Journal of Nano- and Electronic Physics
Vol. **14** No 6, 06012(5pp) (2022)

Журнал нано- та електронної фізики
Том **14** № 6, 06012(5cc) (2022)

Features of Impurity Segregation and Microstructure of Si Ingots obtained by Electron-Beam Purification of Metallurgical Grade Silicon

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(Received 29 October 2022; revised manuscript received 22 December 2022; published online 27 December 2022)

Today, solar-grade silicon (SG-Si) is the most used material for the manufacture of solar photovoltaic converters (SPVC), which are widely used in the renewable energy, industry and households. Improving the efficiency of SPVC while reducing the cost of production and strengthening environmental requirements is the urgent and important task for modern applied science and technology development. The solution to solving this problem is due, among other things, to refining methods: vacuum purification (VP) and oxidative purification (OP) during electron-beam melting (EBM) of metallurgical-grade silicon (MG-Si). The influence of VP and OP on the microstructure of silicon ingots, obtained by the EBM of MG-Si, is studied in the present paper. It is experimentally established that the structure of ingots does not depend on the type of VP/OP refining used during EBM and is determined prefer by the technological/thermo-physical conditions of their solidification/crystallization. The structure of the obtained ingots consists mainly of more frequent crystallites, their main axis is perpendicular to the surface of solidification. In the obtained ingots of upgraded metallurgical silicon (UMG-Si) by EBM, there is a noticeable segregation of inclusions with an increase in their number in the direction from the center to the free surface of the melt that solidified last. The sensitivity of the particle sizes of inclusions according to the type of refining of metallurgical silicon VP/OP is noted, in contrast to the size of crystallites. The absence of segregation of impurities onto grain boundaries, regardless of the selected refining method (VP/OP), is confirmed in ingots of UMG-Si obtained by EBM of MG-Si. Analysis of the chemical composition of impurities in the obtained ingots confirms the presence of the "heredity effect" – majors of impurities are autonomous single-element phases of residual and low-component impurities with a ratio of elements of their chemical composition similar to those in the initial MG-Si.

Keywords: Purification, Structure, Impurities, Segregation, Coagulation, Upgraded metallurgical grade silicon, Electron-beam Melting.

DOI: 10.21272/jnep.14(6).06012 PACS numbers: 81.20, 64.75.Qr

1 INTRODUCTION

Wide and effective use of renewable (green) energy, including solar energy, is one of the important and urgent tasks of human development. Currently, the majority of widely used Solar Photovoltaic Converters (SPVC) made from Solar Grade Silicon (SG-Si), including monocrystalline SG-Si, multicrystalline SG-Si and thin film-Si is also spreading. Special attention is paid to the development of new effective materials, technologies and the improvement of existing ones to increase their efficiency and reduce the cost of production.

Electron-Beam Melting (EBM) is currently one of the promising and effective methods of refining silicon in Ukraine and in the world. Technological features of the EBM application, including Vacuum Purification (VP) or Oxygen Purification (OP), and its effect on silicon refining were presented in papers [1-4].

The features of impurity segregation and microstructure of polycrystalline Upgraded Metallurgical Grade Silicon (UMG-Si) ingots obtained from VP and OP Metallurgical Grade Silicon (MG-Si) during its EBM have been examined in the present paper.

2 MATERIALS AND EXPERIMENTAL

For the research, UMG-Si ingots were produced by VP and OP methods from MG-Si during EBM [3, 4]. During the experiment, melting of MG-Si was carried out by gradually increasing the power of the Electron Beam (EB). Melting and purification/refining was provided at constant EB power with a partial supply of molten material to the water-cooled crucible/casting pot with exposure in a liquid state for a controlled period of time. For the subsequent solidification, the EB power was gradually reduced, providing a temperature difference from the edge to the center of the ingot, which contributed to compensation for the volume expansion of Si to prevent the cracking of ingots during their solidification/crystallization. The crystallization front of the ingot during its controlled solidification ran from the edges in contact with the walls of the water-cooled crucible to the center of the free surface of the ingot, which crystallized last with the formation of a characteristic convexity. The resulting ingots were shaped like a convex disc with a diameter of 95 mm and a maximal thickness of 30 mm.

