Purification of Metallurgical Silicon up to ‘‘Solar’’ Mark Silicon

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Abstract- The paper presents experimental results showing the possibility of obtaining the "solar" mark silicon by recrystallization of metallurgical silicon in low-melting metals on the example of tin and the cultivation of the obtained flakes of single crystal silicon by the Czochralski method. The experiments on the purification of low-melting metal (tin) after the completion of the cycle of the silicon flakes are conducted in order to re-use it. Qualitative and quantitative analysis of raw materials of silicon and tin and the composition after different processing stages were studied by XRF analysis on the instrument Elvax light. Structural features of the obtained silicon flakes were examined using scanning electron microscopy on the device РЕММА106И. The measurements of the conductivity type and electrical resistivity of the obtained monocrystalline ingot of silicon are carried out by a four-probe technique. The obtained monocrystalline silicon has a purity not worse than 5N, p-type conductivity and a resistivity of not more than 2 Ω·cm.

Keywords- metallurgical silicon, monocrystalline silicon, tin, purification, recrystallization.

1. Introduction

Solar photovoltaic energy is currently one of the fastest growing areas not only in the energy sector, but also among other industries [1]. In 2008 the total power of solar photovoltaic setups (solar PVS) in the world was 13 GW, and in the beginning of 2014 more than 140 GW and it is expected that in 2030 their volume should exceed 700 GW. It is expected that the total power of solar PVS introduced in 2015 in the world will exceed 50 GW [2, 3].

Modern production of ‘‘solar’’ mark silicon [4], based on more than 85% of the modern solar PVS is carried out on a simplified "siemens" technology of trichlorosilane or in the process of monosilane pyrolysis in the reactors of MEMS company design. Total production in 2004 was about 7 000 tons, and in 2008 produced more than 70,000 tons of pure silicon. When processing the waste of the production of silicon in the electronics industry in 2004 received about 3 500 tons in 2008 and 15,000 tons of silicon. Projected silicon production capacities available for solar photovoltaic, (solar cells) in 2014, according to various sources, measured between 310 000 and 429 860 tons, from 27 000 to 30 000 tons of silicon used electronic industry [2, 3].

The first two methods are based on environmentally dirty chemical processes, which, given the pace of development of global solar energy, can lead to irreversible negative environmental consequences, while the latter method is limited by the amount of electronic waste, and does not solve the problem of silicon production for the growing need of solar silicon energy sector.

In this regard, particular interest are non-traditional environmentally friendly methods of producing ‘‘solar’’ mark silicon. These include methods based on the use of high-purity quartzite in the process of obtaining metallurgical silicon with subsequent purification by directional crystallization, as well as methods for producing silicon from a mixture of electronic and metallurgical silicon, purified by zone melting. However, these methods do not allow to obtain the ‘‘solar’’ mark silicon for solar cells with efficiency over 15%. Alkoxysilane and aluminothermic methods of obtaining silicon are currently among the promising techniques. They are environmentally friendly chlorine-free technology for obtaining polycrystalline silicon, which can be used either for solar cells or for semiconductor electronics. However, these methods are quite energy-intensive and do not allow to solve the existing problem fully.

It is possible to solve the above problems with the introduction in this area of new, environmentally friendly and less energy-consuming technologies allowing obtaining high-purity silicon for solar cells with characteristics relevant to the modern world standards. We propose to use a new method of obtaining the ‘‘solar’’ mark silicon by recrystallization metallurgy, with the application of solutions-melts of low-melting metals [5-7] and further directed recrystallization of the obtained material. This method also allows recycling of all types of waste when obtaining the solar cells and modules based on them for the purpose of obtaining the ‘‘solar’’ mark silicon (during the production of silicon wafers for 1MW of solar cells 30 tons of sludge is formed, which contains 5 tons of silicon).

The main goals of this work were to solve research and technological problems: with the development of laboratory techniques of purification of metallurgical silicon, and silicon-containing wastes using melts of low-melting metals on the example of tin when obtaining the ‘‘solar’’ mark silicon for the application in solar energy.

2. Analysis

Monocrystalline ‘‘solar’’ mark silicon extraction from metallurgical silicon by recrystallization in low-melting metals can be conditionally divided into four stages.

The first step in the purification of metallurgical silicon is the series of operations to prepare the main and auxiliary materials and tooling of vacuum technological setups.

Original metallurgical silicon is mechanically crushed using a jaw crusher to a grain size of 5.0 – 10.0 mm, then the chemical treatment was carried out in acids mixture HNO_3:HF:H_2O = 1:1:1 at the solution temperature ~ 20 °C [4], thoroughly washed in deionized water and dried in a vacuum dessicator. After drying it was divided into sample and the probe was selected for analysis of this material on the chemical composition.

