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THE S-WEB TECHNIQUE FOR HIGH-SPEED GROWTH OF Si SHEETS

J.G. Grabmaier and H. Föll
Research Laboratories of Siemens AG, D-8000 Muenchen 83, FRG

ABSTRACT

The supported-web (S-Web) technique was conceived as a method to grow Si-ribbons at large areal growth rates. Its central idea is to pull a net made, e.g., from carbon-fibers, through liquid Si. Webs of liquid Si are drawn out within the meshes of the net and kept stable by the high surface tension of liquid Si. The liquid webs crystallize individually some time after their formation and this allows to obtain a ribbon-shaped body of Si at high speed. First experiments with graphite-grids were encouraging and opened the way for more involved experiments with carbon-fiber nets woven on a suitable loom. Ribbons suitable for the fabrication of solar-cells were obtained at low pulling speeds, but problems were encountered at high pulling speeds. The results of the net-pulling experiments are presented and discussed.

INTRODUCTION

The large-scale manufacture of cheap, but efficient solar cells demands not only cheap starting materials and processes, but also high through-put rates at every step in the production chain. With crystalline Si as basic solar-cell material, any production sequence will contain the controlled crystallization of liquid Si; preferably directly in the form of large-grained sheets or ribbons. Most crystal growth techniques utilized so far (for a review see /1,2/) are limited to areal growth rates $\approx 0{,}05\ m^2/min$; a value far below the demands of large-scale production.

The volume of Si crystallizing per time unit is generally given by the product of the area of the solid-liquid interface and the velocity with which this interface moves perpendicular to itself. Attempts to increase areal growth rates therefore aim at increasing the interface velocity (i.e. the "pulling speed" for most processes), the interface area, or both. The first approach requires very large temperature gradients in order to remove the heat of crystallization and invariably leads to problems with the structural perfection of crystals thus obtained (example: roller-quenching /3/). The experimental evidence collected so far indicates that interface velocities

in excess of ≈5 cm/min will not lead to satisfactory crystals. Increasing the area of the solid-liquid interface thus seems to be more attractive and has shown some promise as demonstrated by "horizontal ribbon growth" (HRG) /4/; "low-angle Si sheet growth" (LASS) /5/ and "interface controlled crystallization" (ICC) /6/. However, stability and morphology problems appear to be associated with these approaches.

The "supported-web" (S-Web) technique /7,8/ is a newcomer to this field. The unique and unconventional idea in this technique is to use a net as a kind of supporting substrate for Si ribbons. In the original concept of the S-Web-technique, the net, made from carbon-, graphite-, or carbon-coated quartz-fibres, is to be pulled through a crucible containing liquid Si at comparatively high velocities. Films or webs of liquid Si are spread out within the meshes of the net where they remain stable for some time due to the high surface tension of liquid Si. Each web then crystallizes individually in a "crystallization zone". The shaping of the Si-ribbon and its crystallization thus would be decoupled and the removal of the heat of crystallization would no longer be speed-limiting. High areal growth rates should be possible because the solid-liquid interface area present at any given time is very large compared to the cross-sectional area of the ribbon, but in contrast to HRG, LASS and ICC the total interface area is now partitioned into many independent interfaces.

This paper gives an overview of the experiments performed so far and discusses the potential and the problems of the S-Web-technique.

EXPERIMENTAL STUDIES

Dip-coating of graphite grids

For a first evaluation of the S-Web-technique, dip-coating experiments were performed with graphite-grids instead of the then unavailable net. The grids were laser-cut from high-density high-purity graphite sheets (typically 60 x 40 x 0,5 mm^3) with mesh-sizes between 1 x 1 mm^2 - 4 x 4 mm^2. These grids were dipped into liquid Si kept at a temperature slightly above the melting point and, after a soaking period of 30 sec - 60 sec, withdrawn with velocities between ≈ 2 cm/min and 200 cm/min. The following results merit mentioning:

i) At pulling speeds ≲ 4 cm/min the graphite was uniformly coated on both sides (Fig. 1a).

ii) If the pulling direction was not perpendicular to the melt surface but inclined by ~ 10^o-15^o, the graphite grid was coated at one side only for pulling speeds ≲ 4 cm/min (Fig. 1b).

iii) At pulling speeds between ≈10 cm/min - 200 cm/min the meshes of the grid were still filled with Si which exhibited

a peculiar morphology that did not depend on the pulling angle (Fig. 1c). The surface of the graphite grid, howewer, was not coated.

