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Review

Growth of Si Crystals in Rectangular Shape for the Solar Cell Application

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Conventionally grown Czochralski (Cz) silicon crystals for photovoltaic application are of un-favourable cylindrical shape leading to essential material loss during the wafer cutting process. Additionally, the typical high oxygen concentration promotes the solar cell degradation. In this paper the attemps to grow Cz silicon crystals with both quadratic cross section and relatively low as-grown oxygen content are summarized. A favourable technique is described wich allowed the pulling of 10 cm long rectangular Cz ingots with square coss section of 91×91 mm^2 and interstitial oxygen content of 7×10^{17} cm^{-3} by {110} facetting along the [001] orientation. In order to obtain stable very low radial temperatur gradient at the melt-solid periphery, as a prerequisit of pronounced facetting, traveling magnetic fields (TMF) have been applied. Such non-steady magnetic field is generated simultaneously within the heater around the crucible. It induces a very stable high-speed toroidal convection roll between crucible and growing crystal graduating the temperature distribution along the free melt surface that promotes the apperance of large {110} facet.

1. Introduction

The basic photovoltaic (PV) material during the next decades remains still bulk silicon in the form of multicrystalline (mc) and monocrystalline ingots. Considering the still too high material cost the optimization of the crystal growth process is a focal point. Although structural drawbacks mc-ingots have an essential economical advantage over nearly perfect Cz crystals - the rectangular shape that enables a nearly lossless cut into columns which turn are sawed into quadratic wafers. On the other hand the cylindrical Czochralski geometry implies a considerable silicon loss during crystal cutting. In order to obtain square wafers with edge lengths of 125 and 150 mm, conventional Cz crystals of cylindrical shape with respective diameters of 175 and 200 mm are needed, leading to cutting-related material losses of 25 and 28% of immediately used Cz silicon, respectively. Thus, the growth of perfect Cz silicon crystals with quadratic growth section and, preferable, with reduced oxygen content, would be a rewarding challenge for the today crystal growers.

The idea of shaped crystal pulling from the melt is not new. Especially during the sixties and seventies many efforts have been intensified to grow crystals of such advantage geometry$^{1)}$. For instance, during the period of 1969-1973 Stepanov's group reported the pulling of germanium crystals with cross section of 30×30 mm^2 from a non-wetting swimming die with a rectangular orifice made of graphite$^{2\text{-}4)}$. To form a meniscus of quadratic cross section above the non-wetting orifice the die was slightly pressed into the melt surface. During the seeding process, however, the forming of such meniscus geometry was not yet exercised due to the dash necking. Only after the thin concentric shoulder reached the length of about 12 cm the stable rectangular pulling regime could be started. Jegorov et al.$^{5)}$ mentioned the complicacy to obtain sharp meniscus edges in the non-wetting die corners and proposed their replacement by a wetting material, e.g. tungsten. Probably, the missing of related reports on silicon in the time following was due to the not yet available non-wetting die material for molten Si. Today, the performance of repeating attempts with silicon by using nearly non-wetting BN or Si_2N_2O/Si_3N_4-coated fused silica dies could be of certain interest. However, all crystal growth arrangements applying special meniscus shaper are of enhanced impurity contamination via the die.

An interesting thermal solution has been reported by J.G. Posa in 1979$^{6)}$. The Motorola Inc. used a square die that acted as a thermal shaping device without capillary effect. Additionally, the temperature zones on the melt surface were squarish. As a result the ingot assumed a squarish cross section as it passed through the die as it was pulled from the

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melt. In contrast to the uniform rotation a quick 90° turn was used. The crystal remained stationary and aligned with square die for about 15 seconds while it grew corners and sides. Then it was undergoing a second 90° rotation so as to be in line with the square die again for continued growth. At [001] seed orientation the ingots were 2 inches on a side. Unfortunately, no informations about side orientation, crystal length and quality have been provided. Also, no more additional reports have been found in the literature since that publication.

A contactless electromagnetic shaping was introduced in 1971 by Artyschevskij et al.[7,8] applying rectangular RF inductors during floating zone (FZ) melting of silicon. To form a quadratic cross section of the molten zone an inductor with central rectangular orifice was used. Various inductor designs were tested in order to homogenize the temperature field by current path engineering (see refs. 7,8). Recently, at IKZ Berlin a likewise technique has been reported for successful FZ growth without rotation of dislocation-free silicon crystals with square-like cross section of 100×100 mm^2. If it proves possible to enlarge the area towards 150×150 mm^2, and ensure a satisfactory crystal lenght such PV silicon production would be of certain advantage because FZ-grown material is of highest purity, especially regarding transition metals, oxygen and carbon.