Low-melting metal, as which we use tin, before placing in the crucible also passed chemical preparation and input control.

Quartz products (crucibles and tooling) and graphite products (thermal units in electrovacuum setups and graphite tooling) are prepared according to the standard for the electronics industry technological regulations.

In the second stage, we conducted the primary purification of metallurgical silicon in the low-melting metal (tin) in the electrovacuum setup (the standard setup for crystal growth by "Crystal 3M" Czochralski method was used), using our developed tooling for purification of silicon. Schematic image of the tooling in the heat unit at different stages of the purification process is shown in Fig.1.

Into the crucible (4) which is rotatable relative to the heat unit (2), put the prepared sample of silicon metal (5), and in a container with holes in the bottom (3) having the ability to move relative to the crucible a sample of tin (1) used as a solvent of metallurgical silicon (Fig.1 a). The ratio of tin to metallurgical silicon is 96% weight to 4% weight. Calculation of sample weights is due to the solubility of silicon in the tin at the process temperature of 1200 °C according to the phase equilibrium diagram (Fig.2). The temperature increase of the purification process, and with it the solubility of silicon, is impractical, due to the fact that the increase in the vapor pressure of tin leads to losses and contamination of the working chamber due to the deposition on the walls (the vapor pressure of the tin at a temperature of 1220°C is 10^{-2} Torr). Reducing the temperature of the cleaning process reduces the solubility of silicon in the tin, making the cleaning process less productive. Therefore, we believe this process temperature for these materials is the most optimal and the most effective.

After loading, the process chamber is sealed and vacuumed to residual pressure 10^{-2} Torr. Then heating of the solvent was carried out until the temperature of the process, pulsed blowing of the solution-melt was carried out with gaseous mixture of

inert gas while rotating the crucible. In this case, the formed slag was removed from the crucible. After the dissolution of metallurgical silicon in the solution-melt of tin (7) and homogenizing of the solution-melt the smooth, undulating lowering the temperature was carried out at which the crystallization of the dissolved silicon in the form of flakes (6) on the surface of the melt from the saturated solution-melt (Fig.1 b). The temperature reduction was carried out up to T=900°C, and in the mode off furnace to a temperature of T=700°C, after which the flakes with the grown silicon was recovered from the solution-melt (Fig. 1) and further from the setup. The above cleaning operation was repeated several times. The completion of a cycle of the purification process of metallurgical silicon is performed by extracting the crucible with the used melt of the fusible metal and replacing it with a crucible containing a low-melting metal of high purity. After the process from the flakes of the obtained silicon and used tin the sample was selected for the analysis of materials on the chemical composition. The obtained flakes were washed from the residue of tin on their surface in dilute hydrochloric acid. The appearance of the obtained material is shown in Fig.3.

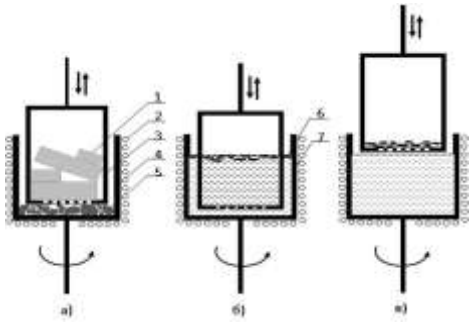

Fig.1. Schematic image of the tooling in the heat unit at different stages of the purification process. a) - before melting, b) - in the process of crystallization of flakes of the purified silicon, c) - the end of the cleaning process.

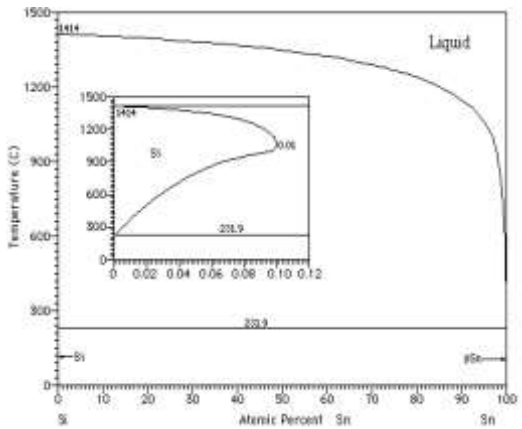

Fig.2. Phase equilibrium diagram of the tin-silicon system.

Fig.3. Flakes of the cleaned silicon after treatment with a hydrochloric acid solution.

In the third stage, cleaning low-melting metal was carried out in two steps. First, the tooling and crucible used for the first reception cleaning were placed in the electrovacuum setup (Crystal 3M). The cleaning process was performed by vacuum degassing of molten tin from the light impurities and then filtered. The second method of purification was carried out by the method of zone recrystallization of low-melting metal on the setup of zone melting. After the process, the purified low-melting metal has passed final inspection and was stored for reuse.