The first two items are easily understood. At low pulling speeds the solid-liquid interface moves downwards with the same velocity with which the grid is withdrawn; i.e. it is stationary. The crystallization thus occurs continuously and the process as a whole is quite similar to the SOC /9/, RAD /10/ or "contiguous capillary coating" /11/ techniques.

The morphology and defect structure of the specimens obtained at high pulling speeds is typical of "mesh crystallization"; i.e. the individual crystallization of a web of liquid Si contained within a mesh of the grid. Detailed investigations by chemical etching, scanning- and transmission electron microscopy, and in-situ photography of the crystallization process lead to an understandig of the mesh-crystallization process as illustrated in Fig. 2 and Fig. 3. In short, a liquid web is indeed drawn out and persists for some time within a mesh of the grid. Its crystallization starts from the outside of the mesh and proceeds towards the interior; several solid-liquid interfaces or crystallization fronts exist at the same time. Whereever two crystallization fronts meet, a highly defected region containing high-angle grain boundaries, dislocations and SiC-precipitates in high densities is formed. The peculiar shape of the crystallized web is a consequence of the non-zero contact angle of solid Si with its own melt as is outlined in /12/.

The experiments with the graphite grids thus demonstrated that the basic idea of the S-Web-technique is valid in principle, but that at the very minimum the crystallization of the liquid Si-webs has to be controlled in order to progress towards a useful morphology of the coated grid or net.

Introducing the net

Up to now, nets were woven from commercially available carbon rovings (Sigrafil R NF 1) on a standard loom which was slightly modified for this purpose and which could also be used for quartz rovings. The carbon rovings contain 1000 single filaments with diameters of ≈ 8 µm /13/. The minimum mesh-size of the net is 2,5 x 2,5 mm^2; larger sizes are possible. As woven, the net is 1 m in width and of arbitrary length (typically 50 m). Smaller nets are obtained by cutting it to size with scissors. The price of the net is about \$ 15/m^2 (for 2,5 x 2,5 mm^2 mesh size) but is expected to decrease if massproduction would be established.

The carbon rovings are covered with a thin layer of a plastic coating for protection. Before using the net, this coating has to be removed; which is simply done by burning it off. The carbon fibers used contain up to 2 % impurities, mainly Ca, Zn,

Mg, Si. In order to evaluate their influence on the S-Web quality, a portion of the net was cleaned by baking it at ≈2700 °C in a halogen atmosphere. These cleaned nets then contained less than 10 ppm impurities.

Feeding the net into the molten Si principally can be conceived in two ways: i) from below the crucible through a slot in the crucible bottom (similar to the RAD-technique /10/) and ii) from above, turning it around a bar of suitable material that is immersed in the liquid Si. The second possibility, however, is untenable because the net embrittles immediately in contact with liquid Si. Therefore the first option was implemented. The problem, of course, is to avoid leakage of liquid Si through the feed-slot. Whereas this is not impossible (cf. /14, 15/), a leakage-proof system employing a slotted die (Fig. 4) was used for first experiments with continuous net-pulling. The contact-area of liquid Si and the net lies higher than the Si-melt level and leakage thus cannot occur. The uphill flow of liquid Si to the net is achieved, as in the EFG-process /16,17/, by capillary action. The slotted die, besides allowing a leakage-free transport of the net, serves also to shape the meniscus and thereby to influence the coating geometry of the net.

Two apparatus have been set up for experiments: S-Web-puller I and II. No. I is a simple but versatile laboratory-model with RF-heating of the crucible and the possibility of chosing any pulling direction desired; the maximum net width is limited to ≈ 4 cm. No. II is a modified Czochralski crystalpuller with resistance-heated crucible, vertical pulling only, and a maximum net width of 10 cm.

