Crystalline silicon solar cells with high resistivity emitter

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The paper presents a part of research targeted at the modification of crystalline silicon solar cell production using screen-printing technology. The proposed process is based on diffusion from POCl_3 resulting in emitter with a sheet resistance on the level of $70 \Omega/\square$ and then, shaped by high temperature passivation treatment. The study was focused on a shallow emitter of high resistivity and on its influence on output electrical parameters of a solar cell. Secondary ion mass spectrometry (SIMS) has been employed for appropriate distinguishing the total donor doped profile. The solar cell parameters were characterized by current-voltage characteristics and spectral response (SR) methods. Some aspects playing a role in suitable manufacturing process were discussed. The situation in a photovoltaic industry with emphasis on silicon supply and current prices of solar cells, modules and photovoltaic (PV) systems are described. The economic and quantitative estimation of the PV world market is shortly discussed.

Keywords: crystalline silicon solar cells, industrial technology.

1. Introduction

The photovoltaics is one of the fastest-growing technologies in the world and photovoltaic (PV) industry shows remarkable progress due to increased world investment an estimated US\$ 10 billion in 2005 up from US\$ 7.5 billion in 2004 [1]. It resulted in 2004 module production 1.160 MWp increased of 32% in 2005 to 1.532 MWp, which makes the total installed capacity is 3.7 GWp of which 95% is on-grid PV systems [2]. Taking the lower reported value, the European installation are estimated at 650–680 MWp with over 600 MWp in Germany – the biggest PV market in EU [3]. In 2006, PV world business employed 12500 people.

In 2005, the world solar cells production by technology substrate types was the following, monocrystalline Si – 28%, polycrystalline Si – 56%, amorphous Si – 4%, ribbon Si – 3%, CdTe – 2%, amorphous Si on Cz-Si – 7%, so that the crystalline silicon captures around 91% share of the world photovoltaics market [4].

To satisfy the market demand, the three main trends exist nowadays in crystalline Si PV field:

- higher conversion efficiencies going from about 15% to 20% for the industrial cells,
- the use of thinner substrates, today 250–300 μm thin gradually is shifting to a thickness of 100–130 microns which determines the specific silicon consumption (SSC) per Watt peak (Wp) of solar electricity,
- growth of silicon supply.

While two first trends, connected with solar cells technology, are incontrovertible, the availability of suitable

solar grade silicon is the key constraint on the growth of PV. Table 1 shows the world production capacities of Si and what is more important, the announcement about the nearest planes in comparison with silicon for IC electronics [5].

Table 1. Current and predicted crystalline Si world production of raw material, solar cells and specific Si consumption trend in PV field (after Ref. 5).

Year	Si production (MT/year)		SSC (g/WP)	Cell production (MWp)
	for IC electronics	for PV sector		
2004	18500	14300	13	1100
2005	19500	16300	11	1500
2006	20400	18850	10	1900
2007	21400	29300	9.0	3250
2008	22500	67500	8.5	7900
2009	23600	86250	8.0	10800
2010	24700	97800	7.5	13000

Industry experts are now reporting a price of between 40 and 70 Euro/kg raw crystalline silicon in long contracts up to 10 years when up to 250 Euro/kg are even being paid on the spot market. The highly unusual development is noticed in China, where polycrystalline silicon production foreseen by 2010 should reach capacity of about 30000 MT/year [5].

The process of crystalline Si from ingot to the solar cell leads to the material losses. Heavily contaminated sides of the raw crystalline silicon ingots are sawn-off and this is the first loss of Si, which equals approximately 15% up to 30% of its volume, but the removed Si is, in this case, recycled.

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Next, the blocks of crystalline Si are sliced into wafers using multi-wire saws and the highest losses occur during the wafering where about 40% of Si is lost as kerf and for the typical wafer 300- μm thick at the present, the kerf loss is 180–200 μm [6]. The slurry is highly enriched with silicon, but there is no data, no knowledge viable process for recovery of the Si from cutting suspension. The mentioned previously factor SSC takes into account the sawn-off, kerf and raw wafer Si material. The saw damage layer on both sides of wafer must be etched before the start of solar cell technology process, which reduces the wafer thickness to 280 μm . Considering the density of Si 2.328 g/cm^3 [7], one can calculate the yield in terms of a wafer surface area per ingot weight as 0.72 m^2/kg , so then the one 100 cm^2 crystalline wafer must be more than Euro 1 per piece.