In the fourth phase the silicon flakes (obtained in the second stage) underwent further purification by recrystallization in growing single crystal silicon ingot by the Czochralski method on a seed crystal with crystallographic orientation (111) by standard techniques.

3. Results and Discussion

The researches of qualitative and quantitative elemental composition of basic materials, namely silicon and tin, were conducted at different stages of the technological process. Measurements were performed using X-ray fluorescence analysis on the Elvax light device (produced by LLC «Elvatech», Kiev). Table 1 displays the results of the analysis of the original metallurgical silicon, flakes of the purified silicon and single crystal silicon obtained by the Czochralski method. As can be seen from the table values, the purity of the purified flakes is not sufficient due to the presence of large impurity content of the solvent (tin), suggesting the need for its further purification. As shown above, the further purification was carried out by the constriction of the molten flakes with the growing of silicon single crystal on a seed by the Czochralski method. The purity of the constricted monocrystalline silicon of the same quality as mark 5N, which corresponds to the "solar" mark silicon.

Table 1. The measurement results of the qualitative and quantitative composition of silicon.

Table 2 shows the results of the analysis of the tin specimens for qualitative and quantitative elemental composition before carrying out the cleaning processes of silicon, after its completion, and after the cleaning process of tin. According to the presented results it is seen that the chosen technological method of cleaning tin is correct. Purified tin has purity sufficient for re-purification process of metallurgical silicon.

The structure of the obtained purified flakes was investigated using scanning electron microscopy on the РЕММА106И device (produced by SELMI, Sumy, Ukraine). The device allows visualizing the sample surface in a wide range of magnifications with resolution of about 10 nm.

Images with magnifications of 150 were obtained in the mode of secondary electrons. The accelerating voltage for the electron microprobe was 20 kV, the probe current – 3 nA, exposure time – 200 sec. The obtained results are shown in Fig. 5. The figures show that the flakes consist of silicon polycrystals, having a visual size of 100÷180 μm.

Table 2. The measurements results of the qualitative and quantitative composition of tin.

Atomic number	Element	The concentration of impurities in the original tin, in wt.%	The concentration of impurities in the tin after cleaning the silicon, in wt.%	The concentration of impurities in the tin after it is cleaned, in wt.%
12	Mg	0,00001%	-	-
13	Al	0,0001%	0,2652%	0,0003%
14	Si	0,0003%	0,85602%	-
20	Ca	0,00001%	0,1309%	-
22	Ti	0,00001%	0,1038%	-
25	Mn	0,00003%	-	-
26	Fe	0,00005%	0,23487%	0,0001%
27	Co	-	0,00001%	0,00001%
28	Ni	0,0001%	0,0815%	0,00001%
29	Cu	0,00001%	0,0721%	0,00001%
30	Zn	0,00001	0,00003%	0,00003%
31	Ga	-	0,00005%	0,00005%
33	As	-	0,0001%	0,0001%
47	Ag	-	0,00001%	0,00001%
48	Cd	0,00005%	0,0564%	-
50	Sn	99,999%	98,0352%	99,999%
51	Sb	0,00001%	0,09075%	0,00005%
53	In	-	0,00001%	0,00001%
79	Au	-	0,00001%	0,00001%
82	Pb	0,00001%	0,07312%	0,00001%

At the grain boundaries in some places you can see remnants of the solvent (tin) which is confirmed by the research of qualitative and quantitative elemental composition of the flakes of the X-ray fluorescent method of analysis.

The electrophysical properties of the obtained single crystal were examined. Measurements were performed according to the method which is used for measuring specific electrical resistance (resistivity) on the end surface of monocrystalline ingots and silicon wafers from $1 \cdot 10^{-4}$ to $1 \cdot 10^{3}$ Ohm·cm according to GOST 19658-1981. The measurements were performed using the Pius – 1УМ-К which has a measuring С2080 type four-probe head with four linearly arranged probes (inter-probe distance of 1.3 mm).