The present paper summarizes the provisional results of facetting-based rectangular Cz crystal growth without any shaping element by using crucible and seed rotations like during standard Cz process but in much lower radial temperature gradients. In 1980 Kuroda et al.[10] described such self-shaping effect of Czochralski silicon crystals. Independently on seed and crucible rotation, a rectangular crystal profile with quadratic-like cross section was formed due to the appearance of the four {110} facets parallel to the [001] growth direction. Wafers with edge widths of ~70 mm cut from such crystals were demonstrated (see Fig. 1 in ref. 10). Unfortunately, no crystal lengths were mentioned in this paper and no further publications were given by this group. Later, our team reported the pulling of 3-4 cm long [001]-oriented GaAs crystals with nearly quadratic cross section defined by four {110} planes of widths of about 25 mm[11, 12]. Also this crystal shape appeared in very low radial temperature gradients obtained by the vapour pressure controlled Czochralski method without liquid encapsulation[11].

It should be noted that polyhedrical growth tendency, called "crystal facetting", is a characteristic feature in growing dielectric crystals[13, 14]. This is due to the low surface energy of the main crystallographic planes corresponding with high entropy of fusion of these materials. Semiconductors show lower enthalpy of fusion and, thus, their main planes are of higher surface energies. There raises question on shape and length stabilities when such growing crystal is formed by self-facetting. Obviously, the cardinal challenge proves to be the achievement of strong stability of the required low radial temperature gradient which can be considerably disturbed by stochastic thermal convection and, especially, turbulences in large crucibles when no additional stabilizing measure is applied.

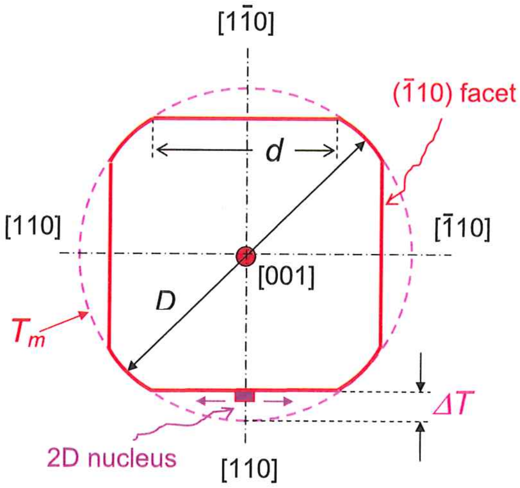

Fig. 1 Scetched cross section of a [001]-oriented Cz crystal with four {110} facets growing in a concentric isotherm field (T_m-melting point isotherm, ΔT-supercooling to be required for 2D-nucleation at the facet center, D-cross section diagonal, d-facet width).

We showed by numerical simulations[15, 16] and proved experimentally[17] that an induced downward directed TMF of certain frequency creates favourable convective prerequisites for a highly stable temperature regime.

2. Fundamentals

Facets form normal to crystal directions for which 2-D nucleation is required in order to initiate the growth of a new layer. On non-facetted ("atomically rough") surfaces atoms can be added singly without the need for nucleation. At a given growth temperature, the crystals will have most surfaces which are atomically rough. However, there are one or more surfaces which are "smooth" requiring nucleation[18]. Early on Jackson[19] provided a simple thermodynamic model which indicated that the magnitude of the entropy of fusion of a material was a guide to its likelihood of forming facets during growth, materials having a low enthalpy of fusion (such as metals) having lowest probability.

The common semiconductor materials, with their covalent bonding, tend to form facets during melt growth only on their most close-packed planes. Following the Jackson criterion[19].

$$a = \frac{\Delta H_{LS}}{RT_m}\frac{Z_A}{Z_V} \tag{1}$$

with ΔH_{LS}-enthalpy of fusion of melt-solid transition, R-gas constant, T_m-melting temperature, Z_A/Z_V-ratio between nearest neighbour sites in the surface area A and in the crystal volume V (Z-coordination number), in silicon the $\Delta H_{LS}/RT_m$ relation is 3.5 (with $\Delta H_{LS} = 50$ kJ mol^{-1}). Hence the Z_A/Z_V ratio decides whether the given face is atomically rough ($a < 2$) or smooth ($a > 2$). Considering an abrupt phase boundary between melt and solid in silicon the {100} planes become atomically rough due to $Z_A/Z_V = 0.5$ ($a \approx 1.7$). The {111} faces, however, tend to be atomically smooth with $Z_A/Z_V \approx 0.8$ ($a \approx 3$) when for the determination of the Z_A/Z_V ratio the zigzag courses of the periodic bond chains (PBCs) between nearest neighbours within the surface double-layers are considered[20]. The determination of the a-factor of {110}, however, is somewhat more complicated due to the "pinnacle" face relief. It can be assumed that a is in the region 0.6-0.7 otherwise no faceting effect would be observed. In fact, we observed that in Cz Si crystals grown in low temperature gradients next to {111} facets also {110} ones do appear (see images in Fig. 5 of ref.17, for example). Note, for us the Jackson-factor serves as a sufficient rule. Of course, for precision a Temkin-Bennema analysis[20], not yet found for the diamond structure, would be recommended.

