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Recrystallization of silicon polygonal tubes using an electric closed molten zone

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ABSTRACT

This article describes a process for generating and controlling a closed molten zone with an induced electrical current, and using it for silicon ribbon tube recrystallization. The silicon tube is the secondary loop of a transformer in which the current is generated by electrical induction. The Joule heat caused by the induced current generates a closed molten line along a cross section of the silicon tube; scanning this molten zone along the tube axis results in material recrystallization, with no contact with foreign materials. From the recrystallized silicon tube faces test solar cells were produced, revealing minority carrier diffusion lengths around 100 μm.

1. Introduction

Shaped crystallization of silicon directly into the form of a ribbon is one of the possible routes to reduce the cost of silicon solar cells [1]. When growing from a melt, a major problem of ribbon growth is meniscus stability, especially at its edges [2]. The solutions of this edge problem are distinguishing features of ribbon techniques. In the "Dendritic Web" technique, the edges of the growing ribbon are supported by silicon dendrites [3]. Of the only two silicon ribbon techniques that reached industrial production, "String Ribbon" uses high temperature strings [4] to support the meniscus edges; however the first technique to be commercialized, EFG (Edge-defined Film-fed Growth ribbons), avoids the edge problem altogether by growing polygonal tubes: the closed meniscus has no edges [5]. For this, EFG uses a polygonal high purity graphite shaper immersed in the silicon melt contained in a crucible; the molten silicon wets the graphite shaper and forms a closed meniscus, from which a polygonal tube of crystalline silicon is pulled.

One can identify a few drawbacks in the EFG technique. One is the high cost of the high purity graphite consumables, especially the shaper. A second problem is contamination: even if high purity graphite is used, carbon will dissolve in the melt and precipitate as carbide in the ribbon; some additional contamination by other elements in the shaper and crucible is unavoidable. A third problem is energy use: it is costly to maintain a large volume of material (crucible, shaper, melt), at the high temperature of molten silicon.

These problems might be solved if the shaper were itself made of silicon, and if, instead of a large crucible containing the melt, one could stabilize a floating molten zone held only between the shaper and the growing silicon tube, a closed ring of melt, contacting only solid silicon, with a very small volume. No foreign material parts would be needed, no contamination would occur, and, in principle, the power needed to keep a very small volume of melt could be very small.

However, maintaining a stable, closed, floating molten zone in a silicon tube shape has never been demonstrated before. The main reason is that it is very difficult to produce the thermal conditions to maintain a ring of molten silicon with a thin, roughly constant cross section, held within the walls of a silicon tube; any slight fluctuation will cause either solid bridges to be established, or a local increase of the melt width and total collapse of the closed molten zone. Previous trials that we know of, using for instance electron beams to produce the melt [6], failed.

Now we have recently shown how an electric current can generate a stable linear molten zone in a semiconductor material [7]. This effect results from a positive feedback mechanism created by the increase of the electrical conductivity of semiconductors with temperature [8]; the result is the formation of a linear capillary of liquid silicon, which is virtually contamination-free, since the melt contacts no foreign substance, and intrinsically resilient, since any change in the melt cross section will be repaired by the negative feedback of the Joule effect. The purpose of the work we report here was precisely to establish whether this effect could be used to create and maintain

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a stable, closed, floating molten zone in a polygonal silicon tube, and whether one could produce crystallization by scanning this closed molten zone along the length of the silicon tube. This is seen as the first step for the development of a new technique for the growth of crystalline silicon tubes; missing steps or further questions to be addressed include (i) how to produce a tube shaped cost effective silicon pre-ribbon, using upgraded metallurgical silicon or other techniques such as the SDS [9] or the SiPoSi [10]) and (ii) how to take full advantage of the segregation effect to improve the quality of the material.

The use of the electrical effect to produce a closed molten zone immediately suggests one should use electromagnetic induction to achieve it: the ring of melt could be the secondary of a transformer, the primary being a radiofrequency coil. We were aware, from the start, that this would be quite challenging, for the following reason: as silicon warms up, and starts to melt, not only is the electrical resistance a non-linear decreasing function of current (as happens in a plasma), but also, and worse, the power needed to maintain the ring of melt can also be a time-dependent decreasing function of current. While it is easy to stabilize the molten zone with an electrical current injected via electrodes, stabilising a closed melt produced with an induced current (and necessarily weak magnetic link between the primary coil and the secondary ring of melt) needs strong active system control. This was also a necessary subject of our investigation.