Results of experiments with continuous net-pulling

After some inital trouble with the net getting stuck in the slotted die, fracture of the coated net, temperature inhomogeneities along the exit surface of the slotted die and the like, a standard slotted-die design for the S-Web-puller II emerged as shown in Fig. 4. The large openings on both sides of the slotted die allow a certain portion of the net to remain uncoated and thus to retain its high mechanical strength, a measure that ensures that pulling can continue even if the coated part of the net fractures. The asymmetric shape of the slotted die results in a onesided coating of the net, as it is preferèd for various reasons.

In contrast to the dip-coating experiments, the meshes of the net are not filled with Si at high pulling rates ($\gtrsim$5 cm/min). This is a direct effect of the geometry of slotted die and net and will be discussed later.

At low pulling speeds, exploiting the continuous crystallization mode, one-sided and (with symmetrical slotted dies) double-sided coating of the net is easily achieved; Fig. 5 shows

typical cross-sections. Grain sizes generally are in the 1-2 mm range. If long and wide ($\gtrsim$5 cm) ribbons are grown, a tendency for fracture along the middle is observed. This is quite natural for ribbons (cf. /18/) and not necessarily connected with the net. The problem can be overcome by periodically raising the pulling speed for a short time period and thus to interrupt the coating process. Coating commences automatically as soon as the pulling speed is lowered again. Rectangular sheets, easily separated by breaking, are obtained in this way; Fig. 6 gives an example.

An uncleaned net with mesh sizes of 2,5 x 2,5 mm^2 or 5 x 5 mm^2 was used for most experiments so far. Contamination of melt and S-Web therefore was unavoidable and manifested itself in an unavoidable conversion of the S-Web to n-type (probably caused by Mg) although p-type Si was used as feed-stock. A detailed evaluation of these n-type samples has not been attempted; but it was found that the minority-carrier diffusion length averaged about 20 μm. This is an unexpectedly high value in view of the contamination that must have taken place.

With clean nets, the original doping of the melt is retained in the S-Web ribbons. First measurements with the Si-electrolyte-contact method /19/ and with test solar-cells based on a MIS-junction technology, gave short-circuit currents I_{sc} under AM1 illumination of $\approx$18 mA/cm^2; i.e. about 60 % of the current obtained with reference single crystals. Because no attempts have been made so far to clean the crucible and the slotted die (both are made from high-density high-purity graphite), this I_{sc}-value is considered to be quite encouraging.

The carbon-fibers of the net react with the liquid Si to SiC. Isolated filaments usually are quantitatively converted to SiC, but the SiC formed initially around the tightly packed filaments in a fiber-bundle "screens" the interior which therefore often contains filaments that are only partially reacted to SiC. Reacted filaments are no longer coherent, but rather strings of small SiC-crystals (Fig. 7). It is thought that this reaction, by breaking up the fibers, relieves some of the stress which is introduced by the incompatibility of the thermal expansion coefficients of Si and the carbon rovings.

The density of dislocations and grain-boundaries is sometimes higher in the immediate vicinity of the net, but frequently the net does not introduce major structural disturbances. Single filaments have often been found to be embedded in the Si (as SiC-crystals) without causing any lattice disturbance.

The net, after incorporation into the Si-ribbon, provides an ohmic contact to the Si-ribbon. This was ascertained by I-U-measurements between the frontside of a sample and unreacted carbon-rovings from the uncoated part of the net at the left- and right-hand-side of the coated region. The net thus may be

used as an integral part of the back-side contact necessary for solar-cells.

Using the smaller S-Web-puller I, experiments were conducted with horizontal instead of vertical pulling of the net. For reasons which will be discussed later, horizontal pulling was thought to promote stable liquid Si-webs within the meshes of the net at high pulling speeds. Whereas this assumption was generally true, the morphology and crystallization of specimens obtained at higher pulling speeds was similar to that of the dip-coating experiments and thus too irregular for further processing. At low pulling speeds (around $\approx$(2-3) cm/min) long ribbons ($\approx$30 x 4 cm^2) with fairly large grains could be obtained; an example is shown in Fig. 8.