A further, geometric, requirement for facet formation during Czochralski crystal growth is that the radial temperature gradient be such that the freezing point isotherm is concentric when viewed along the crystal axis (Fig. 1). This ensures that, if the "atomically smooth" crystal planes starts to lag behind the isotherm, it experiences an increased supercooling which ultimately promotes the nucleation of a new layer. Then, if a [001] seed orientation is used the growing crystal body can be self-profiled by the four {110} facets parallel to the pulling direction. Following Kuroda's estimation[10] in a concentric isotherm field the facet width d becomes.

$$d \approx 5\,\Delta T/G_T \tag{2}$$

with ΔT-undercooling between melting point isotherm and facet centre to be required for 2D-nucleation (~2 K for {110} planes; see Fig. 6 in ref.17) and G_T-radial temperature gradient. As can be seen the facet width increases with decreasing temperature gradient. While for a {110} facet of width of ~100 mm the radial G_T should be around 1 K cm^{-1}, for a size of ~150 mm its value must be reduced to 0.7 K cm^{-1}. This can be well controlled by travelling magnetic fields.

As it was shown by Miller et al.[15, 16] numerically a downward directed TMF of frequency $f = 300$ Hz generates a very fast toroidal convection roll between crucible wall and growing crystal with velocity $v = 115$ mm s^{-1}. Such a fast and stationary rotating convection roll guarantees a stable flat temperature profile at the melt-solid interface periphery caused by the temperature grading along the melt surface between crucible and growing crystal. Even harmful fluctuations are depressed very effectively[15]. As a result stabilized {110} facets of nearly constant width can be developed. On the other hand, when an upward directed TMF is used the radial component of the temperature gradient is increased leading to a cylindric-like crystal geometry without pronounced facetting.

3. Experimental results and discussion

Undoped [001]-oriented Si single crystals of quadratic cross section have been grown. According to the numerically simulated temperature field the radial temperature gradient near the growing crystal periphery was in the range of 1-2 K cm^{-1}. The induction of the TMFs was carried out by applying the KRIST*MAG*® principle[21, 22] whereupon the TMF and melting heat are generated simultaneously in the graphite heater close around the crucible. For that the standard meander-like heater design was changed to a spiral one consisting of subdivided coil segments with contacts for the phase-shifted power supply in star connection. About one order of magnitude of power can be saved when the magnetic field is no longer separately generated outside the growth vessel and a very effective exercise of the influence on the melt flow and interface shape is possible. In order to control the magnetic and heat fields independently such a heater-magnet-module (HMM) is supplied by a respective AC/DC combination which is delivered by a newly-developed power unit and control system[21]. Both, three-phase well-formed sinus AC of the desired frequency with phase shift for TMF generation and a DC component for controlling the melting and crystallization temperature are supplied to the HMM. Such heater-magnet arrangement for growth of rectangular Cz crystals was placed inside an industrial Czochralski puller as was described in detail elsewhere[17, 22]. The TMF parameters could be varied in a wide range, i.e. in the traveling direction (down- or upwards), in frequency $f = 20\text{-}600$ Hz, and in phase shift $\phi = 5 - 120°$. Maximum induction of B ≈ 10 mT could be achieved. The vertical solid temperature gradient at the interface was GT ≈ 30 K cm^{-1} and the pulling velocity $v = 10 - 60$ mm h^{-1}. 2 kg charges of standard high-purity raw silicon from Wacker were used as starting charges in 6-inch fused silica crucibles. For comparison, also test runs with upgraded metallurgical-grade (UMG) silicon were carried out. Rotation rates of $\omega_c = 5 - 10$ rpm and acw $\omega_x = -5$ rpm have been applied for crucible (c) and seed rotation (x), respectively. To fix the melting point isotherm position during the growth run the crucible was translated upwards with rates of $1-4$ mm h^{-1}. Argon gas with flow rate of 5 l min^{-1} was applied as atmosphere. After finishing the growth the crystals were cooled down to room temperature with a rate of 500 K h^{-1}.

