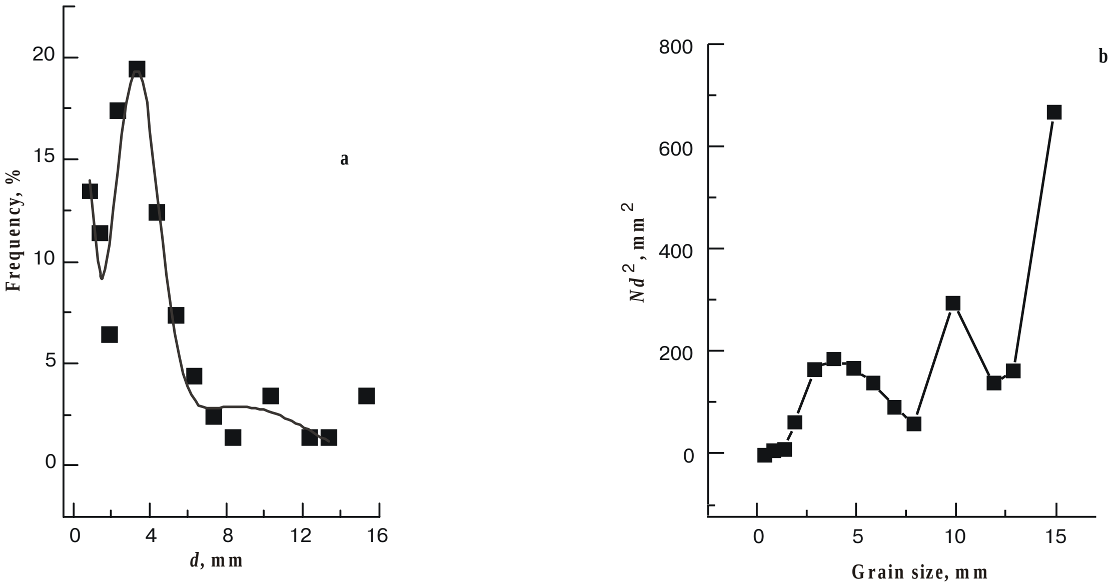

Fig. 3. The histogram of a distribution of grains in a mc-Si sample by sizes. Points – experiment, curve – approximation by the sum of three Gauss functions (a), and dependence of an area, occupied on the mc-Si wafer (see Fig. 3a) by grains of different sizes (approximation by square grains) on grain size (b).

For comparison in Fig. 4b the similar histogram for a monocrystalline silicon sample obtained at the same conditions is shown. These measurements were carried out for the illuminated area of 1×15 mm^2.

The data of Fig.4b can characterize precision of the used experimental setup. Really, the obtained distribution is approximated by the Gauss function (full curve in Fig. 4b). For the Fig. 4b, data the width parameter of a