This article therefore describes how a stable closed molten zone can be established and used for the recrystallization of a polygonal silicon tube, focusing essentially on the control mechanisms of the molten zone.

2. Experimental setup

For the experimental accomplishment of the transformer geometry a radiofrequency generator (RF) was used, using an inductor as the primary of the transformer and the silicon tube acting as the secondary. However some preliminary considerations had to be taken into account:

a) As the electrical conductivity of the solid silicon is relatively low at room temperature, a heat source for initial warming of the silicon is required;
b) As the electrical conductivity increases with temperature the electromagnetic coupling of the transformer also increases, leading to higher current and more heat production, in a positive feedback mechanism that requires a fine-tuned control system, in particular during the solid-liquid transition when the silicon electrical conductivity grows almost twenty five times [11];
c) The silicon skin depth effect can be neglected for the experimental conditions considered (frequencies around 300 kHz and silicon ribbon thickness around 0.30 mm);
d) The expected impedance for the secondary molten silicon loop is dominated by the resistance.

2.1. Optical pre-heating system

The optical heating component of the furnace Fig. 1 is composed of four linear 1000 W halogen lamps, focused using four elliptic mirrors in the silicon tube surface, forming a closed heated line. The water cooled mirrors are made of aluminum and the lamps form a square with 100 mm side. The silicon square tube has 50 mm side and is 125 mm long.

The lamp system provides only initial heating to the silicon to decrease its electric resistivity in order to allow the induced current to grow in the silicon tube heated line. There is no need for a uniform temperature along the line because once the induced current is applied the regions exposed to less lamp power, and thus with higher electrical resistance, will dissipate extra Joule heat, resulting in the establishment of a uniform closed molten line.

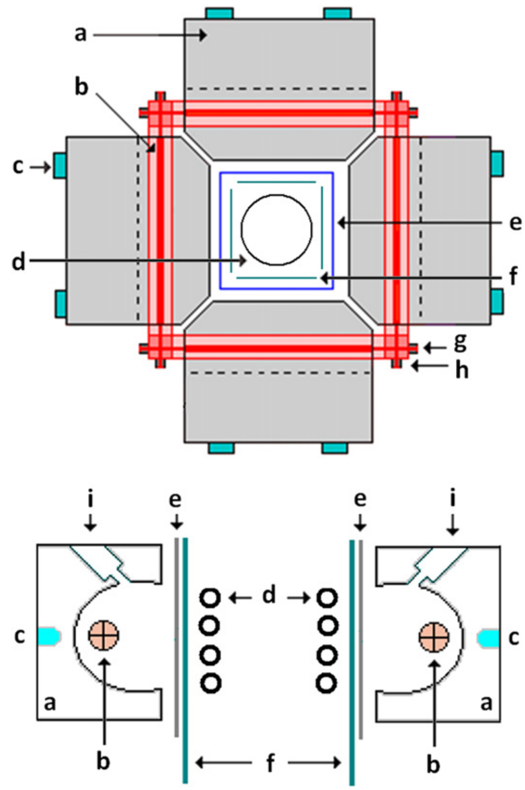

Fig. 1. Interior furnace top and side view: (a) elliptical linear mirrors, (b) halogen linear lamps, (c) water cooling inlet, (d) RF inductor, (e) silicon tube, (f) silicon thermal shields, (g, h) lamp contacts and (i) aperture for visual control of the molten zone.

2.2. RF generator and inductor

A 5 kW RF generator (Huttinger TIG 5/300) with adjustable power was used. The inductor was designed and built from a 6 mm diameter copper tube, 0.85 m long with four turns with an external diameter of 39 mm and a length near 40 mm. The space left between the inductor coils is approximately 3 mm. The inductor electrical isolation was made of quartz rings in the hot regions and a plastic tube in the cool areas.