Samples for tests with a size of 24 × 24 × 4 mm were cut from the obtained UMG-Si ingots for the present research. Cracks were observed on the surface of obtained samples, probably critical internal stresses accumulated in the material during crystallization and cutting. The obtained samples were examined using the SEM JAMP-9500F ("JEOL", Japan) by the methods of Scanning Electron Microscopy (SEM) and spectroscopy: local Auger-electron spectroscopy, electron microprobe

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X-ray chemical analysis of the surface/fractures of samples and micro-X-ray fluorescence chemical analysis.

The chemical/elemental composition of ingots was determined by the method of Glow-Discharge Mass-Spectrometer ("Finnigan Element GD", Germany).

3 RESULTS AND DISCUSSION

VP and OP methods during EBM are based on the separate evaporation/distillation of components that have different partial pressures of saturated vapor (Fig. 1a). At the same temperature and pressure during the technological process, the components with higher partial pressure (vapor elasticity), taking into account their distribution coefficient/activity in the melt/solvent that is more preferable, are refined from the melt [5-9]. The refining kinetics significantly depends on technological parameters, since real processes take place under significantly non-equilibrium thermodynamic conditions.

For a qualitative assessment of the possibility of refining during the evaporation of impurities from molten Si in a vacuum under non-equilibrium conditions, the Olette thermodynamic parameter is used [5, 6]:

$$\alpha = (\gamma_i P_i) / (\gamma_{Si} P_{Si}) \cdot [M_{Si} / M_i]^{1/2},$$

where γ_i, γ_{Si} are Henrian activity coefficients of the i-impurities and Si, respectively, P_{Si}, P_i are the vapor pressures of pure Si and i-impurities at a given temperature, M_{Si}, M_i are the atomic weights of Si and i-impurities.

To study the possibility of refining MG-Si from impurities with low partial pressure (B, P, Bi, etc.) during EBM, the OP method was used. The EBM (OP) method consists in treating the melt with gases/steam containing an oxidant (oxygen, water steam, etc.) with a high chemical affinity for such impurities with the formation of more volatile compounds/oxides, the saturated vapor pressure of which is higher than that of the corresponding pure elements (Fig. 1b) [8, 9].

An additional factor of impurities refining during EBM is their grinding and partial removal due to local overheating of inclusions in a zone of high-energy exposure of EB. In this case, impurities that differ significantly in their thermophysical parameters (thermal conductivity, heat capacity), compared to the main component of the melt (Si), are rapidly overheated, partially sublimated, destroyed and removed from the melt. The described process (in the form of "micro-explosion" with partial removal of material particles from the surface of the melt) is often observed visually during the EBM process of metals and alloys in general and MG-Si in particular.

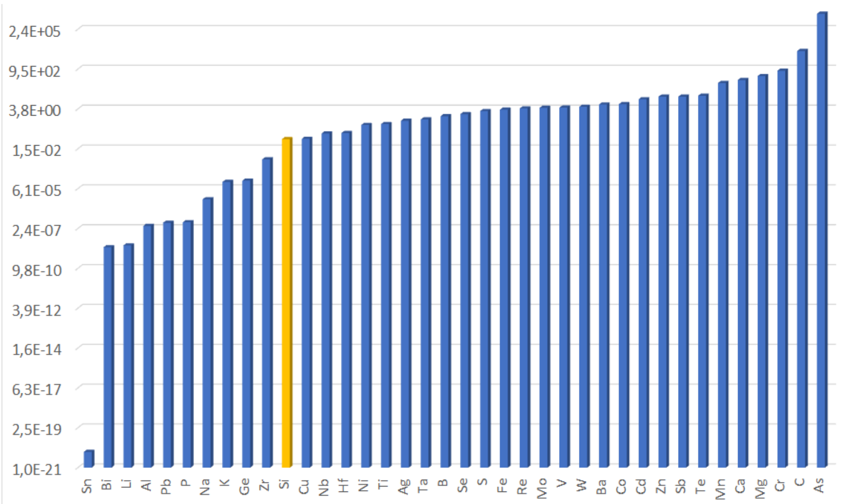
The analysis of the chemical composition of obtained UMG-Si ingots has confirmed the high efficiency of EBM (VP) of MG-Si from metal impurities Cr, Al, Mg, Ca, Ti and also confirmed the promising possibility of refining MG-Si from B and P during EBM (OP) [3].