The 100 cm^2 solar cell manufactured on the basis of this wafer from most producers has 15% conversion efficiency under standard test condition, i.e., light spectrum AM1.5G, normalized to 1000 W/m^2 and at temperature 25°C. This means, that the cell shows the power of 1.5 Wp which sets its market price. The average sales prices for the crystalline Si solar cells are on the level of 2.5 Euro/Wp, for the modules 3.5 Euro/Wp [8,9] while cell fabrication cost is about 0.3 Euro/Wp and module assembly 0.5 Euro/Wp [6].

The cost for the large-scale ground-based or roof-top turnkey systems with the crystalline silicon modules is about 5000 Euro/kWp [10]. The cost of the PV system including not only the module cost but also the balance of system (BOS) cost is summarized in Table 2 [3].

Table 2. Cost drivers for crystalline Si based photovoltaic system [3].

The component parts of PV system		Cost
Modules	BOS (balance of system)	73%
Substructure, framing, installation		8%
DC-cabling		3%
Inverters		7%
Engineering		6%
Other (land area)		3%

The yield of PV systems, for example in Germany, which has average European solar irradiation of 1200 kWh/m^2 per year, achieves 1000 kWh per one kWp. The solar electricity price calculating, taking into account the PV system cost, its interest rate of 7.4% for the capital used, maintenance cost of 1.5% of the system cost and irradiation rate; for Germany gives 0.56 Euro per 1 kWh . This means, that the branch is still far away from achieving the residential grid prices which are between 0.1 Euro/ kWh in Canada to 0.2 Euro/ kWh in Denmark [10]. In order to reach grid parity at the price of conventional domestic electricity, the PV systems would have to cost around 1.5 Euro per 1 Wp which is expected around 2020 by the simultaneous increase in conventional electricity price by 3% each year. Among other

support mechanisms to promote PV a few countries implemented feed-in tariff, which is paid for solar electricity fed into the grid. The feed-in tariff in most cases depends on size of PV systems and for example in Euro per kWh is as follows, Germany – 0.51, Czech Republic – 0.46, Spain – 0.44, Austria – 0.6, and Italy – 0.49 [11].

2. Experimental – crystalline silicon solar cells technology

The emitter is the most important construction part of the crystalline silicon solar cell and its profile determines technology in the next steps as final electrical parameters and has decisive importance for solar cells direct manufacturing cost. The industrial production of solar cells requires chain process, consists of about 25 single process steps, dependent on a solar cell type and technology. However, the essential sequence can be presented in seven main steps which are given in Fig. 1. The solar cells are manufactured by most of the world companies according to this sequence. On this background, the technology elaborated at the Institute of Metallurgy and Materials Science (IMMS) for these particular steps is simple, inexpensive, verified and has a direct potential for mass scale application.

Fig. 1. Chart flow of screen printed contacts and co-fired metalization technology process of solar cells with different time of oxidation.

All the samples were first etched in KOH (30%) to remove saw damage material 10- μm thick from each side of wafers and texturised in IPA:KOH (40%):DIH₂O in volume ratio 3:1:46 solution at 80°C for 15 min and after that rinsed in HCl (2%) and HF (10%). All the chemical processes were completed by rinsing in deionised water and drying in N₂.

The difference in our experiment is in diffusion and passivation temperatures which were applied in particular technological steps to monocrystalline Si (Cz-Si), boron doped p-type, 1 ohm-cm resistivity, 300- μm thick wafers and denoted as sample No. 1, 2, and 3. For the point of reference, the solar cell according to classical technology was prepared [12] and denoted as sample No. 4. The emitter for samples 1, 2, and 3 was generated at a temperature of 825°C for 25 min in an open quartz tube using liquid POCl₃ as the doping source. In this process, a prediffusion duration time was 15 minutes while dopant redistribution time was 10 minutes which resulted in the emitter with a sheet resistance 70 $\Omega/\square$. After diffusion, the parasitic junction was removed by means of a special Teflon clamp in which the wafers were immersed in HNO₃(65%):HF(40%):CH₃COOH(80%) solution in the volume ratio 5:3:3 for 1 min. Then, phosphorus silicate glass was removed by immersion in a bath of HF (10%) for 2 min.

For reference cell No. 4, the surface passivation was achieved by the growth of SiO₂ at the temperature of 800°C for 15 min in a controlled O₂ and N₂ atmosphere and the value of 40 $\Omega/\square$ of the sheet resistance which had been obtained after diffusion at 840°C for 30 min did not change. In the case of samples No. 1, 2, and 3 the silicon dioxide had been deposited for 5 min at 920°C, 880°C, and 840°C, respectively, which caused the change in sheet resistance and donor doped profile (see Table 3 and Fig. 2).