The oscillator circuit configuration was chosen to optimize the generators power use, with working frequency around 223 kHz. A small coil was used to measure the current applied on the external inductor.

2.3. Sample holder

The main requirements for the sample holder design were (i) the need to apply some pressure on the silicon square tube edges in order to maintain the electrical contact of the four independent silicon plates; (ii) low conduction heat loss and (iii) low contamination. Four quartz sticks with carved tops were used to support the edges of the four silicon independent ribbons. The sample holder is made of aluminum (water cooled) with two adjustable springs to maintain the pressure on the exterior ribbons. Silicon thermal shields, which also act as convection conditioners, also supported by small carved quartz sticks, were positioned between the water cooled inductor and the silicon tube.

The furnace has two similar sample holders, one below the square silicon tube and the other on the top, both coupled to a translation system moved by a stepping motor.

The temperature of the wafers near the quartz support should be low enough to prevent the incorporation of impurities from this source since, according to simulation studies [8], 10 mm away from the electrically formed molten zone in silicon the temperature is about 800 K.

2.4. Control system

The process to obtain a closed molten line in the silicon tube is intrinsically unstable due to the positive feedback mechanism that creates the molten zone. This process becomes particularly critical when the silicon melts, because the electrical conductivity increases about 20 times upon the solid-liquid phase transition. The power increment supplied by the transformer leads to a runaway increase of the width of the molten zone. When the limit supported by the superficial tension of the silicon is reached, the molten zone collapses.

In order to avoid the collapse of the molten zone, the power supplied to the silicon loop must be reduced when the silicon temperature (and hence its conductivity) rises. The RF generator allows two different control modes, in current or in voltage. With the current control the silicon heating process leads to a voltage reduction. In the voltage control mode the silicon heating effect translates into a current increase. In both cases the working frequency stays approximately constant.

To investigate both control modes a study of the electromagnetic circuit presented in Fig. 2 was performed.

The circuit impedance Z_g which relates the generator tension V_g and the generator current I_g, may be written in resonant conditions, and for an equivalent resistance R much lower than the ratio of the equivalent inductance L to the equivalent capacity C, as

$$Z_g = \frac{L}{RC} \quad (1)$$

To identify the equivalent resistance, capacity and inductance, the relations between the primary and secondary current and tension (respectively, I_1, V_1 and I_2, V_2) can be written for sinusoidal electrical signals with frequency ω as

$$V_1 = I_1R_1 + j\omega L_{11}I_1 + j\omega L_M I_2 \quad (2)$$

$$V_2 = I_2R_2 + j\omega L_{22}I_2 + j\omega L_M I_1 \quad (3)$$

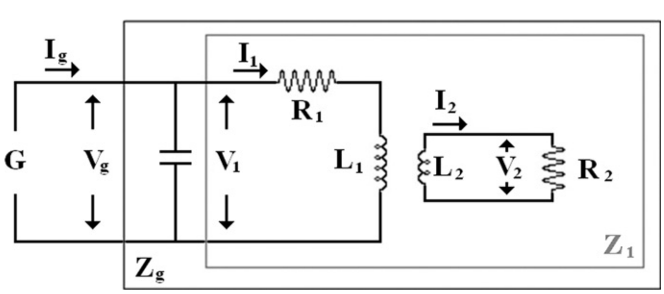

Fig. 2. Electromagnetic circuit, where I_g is the electrical current applied by the RF generator, V_g the potential difference and Z_g the impedance, seen from the generator; V_1 is the potential difference in the inductor L_1 and resistance R_1 (on the transformer primary circuit), where the current I_1 passes; Z_1 is the total transformer primary impedance, which includes the secondary impedance seen from the transformer primary; L_2 and R_2 are the secondary inductance and resistance equivalents, respectively were the I_2 current passes with V_2 potential difference.

where R_1 is the resistance of the primary, R_2 the resistance of the secondary, L_{11} is the self-inductance of the primary, L_{22} the self-inductance of the secondary and L_M the mutual inductance.

