Silicon sheet materials grown by recrystallisation from linear and closed molten zones

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ABSTRACT: As a step in the development of new silicon sheet growth techniques, we have demonstrated that it is possible to form a stable molten zone in a prismatic silicon tube, and use such a closed molten zone (CMZ) in a new recrystallisation process to obtain crystalline silicon sheet material. The main advantage of such a process, as compared to linear molten zones with open side meniscus, is that liquid edge instabilities are avoided. Sheet silicon materials obtained in different conditions, grown from linear or closed molten zones, were characterised by lifetime measurements and by spectral response of test solar cells. Once the main sources of contamination were removed, CMZ materials demonstrated average lifetimes of ~2µs and diffusion lengths of ~100µm in test cells with no BSF nor passivation procedures.

Keywords: Silicon - 1: Ribbons - 2: Recrystallisation – 3

1. INTRODUCTION

Silicon sheet growth techniques may prove vital in the mid and long term development of photovoltaic solar energy applications where low cost and high quality materials are needed. This was realised very early in the modern history of photovoltaics, and much effort has been devoted to the development of an extremely varied array of techniques. That the problem is far from trivial is demonstrated, for instance, by the fact that it is still far from decided today, after several decades of research and development, which techniques will survive the test of industrial production in a competing market: R&D is proceeding, for instance, on the two main classes of processes of growth from the liquid, parallel and perpendicular [1].

Parallel processes, where crystal growth proceeds (almost) parallel to the sheet normal, should permit high area generation rates, but generally require a solid substrate. This substrate can be detached from the silicon sheet and re-used, as in the RGS process, being investigated by Bayer [2], or become part of a final composite sheet, as in the SILICON FILM under development in Astropower [3].

Perpendicular processes, where crystal growth proceeds along a direction in the sheet plane, are generally slower area generators than parallel ones. Interestingly, this class includes the only process that reached well established industrial production, the EFG process [4]. In this process, the problem of meniscus stability is solved with the help of a shaper dye, made of graphite, partly immersed in the liquid silicon bath; and the problem of the free meniscus edges is solved by avoiding them altogether: the dye has a closed polygonal shape, and the final product is a prismatic silicon tube. Among other perpendicular processes, one could mention the String Ribbon [5], where the problem of stability of the meniscus edges is solved by a pair of “strings”, which effectively stabilise the lateral sheet shape; and the Dendritic Web process [6], where lateral collapse of the liquid meniscus is avoided by an acicular silicon dendrite on either side.

A different approach of perpendicular growth from the melt is exemplified by the SSP process [7], where, rather than a liquid silicon bath, only a molten zone is kept liquid.

2. MOLTEN ZONE PROCESSES

Sheet silicon growth from a floating molten zone has interesting advantages when compared to conventional multicrystalline silicon ingot production or other sheet growth techniques: there is no need for a crucible, contamination by foreign materials can be avoided, and, in principle, it can be a low energy process, since only a small volume of silicon has to be kept liquid. The main technical difficulties concern molten zone stability and the need for a pre-ribbon.

Previous work on such molten zone techniques in our group resulted in the development of the STRETCH process, in which a multicrystalline silicon sheet is produced, with area multiplication and thickness reduction, by zone melting recrystallisation of a flat pre-ribbon [8]. Good surface finish, square centimetre grain size and reduction of metallic impurity content were achieved. However, it was shown that the floating zone requires an oxidising atmosphere, necessary for stabilising the free edges by oxide encapsulation of the whole molten zone. This is the main reason why it was not possible to demonstrate a consistent acceptable quality in the samples produced in the presence of oxygen: although the diffusion length of the record sample was quite high (~100 µm), it generally fell below 40 µm. This was not unexpected, since the quality of oxygen containing silicon material is well known to be strongly dependent on thermal history (which includes the thermal profile the sheet is subjected to during the growth process itself). The high oxygen content therefore strongly limits the interest of this growth process.

Edge stability was also found to limit the growth rate to modest values.
Linear molten zone recrystallisation in an argon atmosphere avoids oxygen incorporation and so produces better quality material. However, in argon, no free liquid lateral edges are allowed; the molten zone has to be kept away from the edges in order to avoid the liquid collapse under its surface tension, as was done in the SSP process. This edge problem reduces the interest of such processes for industrial production.
On the other hand, a closed molten zone, without free liquid edges, would overcome this limitation. A process using a closed molten zone (CMZ) would allow the use of an argon atmosphere, thereby avoiding oxygen incorporation; and since no contact of the floating liquid silicon zone with a crucible or shaper is necessary, foreign material contamination can be avoided.
The present article describes the first results on our study of a closed molten zone technique. The demonstration of a stable closed molten zone is considered to be a step for a sheet silicon (tube) production process, that may allow low energy use and produce high quality material.