In this work, as the antireflection layer for solar cells, the titanium dioxide layer was deposited by CVD method with tetraethylorthotitanat (C₂H₅O)₄Ti using purified nitrogen as a carrier gas. The liquid source (C₂H₅O)₄Ti had vapoured at 200°C in a quartz bubbler and was transported via heated lines to a 5-mm diameter teflon nozzle located 10 mm above the silicon wafer heated at the temperature of 300°C.

For the front contact, the Du Pont PV145 paste and for back contact the Ferro CN53-101 Al conductor paste were printed using 330 mesh screens and after drying at 150°C for 15 min the silicon wafers were co-fired in the IR conveyor furnace having 76-cm long three zones heated sector and with 160 cm/min belt speed.

3. Measurements and results

The I–V characteristics of solar cells were measured under standard conditions AM1.5 at a cell temperature of 25°C and the final data are shown in Table 3. A reference cell was calibrated at Wrocław University of Technology at the Photovoltaic Laboratory Solar Lab. using B-class Sun simulator.

Table 3. Main illuminated I–V parameters of solar cells in dependence on sheet resistance adequate to passivation temperature.

Cell No.	Passivation temperature (°C)	R_{sheet} ($\Omega/\square$)	I_{sc} (A)	V_{oc} (V)	P_m (W)	FF	E_{ff} (%)
1	920	20	0.843	0.605	0.369	0.724	14.3
2	880	40	0.888	0.605	0.402	0.749	15.6
3	840	56	0.876	0.601	0.395	0.751	15.3
4 (ref.)	800	40	0.839	0.594	0.370	0.743	14.4

where R_{sheet} is the sheet resistance of an emitter, I_{sc} is the short circuit current, V_{oc} is the open circuit voltage, P_m is the power in the optimum point, FF is the fill factor, and E_{ff} is the conversion efficiency.

The measured I–V curves of a solar cell were described by double exponential model (DEM) [13], defined as follows

$$I = I_{ph} - I_{s1} \left[\exp \left(\frac{V + I \cdot R_s}{A_1 V_t} \right) - 1 \right] - I_{s2} \left[\exp \left(\frac{V + I \cdot R_s}{A_2 V_t} \right) - 1 \right] - \frac{V + I \cdot R_s}{R_{sh}} \quad (1)$$

where R_{sh} is the shunt resistance, R_s is the series resistance, I_{ph} is the photocurrent, I_{s1} is the first diode saturation current from the thermal generation of minority carriers within emitter and base regions, I_{s2} is the second diode saturation current from generation-recombination in space charge region, A_1 and A_2 are the diode ideality factors, V_t is equal to kT/e where k , e , and T have their usual meaning.

The numerical fitting was carried out by SolarFit v1.8 computer program developed at Wrocław University of Technology at the Photovoltaic Laboratory Solar [14]. The values of parameters obtained by fitting the light I–V curves of the described solar cells to the double diode model DEM

Table 4. Solar cell parameters determined from fit of the two-diode model to the illuminated I–V characteristics described in Table 3.

Cell No.	I_{ph} (A)	R_{sh} (k Ω)	R_s (m Ω)	I_{s1} (A)	j_{s1} (A/cm ²)	I_{s2} (A)	j_{s2} (A/cm ²)
1	0.843	0.0198	18.7	2.66e-11	1.04e-16	2.97e-6	1.16e-11
2	0.872	0.0438	10.7	2.91e-11	1.16e-16	2.97e-6	1.19e-11
3	0.869	0.0589	10.1	3.06e-11	1.23e-16	3.99e-6	1.59e-11
4 (ref.)	0.826	0.0375	13.5	3.37e-11	1.35e-16	3.54e-6	1.42e-11

are summarized in Table 4. The sheet resistance was measured by four-point probe technique.

It is interesting to compare cells No. 2 and 4 (ref.) having the same value of R_{sheet} but obtained by the processing at different temperatures. It can be seen that the major difference is a significant increase of I_{sc} and V_{oc} for cell No. 2 with respect to the reference cell.