The results of the study of the microstructure and residual impurities in polycrystalline UMG-Si EBM ingots (VP/OP) are presented in this paper. The obtained UMG-Si EBM ingots had significant internal stresses and were destroyed by a mixed mechanism of brittle fracture. These cracks were noted both on the surface of the grain/crystallite boundary (intercrystallite fracture) and through the grains themselves (transcrystallite fracture) (Fig. 2).

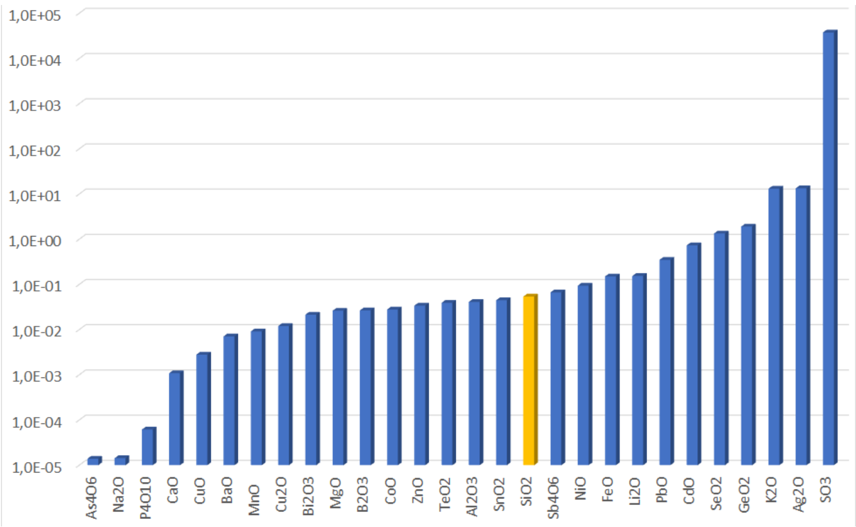
The microstructure of samples cut from UMG-Si EBM (VP) ingots is characterized by columns of columnar grains/crystallites (Fig. 2a). The inner part of such ingots has a wide columnar structure. The cross-section of crystallites with a width of 0.2-0.5 mm and a length of 1-2 mm, their main axis coincides with the direction of crystallization (normal to the surface of solidification). The edge parts of the ingots that were in contact with the copper water-cooled crucible are also characterized by a columnar structure with smaller crystallites (width up to 0.1 mm, length up to 0.3 mm), oriented radially.

Studies of the structure of cross-sections and fracture surfaces of samples cut from UMG-Si EBM ingots (VP) showed that inclusions are randomly distributed in the body of crystallites/grains of Si. The average size of inclusions is about 50 μm.

The microstructure of samples obtained from UMG-Si EBM (OP) ingots is generally similar to the structure of UMG-Si EBM (VP) ingots (Fig. 2b) with a predominance of columnar crystals. In the cross section, such columnar crystallites reach 0.2-0.5 mm with a length of 1-2 mm, their main axis is also parallel to the direction of crystallization.



a- impurities in Si



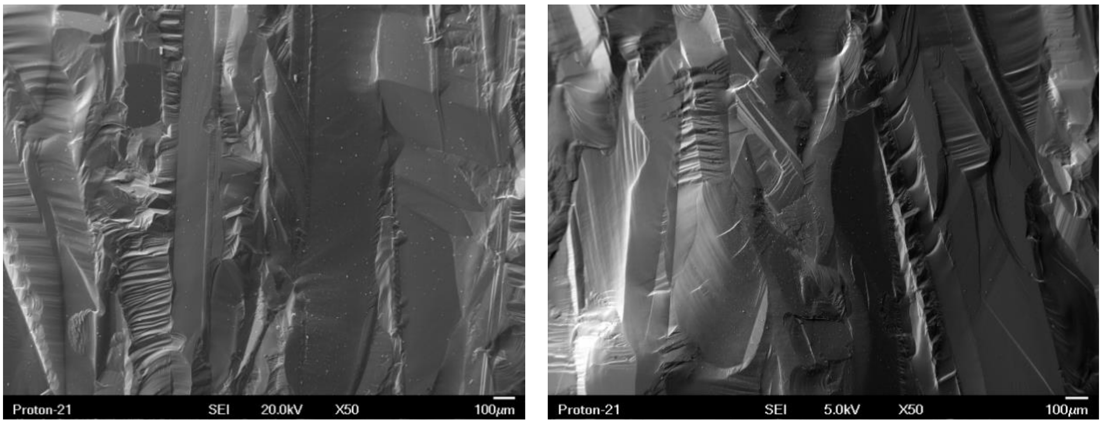
b- impurities in Si (oxides)