Si single crystals with reproducible square cross sections up to lengths of 10 cm have been grown at frequencies $f = 60 - 300$ Hz and a phase shift of $\phi = 90°$ (Fig. 2). Geometrically well-shaped wafers can be obtained by equidistant dissection of the as-grown crystal bodies without considerable material loss (Fig. 2).

In Fig. 3 two snapshots from a live recording during a growth run are presented. Note, in our growth set-up, being yet of markedly reduced scale compared with industrial Si Cz standard pullers, only relatively small crystals with maximum cross section diagonals D up to 107 mm could be grown. Accordingly, quadratic cross sections with rounded corners (see Fig. 2) of maximum area 91×91 mm^2 and side facet widths of $d = 5.6$ cm have been observed. Inserting in Eq. (1) $d \approx 5.6$ cm and $G_T \approx 1-2$ K cm^{-1} becomes an undercooling value of ΔT for {110} facets in the range of $1-2$ K. To take the ΔT from eight puling experiments under a TMF frequency of $f = 300$ Hz a mean undercooling value of about 2 K could be deduced[17]. To the authors knowledge such systematic undercooling studies even on {110} facets in silicon are still missing in the literature. Kuroda et al.[10] assumed a nearly similar value of ≈ 1 K. In comparison to that a lower effectire $\Delta T \approx 0.5$ K has been deduced on crystals grown under a lower frequency (because the facet undercooling should be a material related constant) $f = 180$ Hz or/and from UMG feedstock. Such features could be explained by increased radial temperature gradient due to the reduced vortex rotation velocity at lowered TMF frequency but also to the increased atomical roughness, i.e. enhanced nucleation density, in case of more contaminated UMG material. However, more systematic research is still required.

Fig. 2 As-grown rectangular Si Cz crystal (left) and a wafer cut from such crystal (right).

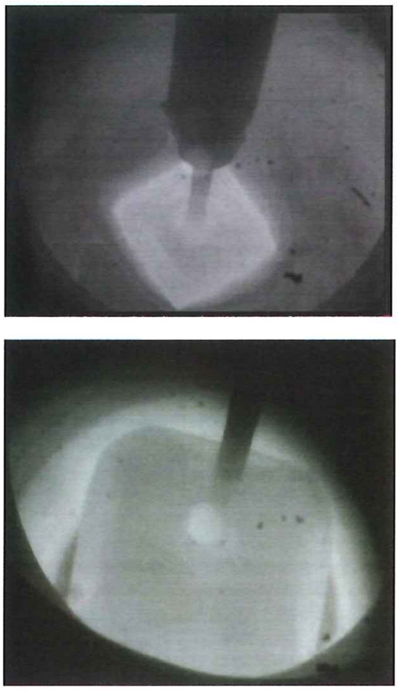

Fig. 3 Snapshots from live recording during a growth run under downward directed TMF. Already the shoulder shows well pronounced squarish shape (above) before the crystal body is growing with nearly constant cross section (below).

In order to study the microscopic morphology the edges of slices cut perpendicular to the {110} facets were investigated by high-resolution transmission electron microscopy (HRTEM). A surprising result was obtained. As can be seen from Fig. 4 the surface is formed by alternating {110} terraces and {111} steps. Such {111} prevailing could be expected due to the obviously higher atomical smoothness of the {111} planes compared to {110}. Strictly speaking, the appearance of {111} steps contributes to a minimal shrinkage of the cross section during the constant pulling phase.

For the measurement of the etch pit density (EPD) the examples were polished and subsequently etched at 300 K by using standard General Electric etchant consisting of 1:2:4 hydrofluoric, acetic and nitric acid, respectively. Densi-

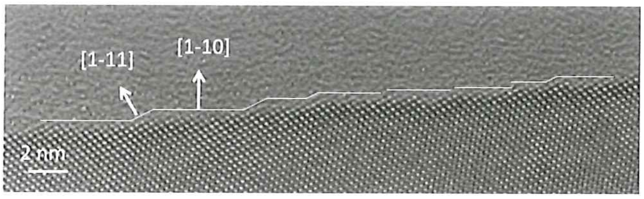

Fig. 4 HTREM image from the edge of a cut parallel to the {110} plane. As it is seen the plane is composed of alternating {110} terraces and {111} steps.

ties between 0 and 10^4 cm^{-2} have been detected. In high-purity crystals, the predominant crystal volume shows zero EPD. Sometimes sporadic dislocation bundles, especially, in the crystal centre have been observed which have, however, no relation to the quadratic growth principle but is rather related to the still omission of special necking procedure after the seed dipping. In crystals from UMG material an enhanced axial EPD between 10^3 cm^{-2} at the top and 10^5 cm^{-2} at the tail has been found. However, already at the present stage of development the crystal structure would meet the demands of conventional solar wafers.

