UDC 621.315.592

T.V. Kritskay [1], professor, d.t.s.
P.V. Kuz'min [2], dep. of general director

MODERN TECHNOLOGIES OF QUARTZ CRUCIBLES FOR SINGLE-CRYSTAL SILICON METALLURGY

[1] Zaporozhe state engineering academy, Ukraine,
[2] LTD. «Polychem», Tula area, Yasnogors, Russian Federation

The analysis of modern technologies of receipt of quartz crucibles is executed for the production of «sun» silicon single-crystals and electronic quality. Influence of kind and concentration of admixtures is shown in material of crucible on the receipt of high-quality single-crystals. Basic technological receptions, allowing to reduce the cost of crucible, promote his mechanical properties and stability to the protracted influence of high temperatures, are adopted.

Keywords: quartz crucibles, polymorphic modifications of quartz, admixtures, gas including, method of electric arc building-up

The great demands to the cleanness, mechanical durability, geometrical sizes, to reactionary ability in touch with fusion of silicon, maintenance of the gas including and other to the crucibles, intended for the process of growing of single-crystals on the method of Chokhralsky are presented. Calculations of sizes and thickness of crucible wall for providing of it durability, carried out on the basis of modeling for conditions of exploitation (distribution of temperature on a surface, duration of melting, axial, radial gradients of temperature, character of convective streams in fusion, presence of overhead after heaters). Leading firms on the production of quartz crucibles in the world were: «Toshiba Ceramics», «Japan Super Quartz Corporation» (Japan), «GE» (USA), «Heraues» (Germany), «Saint-Gobain» (France), «Shin-Etsu» (China). Producible crucibles are used the receiption of single-crystals by diameter from 100 to 450 mm.

The known industrial method of receiption for synthetic quartz crucibles a steam phase hydrolysis of $SiCl_4$ or decomposition of SiH_4 in the stream of oxygen-hydrogen plasma (1100-1300 °C). The maximal diameter of crucibles, produced by this method in the USSR, made a 406 mm [1].

Presently quartz crucibles in the world are produced by the method of electro arc building-up in the revolved form (rotor technology). Thus grouts of natural quartz (sorts, analogical Iota standard, Iota-4 and other of firm «Unimin» USA), exposed to melting in a voltaic arc with simultaneous forming. Mechanical treatment external of surface and edge of crucible provides exact accordance to the set geometrical sizes. For the obtaining crucibles chemical composition is controlled. Chemically attained and washed crucibles must be kept in the vacuumized polyethylene packing [2].

In the process of growing on the border of division the «fusion-silicon crucible-atmosphere of growing» takes place chemical reaction with formation of volatile monoxide of silicon *SiO*. Because of thermodiffusion and existing convective stream in fusion, admixture contained in material of crucible pass to fusion and growing single-crystal. Quartz glass, being mixture of polymorphic crystalline modifications of dioxide silicon thermodynamics unsteadily in a sufficient degree. At heating to the

plastic state (> 1170 °C) glass passes to the stable for this temperature crystalline phase - cristobalite. Along with the increase of mechanical durability of crucible, formation of cristobalite results to the origin of mechanical tensions, appearance of cracks, and at same cases to partial destruction of internal surface of crucible. The scaling particles of cristobalite can be taken by convective streams in fusion and to get in the area of crystallization, resulting at violations of structure of growing single-crystal.

The contents of oxygen in a single-crystal in a substantial degree is determined by speed of dissolution of quartz crucible in fusion of silicon $1{,}38 \cdot 10^{-6}$ g/sm^2·s [3], which depends on the temperature of crucible wall, character of convection in fusion and content of hydroxy-groups *OH*¬ in a quartz.

The gas including (O_2, N_2, *CO*, CO_2 of and other) as bubbles measuring ~ 15-35 mcm there always are in material of quartz crucible. As a result of quartz co-operating with fusion it is appearance of new bubbles and their confluence with already existing.

Admixtures, contained in material of crucible, in the process of growing pass to fusion, contaminating it and growing single-crystal. Therefore an important role at the estimation of quality of quartz crucible is played the factor of its moistening by fusion, qualificatory kinetics of dissolution of quartz. On the pin corner of moistening of meniscus form of fusion and, accordingly, adhesion of silicon depends to the surface of crucible, having influence on speed of growing and accident-freeness of process (because of absence «parasite» crystallization from the crucible wall).