DISCUSSION

The geometry of coating the net

Of particular interest for the S-Web-technique is the relationship between mesh-size, geometry of the slotted die, and the amount of liquid Si that can be spread out as a liquid web within a mesh. The basic quantities and processes governing this relationship are illustrated in Fig. 9 for both pulling the net through a free surface and through a slotted die possessing a meniscus-defining edge. It is clear from Fig. 9 that after a meniscus was attached to a horizontal bar of the net that emerges from the liquid Si, the next bar has to come up before the two menisci overlap and thereby rupture the Si-web. The most important quantity is the meniscus shape, defined by its radius of curvature R as a function of the meniscus height h. In the simple one-dimensional case shown in Fig. 9, R(h) is given by

$$R(h) = \frac{\gamma}{\varrho \cdot g (h_o + h)}$$

with γ = surface tension of liquid Si (720 mJ/m^2), ϱ = density of liquid Si (2.53 g/cm^3), g = 9.81 m/sec^2, and h_o = "effective" height of the die-top with respect to the Si-melt level (cf. /16/). An evaluation of this equation, taking into account various boundary conditions for the meniscus as determined by the precise shape of the slotted die, leads to a relation between the maximum mesh-size and the effective die-top height h_o as shown in Fig. 10. The curves given represent only general trends since the precise relation depends on the exact geometry of die-top and net. It is, however, safe to say that vertical pulling always requires mesh sizes $\lesssim$ 4 mm. This is true even for very small h_o-values because the radius of curvature of the meniscus rapidly decreases when it is pulled upwards. In the case of horizontal pulling, the radius of curvature can be kept large at small h_o-values and larger mesh sizes should be possible. This was the incentive for the hori-

zontal pulling experiments and the standard 2,5 x 2,5 mm^2 meshes were indeed filled with liquid Si in this case. Compared to the dipcoating experiments, however, the filling of the meshes occured more haphazardly and the webs often collapsed before crystallization started. The reason for this is that neither the cross-section nor the wetting-angle of a carbon-fiber is a well-defined quantity (as assumed in Figs. 9 and 10).

Outlook

From the experimental and theoretical results described before, it follows that the original concept of the S-Web-technique as outlined in the introduction, is not easily turned into reality. Whereas ribbon growth at low pulling speeds is possible and even may offer some conceptual advantages in comparison to more established methods, it cannot be considered a decisive breakthrough. The goal, clearly, still must be to utilize the intrinsically high areal growth rates of the net-specific mesh-crystallization without sacrificing quality.

One possible way to achieve this goal is illustrated in Fig. 11. The crucial point is the introduction of a temperature gradient perpendicular to the growth direction. The crystallization front thus will be inclined to the growth direction; its total area is large as compared to the ribbon cross-section, and the general geometry is reminescent of HRG, LASS, or ICC /4-6/. Phrased differently, the thin layer of Si covering the net on one side grows in the continuous crystallization mode, whereas the bulk of the ribbon grows in the (transversal) mesh-crystallization mode. Experiments exploring this possibility are in progress.

