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Solar cells based on multicrystalline silicon

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Abstract. This review comprises modern publications devoted to problems of development and manufacturing photovoltaic solar energy converters (solar cells) based on block multicrystalline silicon (poly-Si). Methods of growing polysilicon ingots, mechanical and chemical treatment, characteristics of polysilicon depending on grain sizes and impurity-defect composition are considered. Methods of improving polycrystalline Si parameters (gettering, treatments in different ambients, passivating treatments) are analyzed. Basic design features of the poly-Si based solar cells and technological modes of their manufacturing are surveyed. It is shown that the efficiency value of such solar cells practically reaches that of similar devices manufactured using single-crystalline Si grown by the Czochralski method. Some problems of measurements of minority non-equilibrium charge carriers lifetime in polycrystalline material are discussed.

Keywords: multicrystalline silicon, solar cell, *p-n* junction, gettering.

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1. Introduction

Crystalline silicon (both single and polycrystalline) is now base material for production of photovoltaic converters of a solar energy (about 50 % of producers and about 90 % of market), [1, 2, 3]. The basic reasons for it are well-known: crystalline Si is the well investigated material; technological processes, well developed for purposes of the Si-based microelectronics, are also usable for production of solar cells (SC); Si is single-component material, a composition and structure of which are easily checked; it can be purified up to a high degree; Si is widely spread in nature, is non-toxic; the efficiency (η) of the silicon photo-converters under the AM 1.5 conditions theoretically can exceed 25 % at the room temperature, as is confirmed experimentally [4, 5].

The basic advantage of polycrystalline silicon (poly-Si) in comparison with the single-crystalline one is its smaller cost. The given factor is rather important, as the cost of such material makes about 40 % of the total cost of SC [6, 7, 8].

Poly-Si can be prepared as thin films, strips, pipes and block material (ingots). For the wide area production only the latter is mainly used now (about 40 % of the crystalline Si-based SC production [7]).

Last years it becomes possible to implement the poly-Si based SCs with $\eta = 19,8\%$ under the AM 1.5 condi-

tions [9] at the device area of 1 cm^2 . Photoconversion units based on such devices have efficiency more than 15 % at the area $\geq 1000\text{ cm}^2$ [10]. In accordance with perfected technologies of the poly-Si ingot growth and their post-treatment, the odds between single- and poly-Si based SCs is steadily reduced.

2. Basic criteria of the poly-Si validity for SC manufacturing. Methods of preparation and characterization of poly-Si ingots and wafers

2.1. Impurity composition

Silicon, suitable for manufacturing SCs of wide application (the so-called «terrestrial solargrade», TSG, or «solar») should have total concentration of background electrically active impurities no more than 10^{-3} at. % [11]. In Fig. 1 drawn by using data of [11], threshold impurity concentrations leading to degradation of *p*-type Si based SCs are given.

2.2. Grain size

The inter-grain boundaries existing in a polycrystal can essentially influence the parameters of SCs. Mechanisms of this influence are various, depending on localization

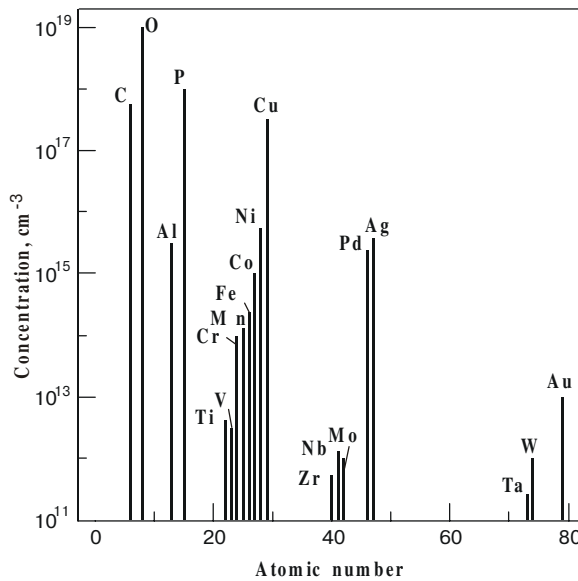


Fig. 1. Threshold impurity concentrations in the p-type Si causing a degradation of the SCs.

and direction of a surface of boundary relatively to the working p-n junction: perpendicularly, in a plane of p-n junction, in a plane of the base. On the whole, the presence of boundaries is a negative factor — they can be traps for non-equilibrium charge carriers, effective recombination centers (with a recombination velocity up to $\sim 3 \cdot 10^4$ cm/s, [12]), sinks for background and doping impurities, which can then diffuse into volume of grains both during technological processes, and at SC operation.

In [12] the theoretical and experimental dependencies for a number of parameters of poly-Si and SCs on its basis as functions of medium grain size, d , are given, as the latter does define the area of inter-crystal boundaries. In Figs 2a, b replotted after [12], the d -dependencies of minority carrier mobility (electrons) and their effective lifetime are given. In Figs 2e-f, [12], the d -dependencies of such parameters, as a diffusion length of minority non-equilibrium charge carriers L_d , short-circuit current, open-circuit voltage and fill factor of a voltage-current characteristic of the SC are given. From these data follows, that the minimum grain size, at which the characteristics of poly-Si and SCs on its basis not so strongly differ from those for a single-crystal material, is $d \approx 1$ mm. Thus, the L_d parameter is still rather small ($\sim 10 \mu\text{m}$) for deriving satisfactory efficiency of photoconversion. In Fig. 3 from [13] the dependencies of η on L_d are given. It is evidently that minimum L_d value at which the high effectiveness can be obtained is about $100 \mu\text{m}$. It, in turn, requires $d > 5$ mm.