Fig. 1 – Saturation vapor pressure of impurities (a) and oxides (b) at a temperature of their melting, Pa

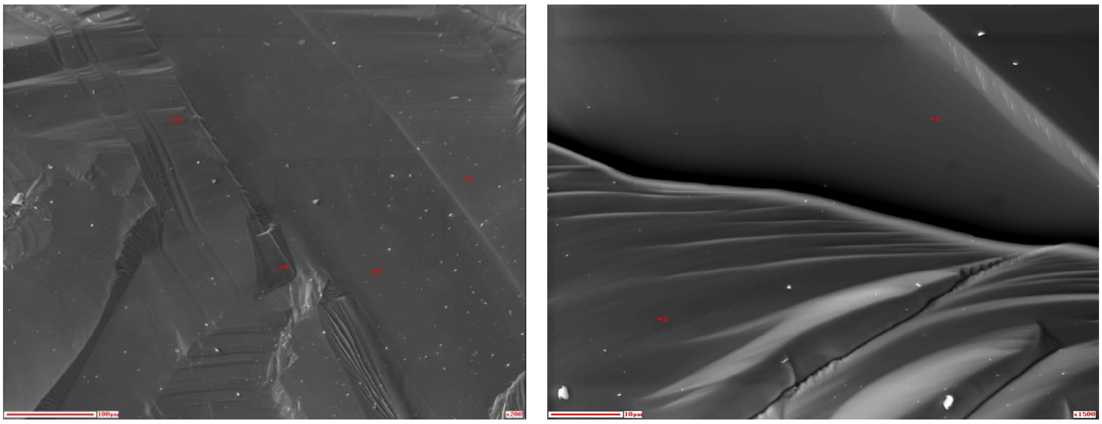
Randomly distributed impurities are also observed in UMG-Si EBM (OP) crystallites. The difference between UMG-Si EBM (VP) is the increased size of such impurities/inclusions to 80-140 µm, which may indicate their coagulation and their total quantity (Fig. 2b).

Comparative studies of the microstructure of UMG-Si EBM (VP) (Fig. 2a) and UMG-Si EBM (OP) (Fig. 2b) showed that the structure of ingots obtained does not depend on the type of VP/OP refining process used and is determined by the thermophysical conditions of their solidification. Impurities/inclusions in ingots are located randomly, mainly in the body of silicon grains/crystallites. Their average size is 50 µm after EBM (VP) and 80-120 µm after EBM (OP).

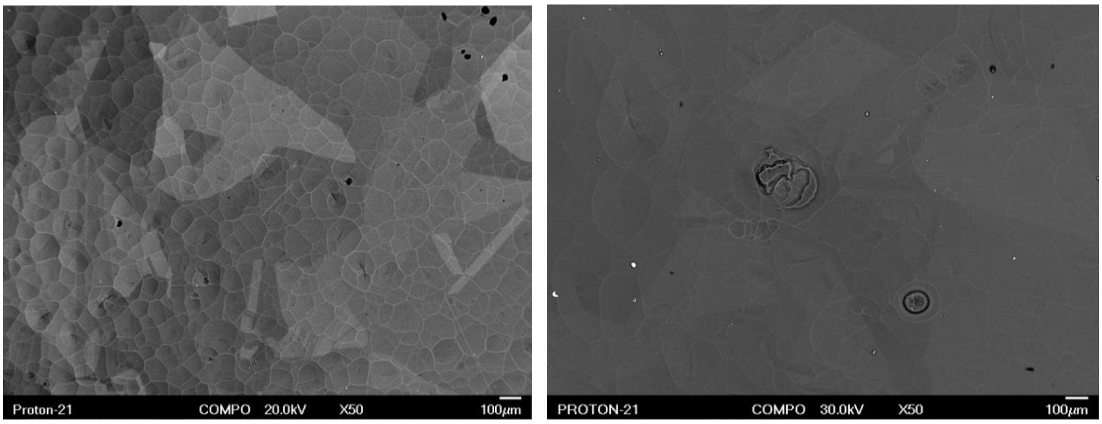
surface of broken (small scale)



surface of broken (large scale)



surface + impurities (COMPO-regime)



a- vacuum purification (VP) b- oxygen purification (OP)