Atomic number	Element	The concentration of impurities in the initial metal. silicon, in wt.%	The concentration of impurities in the silicon flakes, in wt.%	The concentration of impurities in the single crystal silicon, in wt.%
12	Mg	0,0132%	0,00004%	0,00003%
13	Al	0,6221%	0,00007%	0,00006%
14	Si	98,0025%	99,9691%	99,9991%
20	Ca	0,2714%	0,0001%	0,00008%
22	Ti	0,1765%	0,00003%	0,00003%
25	Mn	0,0048	0,00006	0,00006
26	Fe	0,5396%	0,0001%	0,00002%
28	Ni	0,0842%	0,0001%	0,00004%
29	Cu	0,0577%	0,0001%	0,00006%
48	Cd	0,0451%	0,0001%	0,00005%
50	Sn	0,0518%	0,0300%	0,0004%
51	Sb	0,0726%	0,0001%	0,00005%
82	Pb	0,0585%	0,0001%	0,00002%

Electrical resistivity was measured on three samples cut from the ingot of single crystal silicon in the initial, central and caudal parts. The type of conductivity of the obtained samples was determined before measuring the specific electrical resistance by the probe of the same setup. As expected, the doping of silicon by tin, the samples had p-type conductivity. Samples were measured at six fixed points along the diameter of the ingot, in two mutually perpendicular directions, arranged in accordance with Fig.6.

According to the results of measurements of electrical resistivity on the samples cut from the ingot these were calculated:

1. The average value of resistivity in the peripheral ring of the sample by the formula $\rho_p = (\rho_1+\rho_6+\rho_3+\rho_4)/4$.
2. The average value of resistivity in the peripheral center of the sample by the formula $\rho_c = (\rho_2+\rho_5)/2$.
3. The mean value of resistivity in the sample by the formula $P_s = (\rho_p+\rho_c)/2$. The obtained data are systematized in Table 3.

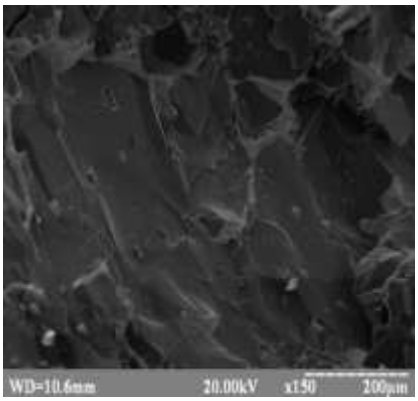

Fig.4. Scanning electron microscopy of purified silicon flakes with magnification 150.

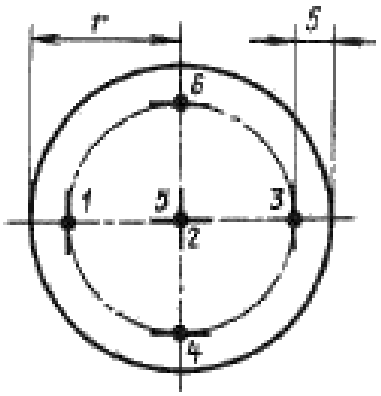

Fig.5. The scheme of control points to measure the electrical resistivity on a silicon wafer.

Table 3. The results of measurements of the electrical resistivity on samples cut from ingot.

№	Sample	ρ_1, Ω*cm	ρ_2, Ω*cm	ρ_3, Ω*cm	ρ_4, Ω*cm	ρ_5, Ω*cm	ρ_6, Ω*cm	P_p, Ω*cm	P_c, Ω*cm	P_s, Ω*cm
1.	The initial part of the ingot	1,972	1,985	2,024	2,008	1,893	1,912	1,979	1,939	1,959
2.	The middle of the ingot	2,004	2,216	2,146	2,184	2,258	2,093	2,107	2,237	2,172
3.	The tip of the ingot	1,396	1,452	1,384	1,408	1,410	1,382	1,393	1,431	1,412

4. Conclusion.

In the course of work the laboratory technique of obtaining of ‘‘solar’’ mark monocrystalline silicon by recrystallization of metallurgical silicon in melts of fusible metals on the example of tin and by a further constriction of the obtained flakes of silicon by the Czochralski method was developed and has been successfully tested.

The technique of purification of low-melting metal (tin) after the cycle to obtain the silicon flakes for the purpose of its re-use was worked out.

The researches of qualitative and quantitative elemental composition of raw materials of silicon and tin as well as their composition on different stages of the technological process were conducted by the method of X-ray fluorescent analysis on the Elvax light device.

The structural features of the obtained silicon flakes were examined using scanning electron microscopy on the РЕММА106И device. The obtained result is consistent with the studies which were conducted by X-ray fluorescent analysis.

The electrical resistivity was measured by four-probe technique on the obtained single-crystal ingot. The measurements were conducted on three samples cut in initial, central and caudal parts of the obtained ingot.

As a result of the conducted research it is shown that the obtained monocrystalline silicon has a purity of not worse than 5N, the p-type conductivity and the electrical resistivity greater than 2 Ω·cm, which is sufficient for fabrication from this material the elements of photovoltaic cells with the characteristics relevant to the modern world standards.

For the purpose of manufacture of purer materials it is planned to pay more attention to the chemical preparation of metallurgical silicon and its washing, to purification processes in low-melting metals, and to improve and further develop the obtained technological methods and the equipment.

Acknowledgements

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