In Table 3, one can see that the best I_{sc} shows the cell passivated at 880°C and further temperature lift, reducing the R_{sheet} , is not profitable for I_{sc} . The second most important parameter for the solar cell V_{oc} , consequently increased together with a passivation temperature which can be attributed to the increase in the active P elements with reduction of material defects in Si crystal lattice. It is further interesting to note that the first diode saturation current diminution while the temperature of passivation increases. For the studied samples, the dopant concentration at the surface after the first step diffusion process is about 1×10^{23} atoms/cm³ (Fig. 2). Depending on the passivation temperature, a sheet resistance changes in the range from 20 to 56 $\Omega/\square$. Along with the increase in the passivation temperature, sheet resistance falls, which is clear and does not require any further explanation. Important thing is that the highest dopant concentration at the surface is for the sample showing the highest sheet resistance. With the increase in passivation temperature, the series resistance increases too. This tendency results in the decrease of FF and in a consequence makes ohmic contact between emitter and front metalisation difficult. The effect can be seen in E_{ff} values. Solar cell of the lowest sheet resistance and the highest series resistance has the lowest value of the fill factor FF , and thus the lowest energy conversion efficiency E_{ff} .

According to the correlation between R_s and R_{sh} , the lowest value of FF has cell No. 1 passivated at a temperature of 920°C.

Among other electronic devices, the distinguishing features of silicon solar cells are very shallow emitters, usually not exceeding $\sim 0.7 \mu\text{m}$. The diffusion profiles presented in Fig. 2 were determined by the secondary ion mass spectroscopy (SIMS) measurements carried out with a Cameca IMS 6F SIMS spectrometer using cesium primary ions and the detection of $^{30}\text{Si}^{31}\text{P}$ negative secondary cluster ions. In Fig. 2, the profiles start from a value of 10^{15} atoms/cm³ which is a bulk detection limit for P elements in Si for SIMS method [7] but the real n-type doped Si is from 1.513×10^{16} atoms/cm³ corresponding to 1 ohm-cm resistivity of p-type Si and this value is marked as dotted horizontal line in Fig. 2.

In Fig. 2, on the axis of abscissae, the characterized point of emitter is laying in $\sim 0.12 \mu\text{m}$ depth. After the passivation process, the original total phosphorus elements from a surface to this point are reduced whereas beyond it the concentration increases.

The spectral response was measured using a Jobi-Yvon H20 monochromator fitted with a 75-W tungsten-iodine lamp. The external quantum efficiency (EQE) of the silicon solar cells was measured with, calibrated by Hamamatsu Si S2281, photodiode and was calculated using its external

Fig. 2. Phosphorous concentration profile after diffusion determined by SIMS and its changes in relation to passivation temperature.

quantum efficiency. In Fig. 3, the dependences of EQE on a wavelength in the 400–600 nm range for samples No. 1, 2, and 3 are shown. The change in the shape of the emitter profile corresponds to the temperature of a second diffusion step taking place during passivation process. The dopant concentration decreases from the surface to the $1\text{-}\mu\text{m}$ depth in bulk Si but deeper the P elements concentration grows systematically.

Cells No. 2 and No. 3 exhibit a better short wavelength response as compared to cell No. 1. With respect to the better short wavelength response, it is apparent that the shallower profile of cell No. 3 results in less absorption within the highly recombinative emitter, and thus a higher collection probability for the short wavelength photons [15]. The degradation of the EQE observed in Fig. 3 is due to increasing passivation temperature and decreasing sheet resistance (see Table 3). The decrease in the surface concentration from $\sim 3 \times 10^{21}$ atoms/cm³ for cell No. 3 to $\sim 1 \times 10^{20}$ atoms/cm³ for cell No. 1 did not cause the EQE reduction in the near surface region. On the contrary, the EQE showed the best value level for cell No. 3.

Fig. 3. External quantum efficiency for solar cells in dependence on passivation temperature and adequate value of a sheet resistance.

4. Conclusions

The new approach of n-type emitter formation by double step process can be used on industrial level without any additional technological step. During the passivation process, taking place above the temperature of 840°C, the shape of an emitter can be formed. The presented results indicate that the electrical parameters of the silicon solar cell depend mostly on the sheet resistance giving information about active *P* elements but not directly on a dopant concentration at the surface region. The emitters with different profiles can be manufactured having the same sheet resistance. In the screen printing technology, obtaining the low resistivity ohmic contact between emitter and front metallization depends mostly on the concentration of a dopant at the surface. The screen-printed solar cells with dopant concentration profiles formed at lower temperatures of passivation process exhibit the higher fill factors *FF*. The presented double step process of formation of a dopant concentration profile in emitter allows the improvement in produced solar cells output parameters.

The solar cell obtained by the diffusion process at a temperature of 825°C and passivated at 880°C show the best electrical parameters and finally the best conversion efficiency which is associated with its emitter profile. It is possible to reduce the cost of a diffusion process by the lowering temperature of a process down to 825°C, and shortening annealing time to 25 minutes.

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