Fig. 2 – SEM microstructures of UMG-Si EBM after VP (a) and OP (b)

In the obtained UMG-Si EBM ingots, there is a noticeable segregation of impurities with an increase in their number towards the center of the free surface of the melt, which solidified last. This is partly explained by the peculiarities of the process of solidification of ingots in a water-cooled crystallizer during EBM with concentration subcooling due to the difference in the solubility of impurities in the melt and solid phase and the effect of directed solidification. At the same time, the convection currents in the melt caused by the scanning/unfolding of the EB on its surface prevent the formation of concentration inhomogeneity of impurities in the liquid phase before the crystallization front, which is confirmed by the absence of segregation of impurities along the grain boundaries in the studied ingots.

Analysis of the Auger-spectrum from the surface of the boundaries and the grain body of the samples obtained by EBM (VP/OP) confirmed their almost identicalness and the absence of impurity segregation along the grain boundaries. A qualitative analysis of the chemical composition of the inclusions in the obtained ingots (Fig. 3) shows that most of them are autonomous single-element phases of residual impurity elements and low-component micro-impurities with a ratio of elements in their chemical composition similar to those in the initial MG-Si – the "heredity effect".

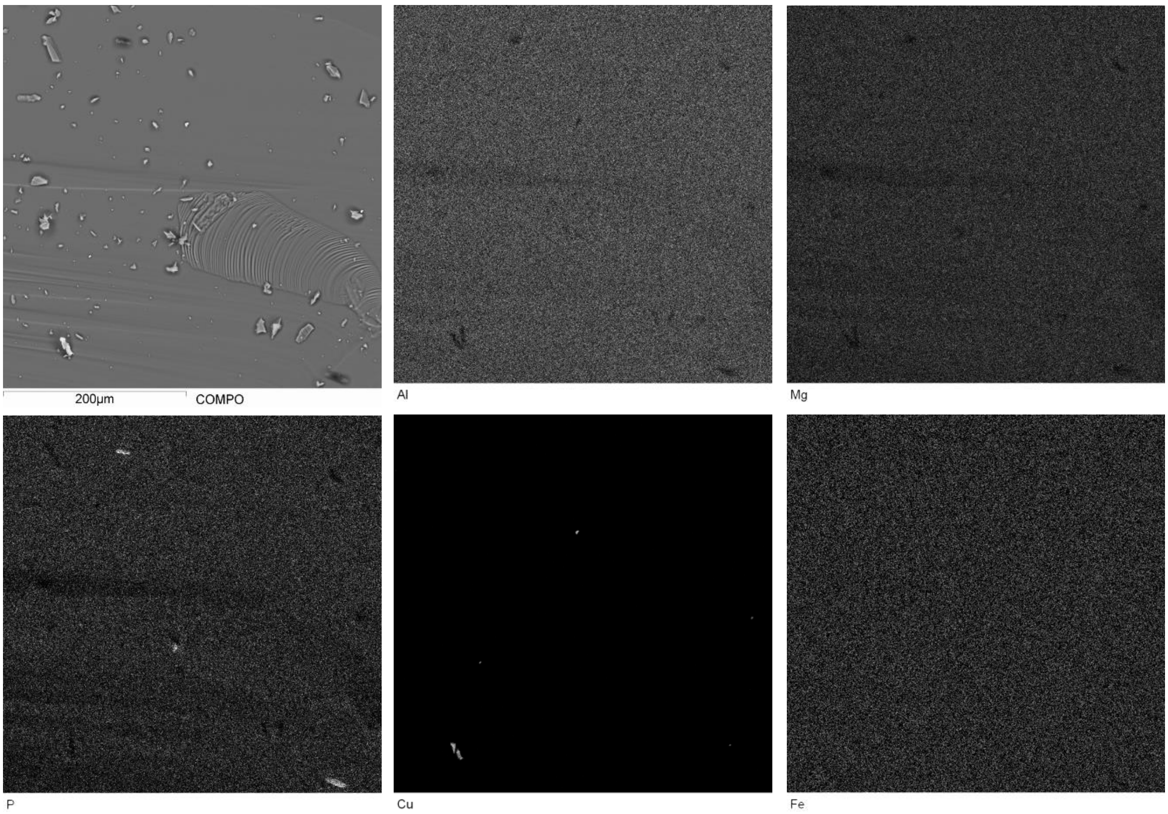


Fig. 3 – Distribution of separate chemical elements by structure/impurities of UMG-Si ingot after EBM (VP)

4 CONCLUSIONS

The structure of UMG-Si EBM ingots is predominantly columnar with a radial arrangement of crystallites on the vertical sides of the ingots and an axial arrangement along the bottom and towards the center and is independent of the EBM method (VP/OR). Most columnar crystallites have a cross-section of 0.2-0.5 mm and a length of 1-2 mm, their main axis is parallel to the direction of crystallization (normal to the surface of solidification).

The results of the research have confirmed the sensitivity of the size of the impurities/inclusions and their coagulation to the method of refining MG-Si (VP/VO) during EBM, in contrast to the size of the crystallites. As a result of EBM (OP) MG-Si, the sizes of residual impurities/inclusions in such ingots are 2-3 times greater than the sizes of impurities in UMG-Si EBM (VP) ingots, while the quality of such impurities is significantly smaller with a corresponding increase in the average electron path length/electrical conductivity of UMG- Si EBM compared to the initial MG-Si.