When the secondary circuit is in open state R_2 is infinite, and the current on the secondary is null, resulting in

$$Z_1 = R_1 + j\omega L_{11} \quad (4)$$

In short circuit conditions the relation between the currents in the primary and in the secondary can be obtained using Eq. (3), and can be used to simplify Eq. (2), resulting for the primary impedance (when the secondary is essentially resistive, $R_2 \gg j\omega L_{22}$)

$$Z_1 = R_1 + j\omega L_{11} + \frac{\omega^2 L_M^2}{R_2} \quad (5)$$

The secondary impedance on the primary appears with a pure resistance form and the impedance increase in the closed circuit can be translated as an increase in the resistance, r_{12}, which comes to zero when the secondary circuit is opened:

$$r_{12} = \frac{\omega^2 L_M^2}{R_2} \quad (6)$$

For the general impedance, Z_g, it is sufficient to consider the primary self-inductance and its resistance added to r_{12}, like

$$Z_g = \frac{L_{11}}{C(R_1 + r_{12})} \quad (7)$$

With this result, the power from the generator can be written as a function of the tension:

$$P(V) = \frac{V^2}{Z_g} = V^2\frac{CR_1}{L_{11}} + V^2\frac{Cr_{12}}{L_{11}} \quad (8)$$

When the secondary is opened, r_{12} is zero and the power is used only on the primary coil; when the secondary circuit is closed (R_2 is finite) there is a power increase proportional to r_{12}.

Considering the silicon at ambient temperature as the opened secondary and the hot silicon as the closed secondary it is clear that the power increase is proportional to the inverse of the secondary coil electrical resistance. That is, the difference between the generator power on the cold silicon and on the hot silicon is the power transmitted to the silicon coil and can be used as a control variable of the process.

If the generator control is in current control mode the power can be written as

$$P(I) = I^2 Zg = I^2\frac{L_{11}}{C(R_1 + r_{12})} \quad (9)$$

When the secondary is opened r_{12} is zero and the power is used only on the primary coil, as in the voltage mode. However when the secondary circuit is closed there is a power decrease; for the same current the voltage decreases, as was experimentally observed.

The power transmitted to the silicon coil can thus be measured as the difference between the generator power when the silicon is hot and the power when the silicon is cold, and this can be the control variable also in this control mode.

For a determinate current the tension can be written as

$$V_g = Z_g I_g = \frac{L_{11}}{C(R_1 + r_{12})} I_g \quad (10)$$

The difference between the opened secondary tension V_g^0 (in cold silicon) and the normalized measurement of the on line tension (hot silicon) can be used as a control parameter X:

$$X = \frac{V_g^0 - V_g}{V_g} = \frac{r_{12}}{R_1} \quad (11)$$

The control system implemented is based on the calculation of this control parameter, which is proportional to the silicon loop conductivity and is related both to the silicon temperature and the molten zone width. The control parameter is calculated by the difference between the power supplied by the RF generator in real time and the one recorded when the silicon was cold, that is the difference when there existes of a resistive load on the secondary transformer loop and the case when the secondary is in open circuit due to the low electrical conductivity of silicon at room temperature.

A computer-assisted control program was implemented applying a differential control algorithm based on the control parameter and imposing new current values to the RF generator on each control cycle, maintaining an adequate power transmission to the silicon ribbon tube.

3. Process description

Four chemically etched silicon ribbon samples, 0.3 mm thick, are mounted in the sample holder, in order to form a square tube with a 50 mm side. The samples are moved into the furnace region and all the system is maintained in an argon atmosphere. The focused lamps are used to create a high temperature 1.4 mm-wide closed region across the tube faces.

The computer controlled RF generator creates a stable closed molten zone in the high temperature region, with 0.5 to 1.0 mm width, promoting the point soldering of the four silicon plates, and thus forming the closed molten zone around the polygonal tube. The silicon tube is moved down with a typical speed of 1-3 mm/min and therefore the closed molten zone travels upward, recrystallizing the silicon tube.

4. Experimental results

Several silicon ribbon tubes were recrystallized, revealing smooth surfaces, long grains (cm size) in the faces central region and smaller ones near the edges; The recrystalized material has the same width as that of the initial ribbon; an example is presented in Fig. 3. An alternative setup based on the Sttrech approach [12] could be envisioned in order to produce thinner ribbons from starting thick material.