2.3. Processes of the «solar» poly-Si ingot growth and characteristics of the material

These processes are based on directional crystallization of Si melt. The metallurgical silicon in melt is purified by

silicate slags and blow-down by active gases and further crystallizes in a crucible from material of high purity. Depending on degree of initial Si purity, process of directional crystallization may be carried out several times, before deriving a satisfactory impurity composition.

A velocity of melt crystallization ranges 0.1-0.5 mm/min (for ingots with the cross-section $50 \times 50 \text{ cm}^2$), a mass of an ingot — up to 250 kg [13, 14]. Several variants of crystallization methods differ by the mode of heat removal from a melt [2].

The Bridgeman – Stockbarger method: a container with a melt moves in a zone with a given temperature profile, so the melt crystallizes from bottom to surface. Crystallization starts from the areas of the melt, adjacent to walls of the container. It protects volume of a polycrystal from further contamination.

Process of gradient cooling: the drop of temperature is set by the program at fixed container. The heat removal is carried out through bottom and upper part of the container. This method allows to receive a homogeneous temperature lateral profile in the section of an ingot. The ingot has column structure along the whole height, with the grain size up to several centimeters.

It is necessary to keep precautions for inhibition of Si adhesion to walls of the container and prevention of a melt contamination, for this the selection of a material of walls is necessary. Graphite, quartz, Si_3N_4 , SiC, $(\text{SiO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ and their combinations are used. For prevention of ingot adherence to container walls the latter are coated with Si_3N_4 , SiO_2 or graphite powder.

The heat removal from the bottom of the container can be forced (for instance cooling by a stream of helium). It is important to provide flat front of a melt crystallization, for what the method of gradient cooling is optimum, though it requires complicated systems for heating and annealing. Computer modeling of crystallization processes allows to calculate optimum modes and to minimize mechanical stresses in crystal. The latter gives, in particular, an increased brittleness of material and major losses at ingot cutting. The process of a crystallization and cooling an ingot takes 20 – 30 hours.

In recent years multicontainer methods of ingot growth were advanced [2, 7]. These are based on partitioning of Si fusion and crystallization processes. It allows to essentially increase the productivity of the process (up to two ingots per day on one installation).

Continuous growth of ingots using high-frequency heating [7] allows to refuse usage of expensive crucibles, to increase the size of ingots and to reduce their contamination.

2.4. Defects in poly-Si

To the defects in poly-Si concern: the grains boundaries, dislocation (the latter will be derivated when cooling) with the density of $10^5 - 10^6 \text{ cm}^{-2}$, precipitates (SiO_2 , SiC, Si_3N_4) with the sizes of 1 to 100 micrometers, microdefects (located inside the grains). Small precipitates should be mentioned (their concentration ranges from 10^{11} to