3. THE CLOSED MOLTEN ZONE TECHNIQUE

Simplicity of the furnace design led to a four-sided molten zone; the end product should therefore be a square prism of recrystallised silicon. During the development of the closed molten zone technique it was found that, in practice, it is impossible to obtain a stable closed molten zone by optical heating alone. Stable growth conditions were achieved with a combination of radiation and

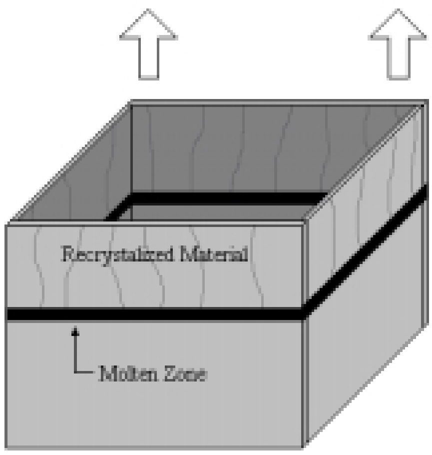

Figure 1: *Schematic diagram of the Closed Molten Zone technique, where silicon is recrystallised into a square tube.*

resistive heating, In the final prototype furnace configuration, the closed molten zone is formed on the heated region and the silicon tube is moved, in order to recrystallise the liquid and feed the molten zone with fresh solid, as shown on the schematic diagram of figure 1.
Since our aim was to demonstrate the principle, study intrinsic limitations and compare produced material quality with that obtained by other known recrystallisation techniques, we limited our choice of starting material to well characterised and reasonably uniform material, namely to high quality commercial multicrystalline wafers from Eurosolare and Bayer.

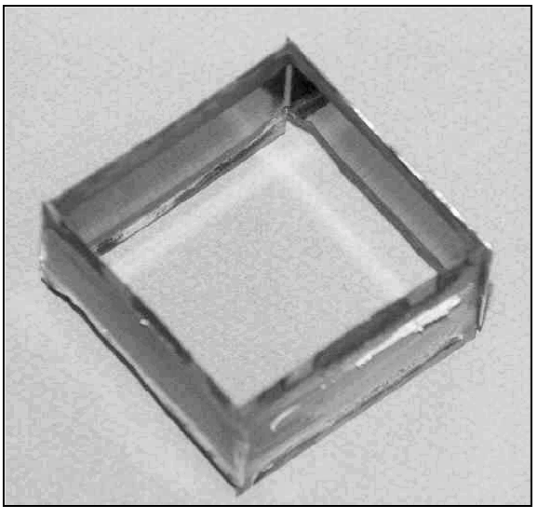

Figure 2: *Top view of a 50 mm wide recrystallised silicon tube.*

Figure 2 shows an example of an as grown square silicon tube of 50 mm side resulting from closed molten zone recrystallisation. Although the atmosphere was nominally pure argon, oxide films and deposits are clearly seen on parts of the surface of the sample, demonstrating that residual oxygen was present. However, no oxygen was incorporated in the bulk of the samples, as verified by infrared absorption spectroscopy. The recrystallised surface is quite planar, almost mirror like, with slight small period corrugations. The recrystallised grain size is around 10 to 50 mm^2 near the centre of the prism faces, while near the edges it is reduced to 5 to 8 mm^2, probably due to the temperature profile and the associated stress generation.
The initial presence of naked carbon at high temperatures in the furnace was found to be a problem. Although care was taken to use very high purity carbon, a severe degradation of the material quality was observed (c.f. next section). This problem was eliminated in the later furnace design.
With this laboratory scale furnace, the possibility of creating a stable closed molten zone, and of using it for the recrystallisation of a silicon tube with no oxygen and carbon contamination, was demonstrated.