In order to characterize the recrystallized material several samples were cut from the tube faces, and simple test solar cells were made, without passivation or gettering treatments.

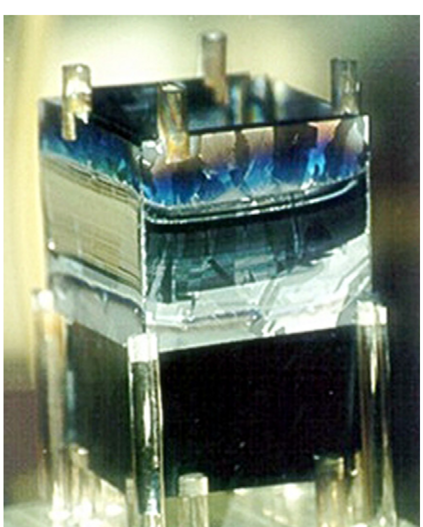

Fig. 3. Photograph of the recrystallized silicon tube mounted on the carved quartz sticks.

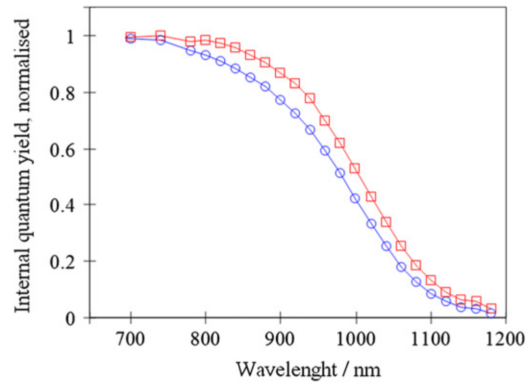

Fig. 4. Internal quantum yield of one of the test solar cells, made on the recrystallized silicon. The internal quantum yield with bias light (squares) shows a greater diffusion length (140 μm) when compared to the measurement with bias light level of 0.2-suns intensity (100 μm).

The results showed diffusion lengths in the order of 100 μm for the samples from the faces central region. Near the edges small grains are visible and lower diffusion lengths, 40 μm, were measured [13].

The measured diffusion length showed some variation with the bias light intensity that was used from 100 μm, with bias light of 0.2 sun intensity, to 140 μm with one sun intensity bias light, as in the example shown in Fig. 4. This behavior suggests that some of the recombination centers, traps, are active in low illumination conditions but become inactive or less active near one sun illumination.

5. Future developments

Careful inspection of the edges of the silicon tube showed only partial melting due to the existence of a small mass accumulation in the interior angle of the square tube, which provides an internal path for the electrical current flow. The total non-recrystallized region is approximately 0.6 mm wide. This mass accumulation in the interior angle results from the thermal conditions and from the unbalanced liquid pressure across the molten zone. The equilibrium is reached when some of the liquid moves to the interior edge angle, increasing the liquid surface curvature ratio, thus balancing the pressure.

Two possibilities can be tried to achieve the melt of the exterior edge of the tube:

a) Increase the internal angle of the tube by increasing the number of sides of the polygonal tube, for instance changing from quadrangular to hexagonal or octagonal tubes;
b) Applying extra heat on the edges of the tube.

The test of these ideas requires the design of a new sample holder and a new heating system.

All the experinces were conducted with 0.3 mm thick, 50 mm wide wafers. Nevertheless it is expected that the control system of the closed molten zone technique can be applied to thinner and larger wafers naturally with suitable modifications on the mechanical arrangement, namely on the samples support.

6. Conclusions

This work demonstrates the possibility of silicon tube recrystallization using a closed molten zone, created by electromagnetic induction. Molten zone stability was achieved through a real time computer aided control. The recrystallization process leads to the welding of the four independent plates, forming a quadrangular tube.

Several samples were cut from the faces of the closed molten zone recrystallized tubes. The characterization main result is the minority carried diffusion length obtained, with values around 100 μm in the central region of tube faces.

Nevertheless the tube was not completely recrystallized: a small external part of the square tube edges had not melted, this fact being related to liquid silicon accumulation on the internal edge angle.

This closed molten zone technique offers an interesting pathway for the crystallization of cost effective silicon wafers for photovoltaic application.

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