As it is well known the oxygen concentration is of critical role in PV silicon. The lower its content the higher is the stability of the start value of solar cell efficiency. During standard Czochralski growth the essential drawback proves to be the partial convective transport of SiO, generated by oxygen release from the crucible wall, under the melt-solid interface and, thus, incorporation into the growing crystal. Hence, it is of highest interest to analyse the oxygen content even in Cz crystals grown under TMF where a stable toroidal convection roll between crucible and crystal periphery is induced. Such convection regime makes the SiO transport to the free melt surface and its removement by evaporation much more effective. In the obtained rectangular crystals the content of interstitial oxygen $[O_i]$ was measured along the growth direction and crystal cross diagonals by local vibrational mode (LVM) IR-absorption at room temperature. Typically, homogeneous distributions of oxygen have been observed, radially and axially17). Table 1 compares the mean O_i concentration in crystals grown under down- and upward directed TMF with standard Cz23) as well as cusp-magnetic field supported Cz material24). We found that from high-purity charges rectangular crystals with relatively low oxygen concentration can be grown. As can be seen at downwards directed TMF with $f = 300$ Hz, being an essential precondition for stable {110} facetting (see ch. 2), an obvious reduction below 10^{18} cm^{-3} has been ascertained. Compared to that the oxygen concentration is somewhat increased up to about 1×10^{18} cm^{-3} in crystals grown under reduced TMF frequency $f = 180$ Hz. Obviously, this is due to the lower rotational SiO transport velocity enhancing the diffusive part from the convective stream region toward the melt-solid interface. The situation can be further improved when an upward directed TMF is applied. Even with UMG material (so far, only such feedstock was used for this TMF regime) a relatively low oxygen concentration of 7×10^{17} cm^{-3}, approaching the results of very costly cusp magnetic field supported Cz growth24). Obviously, the SiO is much effectiver transported away along the crucible wall toward the free melt surface. However, in such case the facetting effect is not more pronounced due to the increased radial temperature gradient as was shown numerically and experimental by Miller et al.16) In general, more detailed experimentally tests are required to find out the optimal TMF parameters for obtaining both large quadratic cross section and lowest oxygen content.

Table 1 Mean interstitial oxygen concentration $[O_i]$ in rectangular Si Cz crystals grown in down- and upward directed traveling magnetic fields (TMF) in comparison with standard Czochralski (Cz) crystals grown without magnetic field and in steady magnetic cusp fields (EG-electronic grade, UMG- upgraded metallurgical-grade).

Method	Experiment number	Feedstock material	TMF frequency, Hz	$[O_i]$, cm^{-3}	Ref.
standard Cz without TMF		EG		$(1.1-1.2) \times 10^{18}$	23)
Cz with cusp magn. field		EG		$(3-8) \times 10^{17}$	26)
rectangular Cz with downward TMF	CMH 034	EG	300 Hz	7.5×10^{17}	present results; see also 17)
	CMH 037	EG	300 Hz	8.6×10^{17}	
	CMH 036	EG	180 Hz	$(8-9) \times 10^{17}$	
	CMH 046	UMG	180 Hz	$(8-14) \times 10^{17}$	
Rectangular Cz with upward TMF	CMH 050	UMG	60 Hz	$(6-8) \times 10^{17}$	
	CMH 051	UMG	300 Hz	$(7-11) \times 10^{17}$	

4. Summary

The paper summarized the previous activities to growth rectangular silicon Czochralski crystals from the melt being of advantage for near kerfless wafer production for solar cells. After the experiment with square die and rectangular hot zone design in 1979 by Motorola Inc. the self-shaping effect by {110} facetting along [001] pulling direction in very low radial temperature gradient has been observed in 1980 by Kuroda from Hitachi Ltd. Only in 2010 next tests were reactivated by the author' s team at IKZ Berlin. Numerous up to 10 cm-long Si single crystals with quadratic cross section up to 91×91 mm^2 and relatively low oxygen concentration of 7×10^{17} cm^{-3} have been grown under TMFs which were simultaneously generated within the heater around the crucible. A stable squarish geometry could be ensured by generation of a high-speed toroidal convection roll without fluctuations in upwards directed TMF of frequency $f=300$ Hz.

All geometrical, structural and chemical qualities of the hitherto grown crystals are still of test character. They are still of relative small dimensions. However, these first results seem to be very hopeful for future Cz material development aiming at photovoltaic applications. For that purpose, as the next step a transformation of the tested growth principle to industrial pullers of at least 200 mm standard dimension is recommended.

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