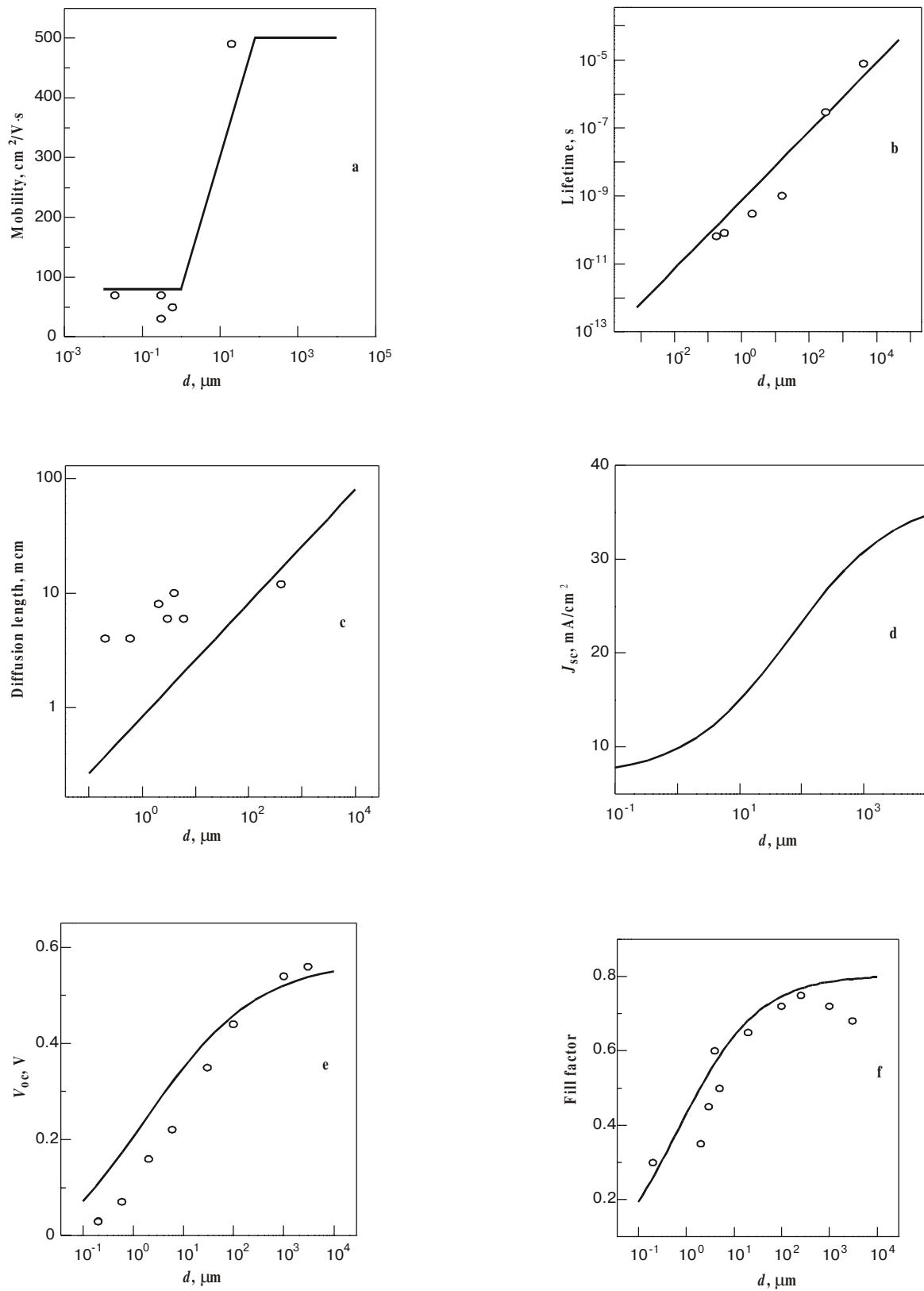


Fig. 2. Dependencies of parameters of poly-Si and poly-Si based SCs on the grain size: a – mobility of electrons and holes, b – lifetime of non-equilibrium carriers, c – diffusion length of carriers, d – short-circuit current of the SC, e – open-circuit voltage of the SC, f – fill factor of SC current-voltage characteristics. Lines correspond to calculations and dots to experimental data.

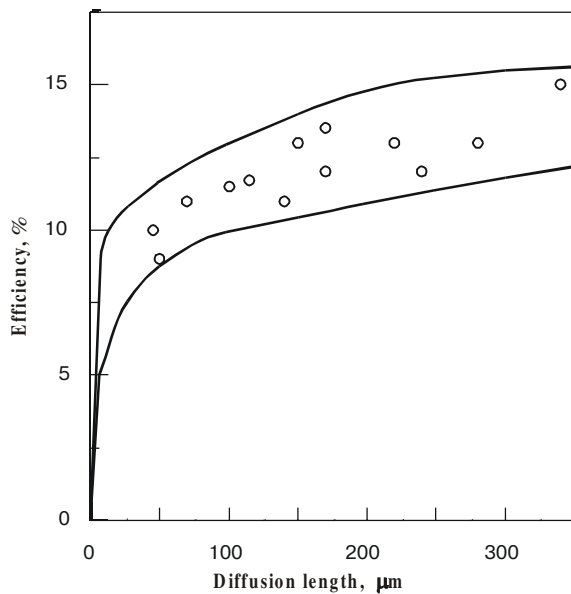


Fig. 3. Dependence of SC efficiency on diffusion length of non-equilibrium carriers. Lines – calculations in different models, dots – experimental data.

10^{13} cm^{-3} at an average distance between them of 0.5 to $2 \mu\text{m}$).

It is necessary to mark that selection of the etchants for investigation of the defects in poly-Si requires to account arbitrary orientation of polycrystals, as the etching velocity for the different planes is different. Therefore it is necessary to select such etchant, that etches different crystal planes whenever possible with close velocities.

2.5. Impurities

Now, as a rule, wastes of silicon, appearing at the single-crystal Si growth are used as a feed stock for the «solar» poly-Si production. Therefore, gained material is pure enough. The basic impurities in poly-Si are oxygen, carbon, nitrogen and impurities of metals. The impurities have characteristic distributions along the ingot height, which is connected with their segregation coefficients. So, oxygen has maximal concentration at the bottom of an ingot, carbon, nitrogen and transition metals – in the upper part. Typical oxygen concentration – from $5 \cdot 10^{16} \text{ cm}^{-3}$ up to $1.3 \cdot 10^{18} \text{ cm}^{-3}$, nitrogen – from $2 \cdot 10^{14} \text{ cm}^{-3}$ up to $9 \cdot 10^{15} \text{ cm}^{-3}$, carbon – from $5 \cdot 10^{16} \text{ cm}^{-3}$ up to $4 \cdot 10^{17} \text{ cm}^{-3}$. In a set of cases the concentration of carbon in an ingot exceeds a limit of its solubility. So considerable concentrations of the indicated impurities essentially rise the probability of their precipitation at subsequent heat treatments. However, because of rather low diffusion constants of oxygen and nitrogen in Si, the precipitation velocity is rather low even at high temperatures. At oxygen and nitrogen concentrations $\sim 10^{17} \text{ cm}^{-3}$ typical sizes of their precipitates, according to calculations of [13], range about 1 nm. As this value is close to a critical radius of precipi-

tates, the probability of their formation at such impurity concentrations appears inappreciable. At the O and C impurity concentration increase up to 10^{18} cm^{-3} radius of precipitates reaches $\sim 10 \text{ nm}$.

The main metal impurities in poly-Si are Fe, Ni, Cu, Cr. These impurities occupy interstitial positions in crystal, that explains their high diffusion constants. Besides the Me_nSi_m (Me – metal) precipitates and Me-B pairs (in *p*-type material that is usually used for SC manufacturing) are formed.

The transition metals also interact with the grain boundaries, dislocations and precipitates. They can be dissolved on extended defects, or precipitate on them, depending on concentration and temperature. The given problem requires additional investigations.

About half of ingot material (several centimeters bordering with walls of a crucible) are unsuitable for the SC manufacturing because of considerable contamination. It stimulates researches for development and improvement thin-film SCs (see for example, [15]) and, on the other hand, requires further perfecting the poly-Si ingot growth and purification methods.