In connection with passing to the processes of growing from fusion of large mass the methods were worked out, controlling speed of formation of cristobalite, in particular, there are applied coverages, containing activators of crystallization. As activators a barium, magnesium, strontium, titan, zirconium, hafnium, can be used. Activators can be used in many chemical forms of organic and inorganic compounds, including., oxides, hydroxides, peroxides, carbonates, carboxylates, silicates, oxalates, acetates, propionates, salicylates, stearatess, fluorides, chlorides of and other. In particular, at formation of coverages by causing of oxides *Ca*, *Mg*, *Sr*, *Ba* their quantity on the square centimeter of surface is $1 \cdot 10^{-9}$-$1 \cdot 10^{-6}$ moth/sm^2. Sintering of oxides is produced at 400-1200 °C, thickness of coverage – 0.01-0.10 mcm. For the increase of coverage firmness furnace-active matters add to solutions and suspensions in crucible subject a microwave radiation (800-1500 MHz) and it maintain at a temperature 600-800 °C. Coverage can be inflicted both on the internal and on outward surfaces of crucible. Coverages on the internal surface of crucible, containing connections of *Zr* or *Hf*, additionally render the regulative affecting at concentration of oxygen in single-crystals. Life cycle of crucibles with coverages increases on 18-20 hour, as compared to ordinary crucibles, at conditions of exploitation [4-6].

The modern technology of multi-layered crucibles is provided necessary quality. For example, the double-layer crucible has an opaque external layer, formed from the fire-polished groats of natural quartz, and transparent layer on the internal surface of crucible from a fire-polished specially inflicted synthetic quartz. Through a

fire-polished layer bubbles do not pass practically, and at the special alloying of layer for synthetic quartz in general in him fail not appear.

Conclusion. Leading world companies are produce quartz crucibles with the use of method of electro arc building-up (rotor technology) and wide nomenclature of high-quality parameters. The use of mixtures of different sorts of groats from a natural and synthetic quartz which strengthens the catalytic action of activator of crystallization is possible. The different kinds of coverages from the alloyed quartz provide realization of processes of growing during 60-100 hour, including the cycles of meltback and loading charge.

LIST OF LITERATURE

1. Способ получения синтетических кварцевых тиглей [Текст]: пат. 2061111 Рос. Феде-рация: МПК С 30 В 29/00, С 30 В 15/00 / Петрик А. Г., Кононенко Е. К., Пометун Б. В. и др. ; заявитель и патентообладатель Запорож. титано-магниевый комбинат (Украина). – заявл. 31.03 1992; опубл. 27,05.1996.
2. Технические требования к кврцевым тиглям производства ПХМЗ [Электронный ресурс] – Режим доступа : \www/ URL http://pcmp.ru/catalogue/show_product/5/. – Загл. с экрана.
3. *Львов*, *А. Ю*. Взаимодействие кварцевого стекла с расплавом высокочистого кремния [Текст] : автореф: дисс. … канд. хим. наук : 02.00.19 / А. Ю. Львов ; [Ин-т химии высокочистых веществ РАН]. – Нижний Новгород, 1993. – 21 с.
4. Способ подготовки тигля для выращивания монокристаллического кремния по методу Чохральского [Текст]: пат. 2354761 Рос. Федерация: МПК С 30 В 15/10, С 30 В 29/06 / Берингов С. Б., Шульга Ю. Г., Куликовский Э. В. и др. ; заявитель и патентообладатель ЧАО «Пиллар» (Украина). – заявл. 26.09.2005; опубл. 27.02.2011.
5. Способ подготовки кварцевых тиглей для выращивания монокристаллов кремния [Текст]: пат. 2354761 Рос. Федерация: МПК С 30 В 15/10, С 30 В 29/06 / Супоненко А. Н., Соколов Е. Б. ; заявитель и патентообладатель ООО «Русский кремний». – заявл. 18.12.2007, опубл. 10.05.2009.
6. Способ подготовки кварцевых тиглей для выращивания монокристаллов кремния [Текст]: пат. 2355833 Рос. Федерация: МПК С30В15/10, С30В29/06 / Супоненко А. Н., Соколов Е .Б. ; заявитель и патентообладатель ООО «Русский кремний». – заявл. 18.12.2007, опубл. 20.05.2009.