4. MATERIAL CHARACTERISATION

Material quality characterisation was done by surface photovoltage (SPV) and by microwave reflectance decay (MRD) in as grown samples, and, after diode formation, by spectral response (SR). For diode formation, the material, which was p-type, typically 0.5 to 2 Ω.cm, was subjected to phosphorous diffusion from a solid source (30 to 60 minutes at 900C). After mesa etching, continuous aluminium back contacts and a grid of Ti/Pd/Ag front contacts were deposited by evaporation, followed by contact annealing (15 min at 450C in nitrogen). The cells were thus formed purely for minority carrier diffusion length measurement from their spectral response at long wavelengths, as close to as grown conditions as possible. No back surface field, no emitter doping optimisation, no passivation nor gettering procedures were attempted: no high efficiency cell process was attempted yet in this material. The rather poor spectral response at low wavelengths, for instance, should be disregarded, since no particular care was taken in the emitter formation step. Only the long wavelength behaviour is considered significant, since it should reflect the bulk material quality as characterised by a minority carrier diffusion length, Ln.

Several series of samples, corresponding to (i) successive stages of development, and trial runs, of the closed molten zone technique, and to (ii) samples grown by other processes, namely in our linear molten zone furnace, for comparison purposes, were prepared for characterisation.

One of the studies carried out concerned the effect of high oxygen content. In fact, an oxidising atmosphere makes it easier to stabilise molten zone growth processes, both because of the capping effect of the natural oxide and of the increase in viscosity of the liquid silicon. In the past, in spite of usually modest minority carrier diffusion lengths Ln (7 to 40 µm), a few surprisingly good results occurred, with a few cells revealing diffusion lengths of the order of 100µm. A study of samples produced under argon and

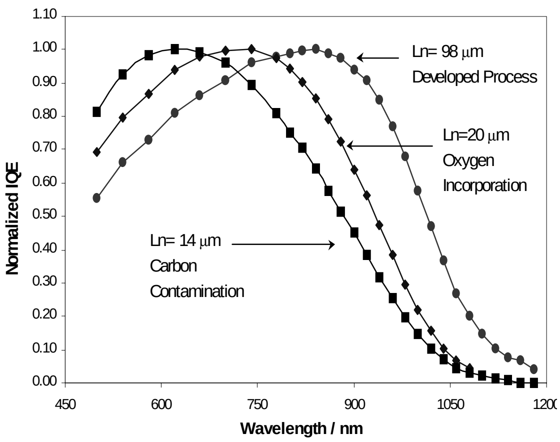

Figure 3: *Normalised internal quantum efficiency of simple test cells made from silicon sheet obtained in different growth conditions. The degradation due to carbon contamination and oxygen incorporation is compared with the result for the developed CMZ process.*

under oxidising atmosphere was therefore undertaken, to check whether high diffusion lengths might occur under the new thermal profiles of the recently developed systems. The results on diffusion length in oxygen containing silicon revealed always very low diffusion lengths, the best Ln being 20 µm, shown in Figure 3.

These consistently lower diffusion lengths are tentatively attributed to different post-crystallisation temperature distribution in the new systems. Whereas in the past we could find growth conditions which avoided severe degradation by oxide precipitation, this was not possible in the present growth systems.

In view of these results, oxidising atmospheres were definitively ruled out, and we concentrated our studies in pure argon atmosphere. This is, in any case, a more straightforward and attractive proposition for future industrial application, even if it proves experimentally more difficult to realise.

As an example of the problems met in early attempts at combined heating for obtaining a closed molten zone, we describe the case of the poor material produced when naked carbon at high temperature was present inside the furnace. Although care was taken to use very high purity carbon, a severe degradation of the produced material is well illustrated in Figure 3, where we display the comparison of the spectral response of a cell made on such a material (Ln~14 µm) and that of a last generation closed molten zone typical sample. The obvious conclusion is that carbon contamination was responsible for the severe degradation of those early samples.

As mentioned above, we found that it was impossible to obtain a stable closed molten zone by optical heating alone with the furnaces we designed. This was expected from previous experience, and from the beginning of the furnace design we had foreseen the need for extra heating systems. Several were tested, until finally stable growth from a closed molten zone was obtained with a combination of radiation and resistive heating. Now, previous experience with furnaces with optical heating alone had shown the possibility of producing good quality material. Would the material produced by closed molten zone, with combined heating as designed (with different temperature distributions and potential contamination sources), produce a material of similar quality to that produced by optical heating alone (no closed molten zone formed), or show an obvious degradation? For the purpose of checking this point, we grew several samples by optical heating alone from the same starting material as that used in the closed molten zone process, and compared the relative quality, using again as a figure of merit the minority carrier diffusion length as measured by the spectral response of simple diodes. Some of the results obtained are shown in Table I. We include here only the last generation closed molten zone samples, since previous samples were rather poorer in quality for known reasons.