2.6. Electrical properties of poly-Si

The presence of defects and impurities in poly-Si leads to formation of energy levels in a forbidden zone, which essentially influences on electrical (including recombination) parameters of a material. The extended defects can trap charge carriers, that causes formation of local electric fields and potential barriers interfering current flow. The capture of majority carriers diminishes conductance of poly-Si. The scattering of carriers on defects diminishes mobility and, accordingly, conductance of a material. However, because of poly-Si wafers are cut perpendicularly to bar crystallites, the main current generated by the SC, proceeds collaterally to grain boundaries, therefore their influence on SC parameters, ultimately, is not so significant. It is confirmed, in particular, by proximity of parameters of SCs, manufactured using single- and polycrystalline Si.

The recombination activity of dislocations becomes dominant at their density exceeding $10^5 - 10^6 \text{ cm}^{-2}$.

Metal impurities, by decorating dislocations and grain boundaries, rise the recombination activity of them. In Fig. 4 from [13] the L_d dependencies on the of metal impurity content in poly-Si are given.

Oxygen in poly-Si, forming precipitates, creates a series of electrically active defects, similarly to the case of Si, grown by the Czochralski method (Cz-Si). The L_d dependence on carbon concentration is also observed, and the L_d dependence on the difference between oxygen C_O and carbon C_C concentrations has a maximum at small C_C excess above C_O [13].

Poly-Si heat treatments at $800 - 950^\circ\text{C}$, necessary for *p-n* junction preparation, can essentially influence electrical parameters of material. Thus, initial thermo-donor centers can have concentration comparable to that of a doping impurity. In Fig. 5 replotted after [13] the de-

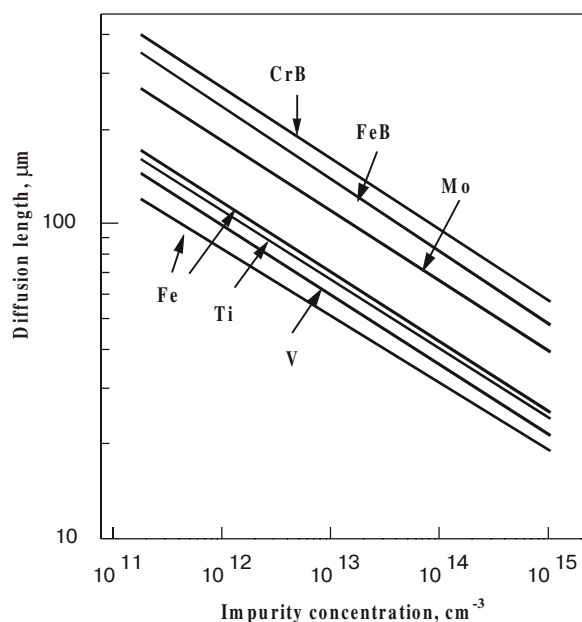


Fig. 4. L_d dependencies on impurity level of metals and their complexes with boron (data on Fe_i – by different authors).

dependencies of interstitial oxygen concentration O_i in poly-Si, conductance of material, and also resistance and concentration of majority charge carriers on annealing temperature are given. One can see that the change of values of the two last parameters legibly correlates with O_i change caused by growth/decay of SiO_2 precipitates of different structure, shape and sizes (in a temperature dependence). In comparison with Cz-Si, oxygen precipitation velocity in poly-Si is increased. The possible reason of this may be carbon concentration increased in poly-Si, that stimulates precipitation of O_i . In [16] the results of experimental study of oxygen precipitation processes, and also numerical modeling of this process for the case of poly-Si are given. It is shown, that precipitation is affected by the carbon content, dislocation and grain boundaries densities, temperature schedule of ingot growth, and also emission and annihilation of interstitial silicon at heat treatments.

2.7. Gettering of impurities in poly-Si

The heightened impurity level in poly-Si makes actual development of gettering methods, which would delete impurities from the active working area of the SC and would bind them in the getter region. In [17] the most spread methods of a gettering, designed earlier for Cz-Si, and their applicability for poly-Si are surveyed.

The feature of gettering methods usable in the technology of SCs, is the necessity to purify all the thickness of a Si wafer. Taking into account presence in poly-Si of considerable structural infringements, it is necessary to expect that gettering methods based on creation of defect areas in local sites of the wafer, on which at the subse-

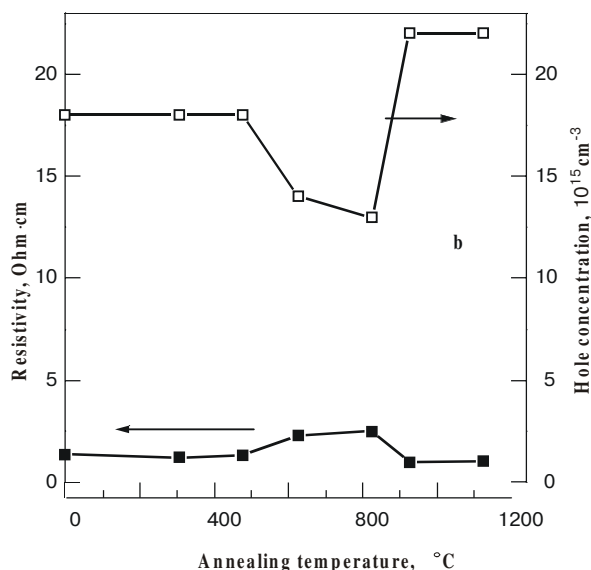
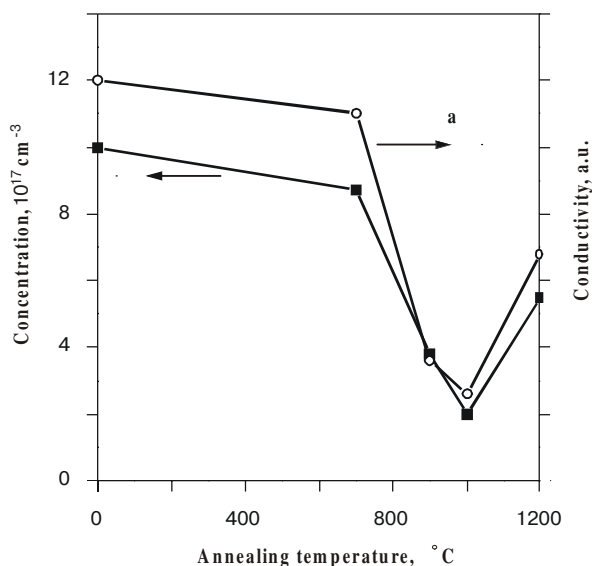