The use of the sensitivity to coagulation of impurities makes it possible to exert a controlled influence on their distribution in the melt during EBM of MG-Si by choosing/combining the required refining method (VP/OP).

The lack of segregation of impurities on the grain boundaries in UMG-Si EBM ingots has been confirmed experimentally.

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Особливості сегрегації включень та мікроструктура зливків кремнію, отриманих електронно-променевим рафінуванням металургійного кремнію

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Насьогодні кремній сонячної чистоти (SG-Si) залишається головним матеріалом для виготовлення фотоелектричних перетворювачів (ФЕП), які широко використовуються у відновлювальній енергетиці. Підвищення ефективності ФЕП при зниженні собівартості виробництва та посиленні екологічних вимог є актуальною задачею для прикладної науки й розвитку технологій. Рішення цієї проблеми пов'язано у тому числі з методами вакуумного (VP) та окислювального (OP) рафінування під час електронно-променевого переплаву (EBM) металургійного кремнію (MG-Si). У роботі досліджено вплив VP та OP на мікроструктуру зливків кремнію, отриманих електронно-променевим рафінуванням. При цьому експериментально встановлено, що структура зливків не залежить від виду використаного рафінування VP/OP при EBM та визначається виключно технологічними/теплофізичними умовами їх тверднення. Структура отриманих зливків складалась переважно із стовбчастих кристалітів, головна вісь яких є перпендикулярною/нормальною до поверхні кристалізації. В отриманих зливках покращеного металургійного кремнію (UMG-Si), отриманого EBM, відзначається помітна сегрегація включень/домішок із збільшенням їх кількості в напрямку до центру вільної поверхні розплаву, який тверднув/кристалізувався останнім. При цьому відзначено чутливість розмірів включень до використаного способу рафінування металургійного кремнію VP/OP, на відміну від розмірів кристалітів. У зливках кремнію, отриманих електронно-променевим рафінуванням, підтверджена відсутність сегрегації домішок/включень до границь зерен, незалежно від обраного способу рафінування (VP/OP). Аналіз хімічного складу включень в отриманих зливках підтверджує наявність ефекту «спадковості» – переважна більшість включень являють собою автономні одноелементні фази залишкових домішкових елементів та малокомонентні мікровключення зі співвідношенням елементів їх хімічного складу, подібним до таких у вихідному MG-Si.

Ключові слова: Рафінування, Структура, Включення, Домішки, Сегрегація, Коагуляція, Металургійний кремній покращеної якості, Електронно-променеве переплавляння.