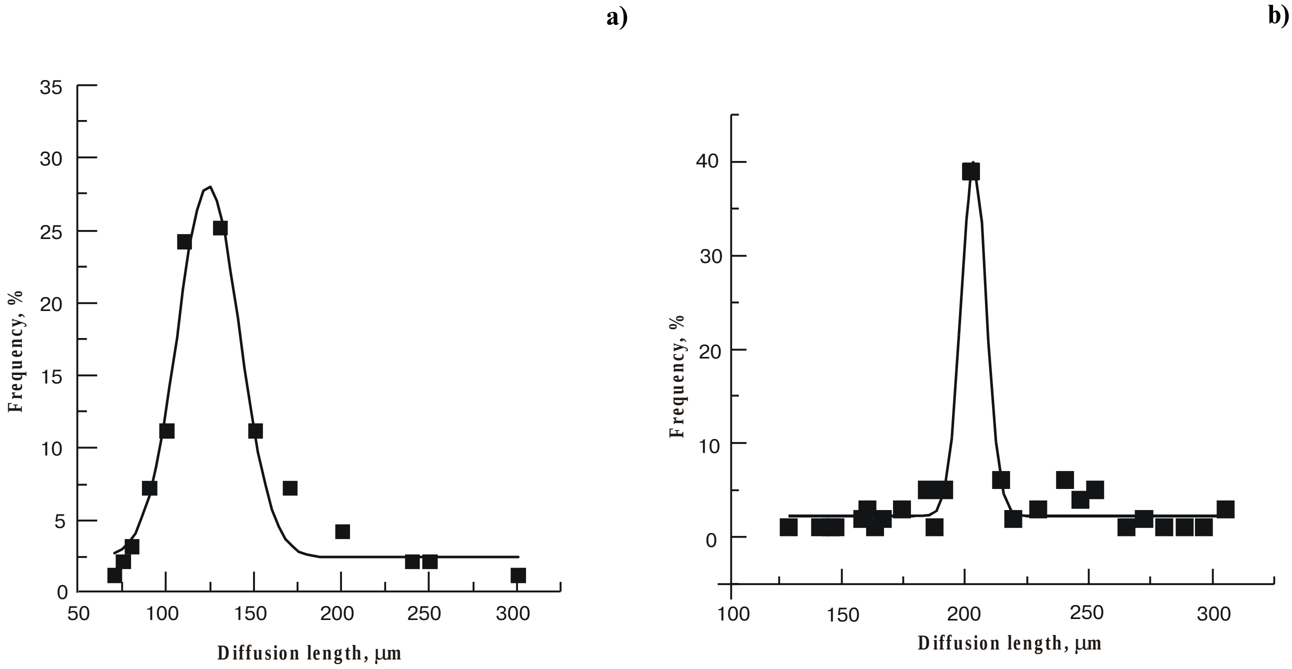

Fig. 4. Histograms of L_d value distributions for mc-Si (a) and monocrystalline Si (b) samples. Points – experiment, curves – approximation by the Gauss functions.

normal distribution is $2\sigma = 10.271$ µm at the mean L_d value of 200.93 µm. From this, according to [7], the standard deviation ($\sigma = 5.13$ µm), arithmetical mean error ($r = 0.8\sigma = 4.11$ µm) and relative error (2.04 %) can be determined. It is necessary to underline that data of Fig. 4b are obtained on a sample of monocrystalline silicon not subjected to any thermal and other treatments, which, according to [8], can increment planar inhomogeneity of L_d and other parameters.

For the Fig.4a, data the width parameter is 35.71 µm at mean $L_d = 123.40$ µm. Accordingly, the standard deviation is equal to 17.85 µm, arithmetical mean error – 14.28 µm, and the relative error – 11.6 %.

Thus, the histogram shown in Fig. 4a contains the information on a statistical distribution of L_d values for a concrete mc-Si sample. However, for its deriving, the considerable amount of measurements (by our data - not less than 80...90) is necessary, which essentially reduces productivity of operation, especially at lack of computer system for measurements and data processing. For diminution of amount of measurements, an ideal variant would be diminution of their locality (output of a signal from the all sample at irradiating of all its surface), as it is made at measurements of the parameters of final SCs. However, for the majority of experimental techniques this approach, owing to the different reasons, is inapplicable. Further, we have carried out the examinations of the L_d distribution as at larger (4×15 mm^2), and smaller (1×4 mm^2) areas of an illuminated surface, at the invariable area of a field electrode. It has found that the L_d distribution practically does not vary. The main reason of this, in our opinion, is influence of a surface space charge region on a planar spreading of non-equilibrium charge carriers. Influence of light scattering on a rough surface of a sample and multiple reflection echoes in a «sample – field electrode» system is also possible.

It is known [9] that if the distribution of values of a physical parameter is featured by the Gauss function, the probability that, at the single measuring, the result obtained will differ from its mean value no more, than by the standard deviation, makes about 0.68. With the probability of 0.32 results (for concrete data of Fig. 4b) can lay in the range from 70 up to 300 µm, i.e. does not content almost any useful information. Even more errors arise if it is necessary to check L_d changes in the samples after different technological treatments (gettering, annealings etc.), as if the required value is equal to a difference of two quantities, its dispersion σ^2 is equal to the sum of dispersions for each of these quantities [7]. For the Fig. 4a data, for example, the mean standard deviation of single measurements of a difference of L_d values reaches ±25 µm. It is clear that all L_d changes smaller than this error at the single measurements can not be correctly captured at all.

The indicated difficulties can be overcome using magnification of the amount of measurements. If the parameter distribution is featured by the Gauss function, as it takes place in all investigated mc-Si samples, according to [9] the mean error of N measurements Δx_{Nm} diminishes under the law

$$\Delta x_{Nm} = \Delta x_m / \sqrt{N} \qquad (3)$$

where Δx_m is the error of the single measurement.

Thus, making up the desirable quantity of a mean error for L_d (or for the difference of L_d values for an initial sample and the sample after any technological treatment) and beforehand knowing the parameters of a typical statistical L_d distribution for the samples of the given batch, it is easy to determine the necessary amount of measurements. By our data, for determination of L_d with the precision of 15...20 %, it is enough to perform from 5 to 10 measurements. For a sample with the mean L_d value of 123 µm (approximation by the Gauss function in the result of 100 measurements) the results of averaging for the different amount of measurements are given in Table 1.

One have to bear in mind that the errors calculated from the results of few series of the identical local measurements of non-uniform sample are not the same, but, like measured parameter itself, have some statistical distribution of values.