As can be seen from the table, the combined heating closed molten zone material attains a quality which is already quite comparable with that of the material obtained by optical heating alone, although still a little inferior on average. In fact, if we take averages of the measurements of diffusion length obtained with each of the three techniques used (SPV, SR with no bias light, and SR with bias light) the closed molten zone material consistently produces slightly lower values. However, the average Ln=100µm that one obtains for this last generation of closed molten zone material samples, still with no gettering (except that due to the phosphorous diffusion process) or hydrogen passivation, already confirms that - although thermal profiles can still be improved, and perhaps residual contamination sources removed - this technique will be compatible with high efficiency solar cell production.

Table I - Diffusion lengths measured by spectral response of simple diodes. Samples were recrystallised (i) by optical heating alone or (ii) by combined heating as used in the Closed Molten Zone furnace. The diffusion length on the "Average" column was obtained with all the diode area under uniform illumination.

		Diffusion Lengths in µm		
	Id.	No bias light	bias light (0.2 Sun)	Average (0.2 Sun)
Optical heating alone	J1B	51	86	77
	J1C	182	224	150
	J3B	187	214	166
Combined heating, CMZ	R5B	61	109	89
	R7A	99	141	100
	R7B	65	86	98

The change of spectral response with bias light (soaking the sample with continuous, non-chopped light) is interpreted in terms of change of carrier occupation of recombination centres. Bias light can decrease the recombination effectiveness of some of these centres, which may result in an increase of the measured diffusion length. Such an effect is obvious from Table I. The bias light used was approximately equivalent to only 0.2 suns. (A study of the evolution of the measured diffusion length with increasing bias light intensity was carried out on R7A cell. The results showed, in the conditions of columns 1 and 2 of Table I, an increasing diffusion length from 44µm in total darkness – column 1 of the table was obtained with a little ambient light - to a saturation value of 150µm at 0.7 Sun and higher. At 0.2 Sun Ln already approaches the saturation value.)
Carrier lifetime (as measured by Microwave Reflectance Decay) mapping of a few samples without bias light was also carried out. In Figure 4, we show the results of such a mapping in a sample obtained by Closed Molten Zone recrystallisation.

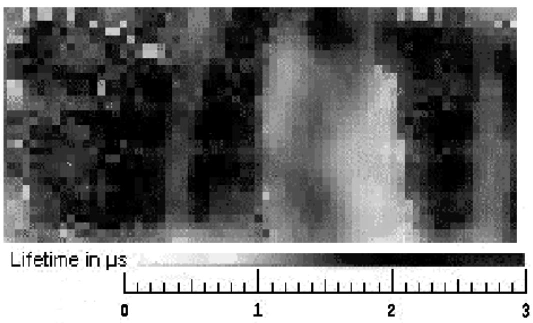

Figure 4: *Carrier lifetime map of a closed molten zone sample (R5B) as measured by Microwave Reflectance Decay. Area displayed is about 220mm^2 and the average lifetime is about 1.7 µs, consistent with the average diffusion length of 83 µm obtained in similar conditions (no bias light).*

Grains with quite different lifetimes are visible, ranging from about 0.7 to 3µs, with an estimated average of 1.7µs. A low resolution LBIC (Light Beam Induced Current) map was also made on the same cell and under the same conditions (no bias light). This confirmed the quality pattern and showed an average diffusion length of 83 µm, which is consistent with the measured lifetimes.

5. CONCLUSIONS

A new process of silicon sheet recrystallisation, based on a closed molten zone, was developed. A laboratory scale furnace, aimed at demonstrating the possibility of silicon tube growth from a molten zone, was built. Conditions have been found for establishment of a stable closed molten zone, and for the recrystallisation of silicon sheet material with quality compatible with high efficiency solar cells.
In the samples produced with the last generation system, minority carrier diffusion lengths averaged ~100 µm, as measured in test cells with no back surface field, no gettering, nor hydrogen passivation.
This study is considered a step for a silicon ribbon production process, that would allow low energy use and high quality material production.

6. ACKNOWLEDGEMENTS

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