Fig. 5. Dependencies of interstitial oxygen concentration and material conductance (a), resistance and hole concentration (b) on temperature of poly-Si annealing for a material with high oxygen content a – initial concentration of oxygen of 20 ppm, b – > 10 ppm.

quent heat treatments a sink and localization of impurities will be occurred, will be less effective for poly-Si. It is particularly confirmed by the data of [18]. Therefore preferable are the gettering methods based on usage of a different solubility of impurities in an active area of a wafer and in specially formed getter region (segregation methods). From these methods the most spread are gettering by phosphorous from the working side of a wafer, aluminum from the rear side, and also their combinations. The criterion of getter efficiency is the magnification of L_d parameter and/or maintenance of its value after heat treatments.

Examinations [17, 19] have shown that the indicated methods have small effectiveness in a case of poly-Si, being applied separately, though operate well for single-crystalline Si at the same gettering modes. The comparison of results for dislocation (dislocation density $\sim 10^8 \text{ cm}^{-2}$) and dislocation-free poly-Si allows to draw a conclusion that the basic contribution to recombination activity is imported by inter-grain boundaries decorated by metal impurities. The combined gettering by phosphorous and aluminum in a combination with a thermal oxidizing has allowed to receive the best results (L_d up to 290 μm). Optimum gettering temperature is 1000°C [19].

Impurity gettering in solids is the multi-stage process: liberation of impurities from structural defects, their diffusion to a getter region and, at last, trapping of an impurity by the getter. Each of these stages requires optimum temperature. At lower temperature the processes of a diffusion are retarded, and at heightened - the process of impurity trapping by the getter is hampered. The feature of poly-Si is that the first stage of the process - liberation of impurities from structural defects (grain boundaries) - is the most determining one. To overcome this difficulty, a perspective way is a short-time high-temperature treatment before gettering process, which can delocalize impurity atoms. The given problem requires additional study and development of new gettering methods, specially for poly-Si.

An example of such approach are the papers [20, 21], where, in addition to discussed above getters, annealing in hydrogen-containing (10 % H_2) forming-gas is used. Thus, key is the presence of Al getter, as at the response of forming-gas reaction with Al, atomic hydrogen, effectively penetrating into volume of a wafer and passivating structural defects, is *needed*. Such treatment, according to [20], in a combination with passivating oxide application, has allowed to increase the L_d parameter from 134 μm to 187 μm , and the efficiency of test SC has increased from 7.8 % (without getter treatment) up to 14.1 %. It is shown in [21] that the further increase of gettering efficiency can be achieved using additional preliminary gettering by phosphorous (diffusion from POCl_3 at 850°C, 1 hour) and subsequent etching of a wafer by the depth of $\sim 20 \mu\text{m}$. Combination of above treatments allows to increase SC efficiency from 11.5 % up to 17.5 %. It is necessary to note that the process of gettering by phosphorous and aluminum is attractive, because, in the case of p-Si, it simultaneously allows to create working p - n junction and rear p - p^+ barrier. Therefore searching the ways to optimize this method is in progress.

Treatments in hydrogen-containing ambients, including plasma, is the conventional method of improving the recombination parameters of poly-Si. In [6] the variant of such method integrated to the standard line for SC production is offered. Such methods are especially effective for poly-Si wafers cut from peripheral areas of an ingot where the impurity and defect concentrations are increased.

Hydrogen can be injected into poly-Si during deposition of antireflecting coating $\text{SiN}_x\text{:H}$ by plasma-en-

hanced CVD method [22]. A shortcoming of such approach is high cost of necessary equipment and restrictions on the type of antireflecting coatings, and advantage - good passivating properties of SiN_x .

Direct treatment of the poly-Si wafers in hydrogen plasma as well as implantation of H^+ ions are not optimum, as damage a surface of a structure with already formed p - n junction. Therefore, spatial separation of atomic hydrogen generation and wafer arrangement places is more preferable. Thus, it is also necessary to prevent hit of hydrogen plasma ultraviolet radiation on a wafer. After treatment in hydrogen (350°C; 0.5 hours, pressure ~ 1 Torr) a necessary antireflecting coating and contacts are deposited. The process of treatment by hydrogen can be combined with the operation of the structure annealing.

A non-conventional method of improving the L_d parameter in poly-Si is the ultrasonic treatment (UST) [23]. It is known that the UST influences properties of point and extended defects in the wafers (generation of Frenkel pairs, dissociation of point defect complexes, change of constants of point defect interaction with dislocations and grain boundaries). UST can lower energy barriers for diffusion of point defects (in particular, atoms of metal impurities conceits to the latter ones) and their trapping on sinks. UST during treatment of a material in hydrogen plasma can essentially increase efficiency of hydrogen action.