It is interesting that the mean L_d values, given in Table 1, are always some higher, than the L_{dm} value obtained as a maximum of the Gauss fit (Fig. 4a). The ΔL_d values also are some higher that that calculated using formula (3). These discrepancies are connected with the contribution of the extra large mc-Si grains to the statistical distribution of L_d values [2]. This effect shows itself by spreading the distribution to higher L_d values, Fig. 4a.

In Fig. 5 the histogram of a statistical distribution of the parameter R values for a mc-Si sample is given. Also shown are the R values (for the some concrete geometry of the experiment) for a reflection from surfaces of monocrystalline Si wafer. As the reflectivity of Si does not depend on a surface crystallographic orientation, any R difference from its value for a single-crystal polished surface is connected with additional light scattering on surface roughness. It is confirmed by the comparison of the R values for polished and ground surfaces of a monocrystalline sample (Si wafer with the standard treatment of surfaces used in microelectronics production), see Fig. 5.

Contrary to a single crystal, the R parameter for mc-Si has straggling values at measurements in different sites

Table 1. The mean L_d and ΔL_d values in their dependence on number of local measurements of the mc-Si sample.

Number of measurements	L_d, µm	ΔL_d, µm
5	142	19
10	138	15
25	126	3
50	129	6
75	128	5
100	127	4

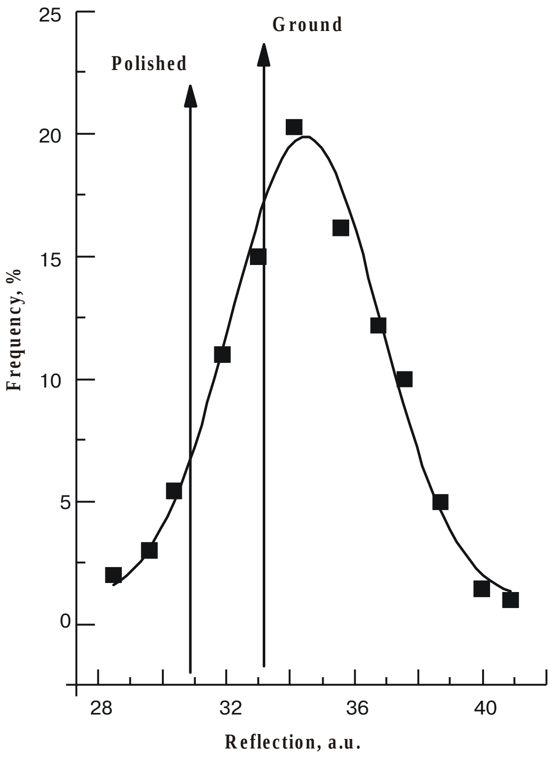

Fig. 5. The histogram of the *R* parameter distribution for mc-Si sample and *R* values for monocrystalline Si with polished (front side) and ground (rear side) surfaces (arrows). Points - experiment, curve - approximation by the Gauss function.

of a surface, and their distribution is featured by the Gauss function (full curve in Fig. 5). This effect is caused by different light scattering from crystal grains of different orientation, owing to selectivity of a chemical etching for the different planes.

The knowledge of *R* parameter and its statistical distribution is important at development of texturization and antireflection technology optimization for mc-Si in the SC production route. The described method of *R* measurements is attractive by virtue of its simplicity and expressness.

Conclusions

1. It is experimentally shown that at carrying out of single local measurements of a «solar» multicrystalline silicon parameters it is impossible to receive the correct values of these parameters due to distinction of their values in different (even close located) sites of the sample.

2. The statistical distributions of grain sizes on a mc-Si surface are explored. It is shown that it is possible to distinguish 4 groups of the crystal grain sizes; distribution of the sizes in three groups (excluding extra large grains) is described by the Gauss functions.

3. The statistical distributions of the values of a diffusion length of minority non-equilibrium charge carriers and effective reflectivity of light from a mc-Si surface are explored. It is shown that these distributions are approximated by the Gauss functions.

4. The algorithm of mc-Si parameter determinations by the local measurements is described that permits to determine amount of measurements, necessary for deriving a parameter value distinguished from the mean one by the specified value of mean error. This procedure consists in measuring a statistical distribution of required parameter for 1–2 test samples of the batch, from which we gain a distribution dispersion and the values of the single measuring errors. The reaching of desirable precision is carried out by magnification of amount of measurements, according to the formula (3).

5. The described techniques of measurement and handling of the results obtained differ by a simplicity and expressness, and allow to optimize the processes of the mc-Si characterization, that is important for the development and manufacturing the mc-Si based solar cells.

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