Availability of UST, as is shown in [23], consists in an opportunity to increase the L_d parameter for the wafers with its low values ($< 50 \mu\text{m}$), that is not always possible at the application of traditional gettering methods. The authors managed to increase L_d values in such samples by 20 - 40 %. The probable mechanism of this effect consists in US-stimulated decay of Fe-B pairs with the subsequent trapping of Fe atoms to sinks. The negative feature is the presence of a relaxation of UST effect.

Good gettering properties show the films of porous Si, grown on a surface of poly-Si at treatment in HNO_3 : HF solution [3, 24, 25]. The porous Si film can simultaneously serve as antireflecting coating (reflectivity of 5 - 6 % in the spectral range of 300 to 1000 nm, [25]) and to passivate the SC surface [24].

To the perspective ones, but insufficiently investigated methods of poly-Si gettering it is possible to refer usage of the complex procedure of getter layer (Al, Ge) deposition on the rear side of a wafer with subsequent ion implantation (Ar^+ , H^+) on the «getter-semiconductor» boundary. As it is shown in [26], such approach is rather effective for Cz-Si with small L_d values ($\sim 20 \mu\text{m}$). At the same time, it is necessary to take into account, that the application of ion implantation in the technology of manufacturing of the SCs of wide application is justified only in the case of wide-scale production [27] and high getter effectiveness. The interesting results may be expected for a complex gettering process (external getter + ion implantation or treatment in atomic hydrogen) at simultaneous US action.

2.8. Features of poly-Si ingot cutting

The process of ingot cutting to columns with a cross-section of $100 \times 100 \text{ mm}^2$ and, further, these columns to wafers are important stages in SC manufacturing. As it was scored in [28], the poor attention has been given to this process. At the same time, it substantially determines quality of gained wafers. For ingot cutting, according to [28], the tape saws are the most perspective, as they allow to handle ingots of the large sizes. The exact choice of the carrier (infinite chain) parameters is important: width, thickness, distance between saws and their shape; its material (usually the low carbon containing steel is used), and also the concentration and aggregate size of an abrading (synthetic diamond with a mean grid size is recommended). The installation for cutting should ensure absence of vibrations of the cutting instrument and its parallel/plate moving. Cutting velocity reaches $120 \text{ cm}^2/\text{min}$.

For cutting the poly-Si columns to wafers some methods are used: traditional cutting by diamond disks (the expensive method), wire cutting (using abrasive SiC suspension or with a diamond coating of wires), multi-blade cutting with abrasive suspension feeding. The optimum selection of feed rate of the cutting instrument and force applied to it is important. The last two methods, at the optimum regimes, do not introduce considerable surface damages of poly-Si wafers.

3. Design and technology of solar cells based on poly-Si

The solar cell represents $p-n$ junction of the large area. For the poly-Si based SCs all the stores of the developments that have been carried out for the single-crystal silicon – based SCs (see, for example, [4, 5, 29]) are used. The record photoconversion efficiency values are obtained using more complicated design and technologies, and more simple design and technologies give lower η . In Fig. 6 from [30] the data on η growth for the large area SCs by the years are presented.

The manufacturing process for the SCs of wide application includes the following basic operations. On one side (working) of the Si wafer emitter (n^+ layer) is formed by phosphorous diffusion (for usually used p -Si substrates). The wafer is preliminarily exposed to chemical etching (NaOH or CP-4) for defect layer removal. Also surface texturization (by etching, or mechanical treatment + etching) can be done. On the rear surface the $p-p^+$ barrier can be formed by aluminum deposition and subsequent annealing. Antireflecting layer is created on the work side, a contact grid is superimposed by the screenprinting method and contact firing is carried out. At the use of the photolithography technique the contact grid is shaped before antireflecting coating deposition. On intermediate stages of the route treatment in hydrogen-containing ambients can be made. Some operations can change places or be combined.

We shall consider the basic approaches and regimes of technological processes for the SC manufacturing.

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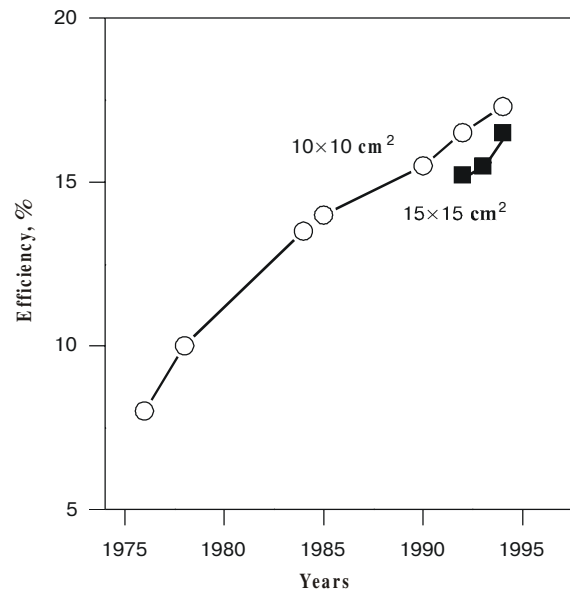


Fig. 6. The dynamics of efficiency growth for the large-area SCs.

3.1. Optimization of the optical characteristics

For optimization it is necessary to reduce light reflection from the front surface, to modify light pass in the bulk and to provide the light reflection from a rear surface.

For solution of the first problem an anisotropic etching in alkaline solutions is commonly used, but in a case of poly-Si this method does not yield a regular texturing. The surface texture can be created also by laser treatment (ensures reflection losses no more than 5% in the wavelength range of 500 to 900 nm, or the method of mechanical treatment of a surface by the relevant abrasive instrument, [22, 30]. After laser or mechanical texturing the etching of a surface to remove the surface defect and contaminated layer have to be used. The qualitative surface texture can be created using an etching through a mask (SiO_2 or Si_3N_4). Such process requires usage of photolithography, though it is possible to superimpose a mask by screenprinting. The lowering of reflection can be reached also by creation on a surface the layer of porous silicon by dipping the $p-n^+$ structure by some seconds in water solution of the mixture $\text{HF} + \text{HNO}_3$ [24, 25].

As antireflecting coatings of the SCs the ZnS/MgF_2 , Ta_2O_5 , Si_3N_4 , SiN , TiO_x , $\text{TiO}_2/\text{SnO}_2$, ZnO , ZnS and other compositions are used.

The interesting perspectives are disclosed by the application of diamond-like carbon films a-C:H [31]. The optical parameters of such films can be modified both during their synthesis and subsequent active treatments, for example, ion implantation.

Antireflecting coatings usually are deposited using the different modifications of the CVD method.

3.2. Contacts

The technology of a contact grid patterning on the SCs front side should be compatible with such parameters of the structure as concentration of charge carriers in emitter and the p - n junction depth. For a contact grid patterning the techniques of photolithography in a combination with metal evaporation by electron beam can be used, as well as electrodeposition, and also screenprinting method. For the SCs of the small area ($< 4 \text{ cm}^2$) the fine ($< 10 \text{ }\mu\text{m}$) stripes are required. Their width varies from 3 up to 25 μm , when using photolithography and from 50 up to 200 μm in case of screenprinting. For high-quality SCs a triple composition Ti/Pd/Ag is generally used. Thickness of Ag layer may run from 8 to 10 μm .

Since carrier recombination lower under metallization, the ultra-thin ($< 2 \text{ nm}$) SiO_2 underlayer may be used. Under the wide fingers the narrow ($< 2 \text{ }\mu\text{m}$) openings in the passivating oxide also may be formed, so the majority of a surface of the finger contacts with SiO_2 or ITO film, and only part — with Si.

The method of an electroplating of metals (Ni, Cu, Sn, Pb and their compositions, from solutions of metal salts in H_2PO_3) allows to achieve smaller damage of Si surface, in comparison with electron-beam evaporation [30]. A shadowing by a contact grid comprises from 3 to 6 %, depending on technology of its deposition [29].

3.3. P - n junction formation

For the high efficiency SCs the impurity diffusion for p - n junction formation usually is carried out in two stages, so that under a contact grid the n^+ layer thickness (for p -type base) was greater. Resistance of the n^+ layer under contacts have to be of 15–20 Ohm/\square , and in remaining sites 80–120 Ohm/\square [29, 30]. Simultaneously to the n^+ layer formation there occurs gettering by phosphorous. Impurity diffusion can be carried out both under the classical scheme, and with application of solid diffusants as well as diffusants superimposed on a surface using spin-on deposition, spraying or screenprinting (phosphorous concentration of 10^{20} – 10^{21} cm^{-3}).

Annealing is yielded in furnaces (temperature about 950°C, time - about 30 min) or setup for rapid thermal treatment, during the time from seconds to minutes, depending on concrete requirements [32].

The p - n junction depth varies from ~ 0.15 to $\sim 0.6 \text{ }\mu\text{m}$, depending on technology of its fabrication. In some cases removal of a part of n^+ layer by chemical etching may be used for optimization of surface resistance and lowering recombination losses [29].

3.4. Formation of the back isotype p - p^+ barrier and back contact

P^+ -layer may be created by boron diffusion from solid sources of BN, BBr_3 , $\text{SiO}_2\text{:B}_2\text{O}_3$. In serial production this operation is usually omitted, being changed by diffusion of Al ($T \leq 850^\circ\text{C}$).

Rear contact, as a rule, is Al. The local impurity diffusion in a rear surface of the poly-Si based SCs as a rule is not used, however back Al contact can be non-continuous, which reduces the back-surface recombination.

3.5. Passivation of defects

For this purpose SiO_2 (obtained by thermal oxidizing, CVD, rapid thermal oxidizing, [29]) combined with heat treatment in hydrogen-containing ambients, as well as Si_3N_4 and SiN_x [22, 32], are used. The application of a-C:H films is also promising.

3.6. Usage of screenprinting techniques at SC manufacturing

Such techniques are applied for the industrial cost-effective large-area SCs. It is possible to deposit dopant-containing layers, to shape a contact grid, back contact and antireflecting coatings using this method. Pastes, containing a necessary impurity and binding substance are used. Printing is yielded by paste squeezing through openings in the screen, made using photolithography. The heat treatment is carried out after printing.

The rear contact is formed by screenprinting of Al-containing pastes. Further firing is then executed, usually by rapid thermal procedures. Simultaneously there occurs gettering and p - p^+ junction formation.

For a front contact grid usually Ag-containing pastes with subsequent firing are used. Temperature and time of this operation should be carefully selected to provide necessary contact parameters, but not to damage the p - n junction [29]. The modern technologies allow to provide width of contacts $\leq 50 \text{ }\mu\text{m}$. Contact thickness is about 15 μm , surface resistance 4 - 10 mOhm/\square [29, 30].

3.7. Multicrystalline silicon — based SC with 19.8 % efficiency [9]

This device has PERL (passivated emitter, rear locally diffused) structure [33] and special honeycomb texturing of the front surface. It is shown in a diagram form in Fig. 7 from [9]. Honeycomb texture essentially reduces reflection losses and increments light trapping in a device. Texturing was carried out using masking SiO_2 , photolithography technique and acid etching (HNO_3 : $\text{HF} = 50:1$). The openings in masking SiO_2 have a diameter of 4 μm , distance between them is 14 μm . The p -type poly-Si with a specific resistance of 1.5 $\text{Ohm}\cdot\text{cm}$ have been used. Substrate thickness was of 260 μm .

The passivating thin oxide on the working and rear surfaces was grown by thermal oxidizing. The front metallization had finger width of 3 μm . To lower recombination under contacts an additional doping was used (see Fig. 7). The dots in the rear-side passivating SiO_2 have a diameter of 10 μm and distance from each other of 250 μm . As antireflecting coatings ZnS/MgF_2 is usually used.

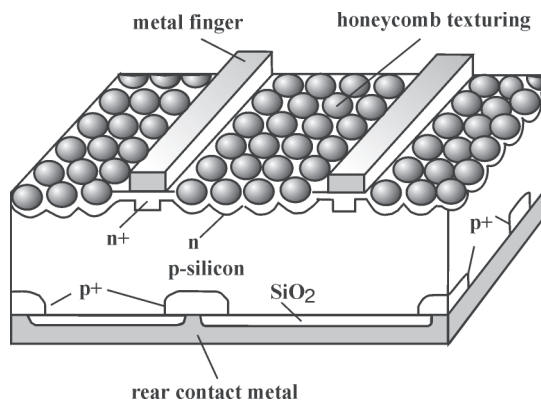


Fig. 7. The sketch representation of the 19.8 %-efficient SC design.

The temperatures used at this SC manufacturing in some cases exceeded 1000°C. However, no degradation of poly-Si parameters was observed, that is associated by the authors with progress reached by the material producers, and also with improved techniques of substrate preparation (Eurosolare Inc. Corporation, Italy).

The parameters of this SC with the area of 1 cm² at AM 1.5 conditions and 25°C: open-circuit voltage 654 mV, short-circuit current 38.1 mA/cm², current-voltage characteristic fill factor 79.5 %, efficiency 19.8 %. Lowered fill factor, in the authors' opinion, is connected with non-optimum distance between contact dots on the rear side of the device.

4. Some problems of charge carrier lifetime determination in poly-Si

A lifetime τ of non-equilibrium carriers in the SC base and bound with it diffusion length of carriers L_d ($L_d = (D\tau)^{1/2}$, where D is the diffusion constant of minority non-equilibrium carriers) are the important parameters of a material. These parameters define quality of the initial Si, and also are subject to changes as a result of carrying out of high-temperature technological operations because of recombination center generation (impurities, defects and complexes of the latter).

One of the conventional methods of the L_d parameter determination is the method of spectral dependencies of a surface photo-voltage (SPV), for the first time proposed in [34]. A series of installations, based on this method, is serially produced now, where the measuring process is completely computerized. The method does not require drawing contacts or carrying out other operations with samples, it is insensitive to processes of carrier trapping (as, for example, the method of photoconductivity transients), is the express one, allows to carry out measuring on the whole Si wafers in different sites. For correct L_d determination by this method the knowledge of the light wavelength (λ) dependencies of absorption constant (α) and light reflection in Si is necessary. If for monocrystalline Si these dependencies are well enough investigated

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(see, for example, [35]), in a case of poly-Si the latter are additionally influenced by internal fields of mechanical stresses, and also surface roughness of material. In [36] the influence of these factors on correctness of L_d determination in poly-Si by the SPV method is investigated. It is shown, that usage of the $\alpha(\lambda)$ dependence for monocrystalline Si in L_d calculations gives considerable errors (the L_d is overestimated). This error is especially significant for the case of small L_d values (20–50 μm). The authors have shown, that correct results may be obtained using a long-wave spectral region ($1/\alpha < 50 \mu\text{m}$).

The $\alpha(\lambda)$ values for Si without regard for the mechanical stresses, as the authors [35] state, most precisely are featured by a relation $\alpha(\lambda) = (85.015/\lambda - 77.104)^2$, where α is expressed in cm⁻¹, and λ — in micrometers. For a case of mechanical stress presence, the relation $\alpha = -10696.4 + 33498.2/\lambda - 36164.9/\lambda^2 + 13483.1/\lambda^3$ is given in [36]. It is necessary, however, to note, that according to the experimental data of [36] for different poly-Si samples the $\alpha(\lambda)$ dependencies are practically identical only in the long-wave region, and in the short-wave region they can substantially differ.

Another widespread method of τ determination is the method of photoconductivity transients. In the classical variant it requires the preparation of samples with two ohmic contacts. Measured τ in general is an effective value reflecting both volume and surface recombination, as well as non-equilibrium carrier trapping [37]. In experiment the contribution of surfaces and traps as a rule may be cut off, excluding the short-time region of the signal relaxation and using a stationary illumination of a sample. It, however, superimposes restrictions on lower limit of measured τ values (some microseconds). For a comparison, the SPV method allows to determine $\tau \leq 20 \text{ ns}$ [38]. The restriction of upper limit of the measured t is determined in both the methods by a relation between L_d and sample thickness. As it is shown in [35], at the correct account of all these factors the L_d and τ parameters, measured by both methods, practically coincide. In the case of the SPV method use, as it was already scored, it is necessary also to use correct $\alpha(\lambda)$ values for the material investigated, and to take into account the influence of poly-Si surface roughness.

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