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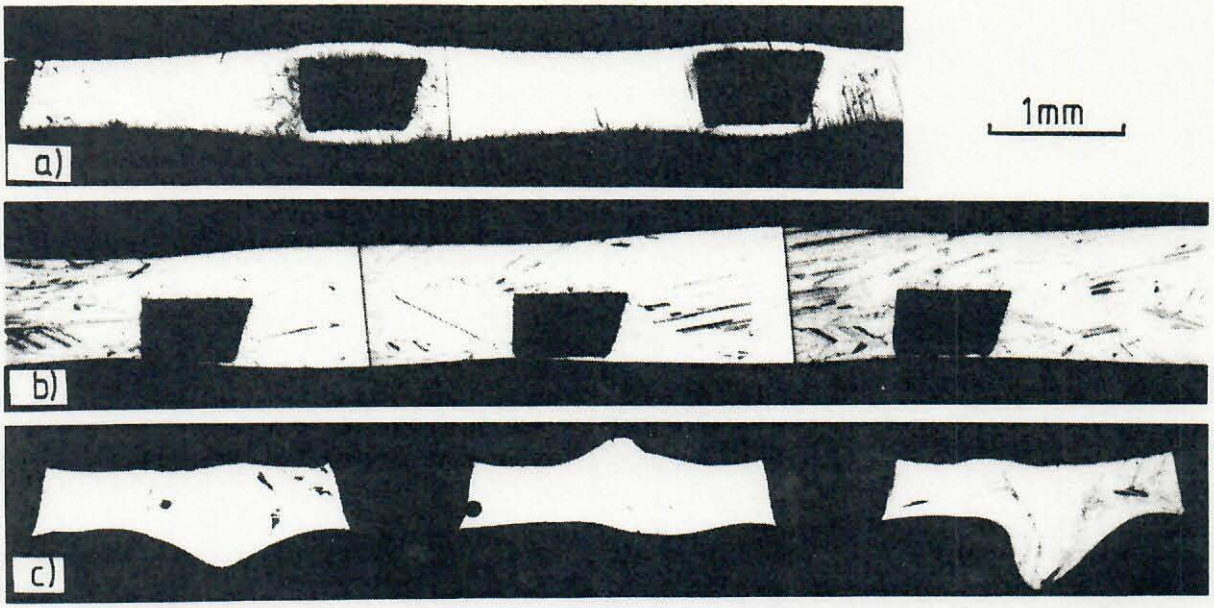

Fig. 1
Coating geometry of graphite grids for a) vertical pulling; b) inclined pulling at low speed; c) pulling at high speed.

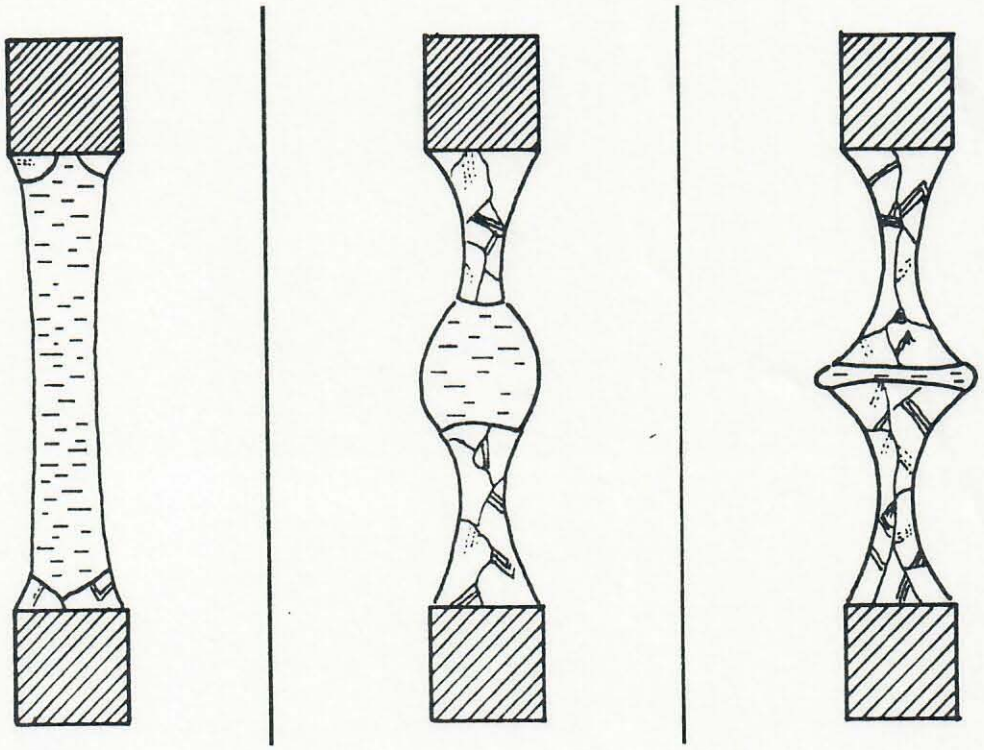

Fig. 2
Subsequent stages of mesh crystallization. For details see text.

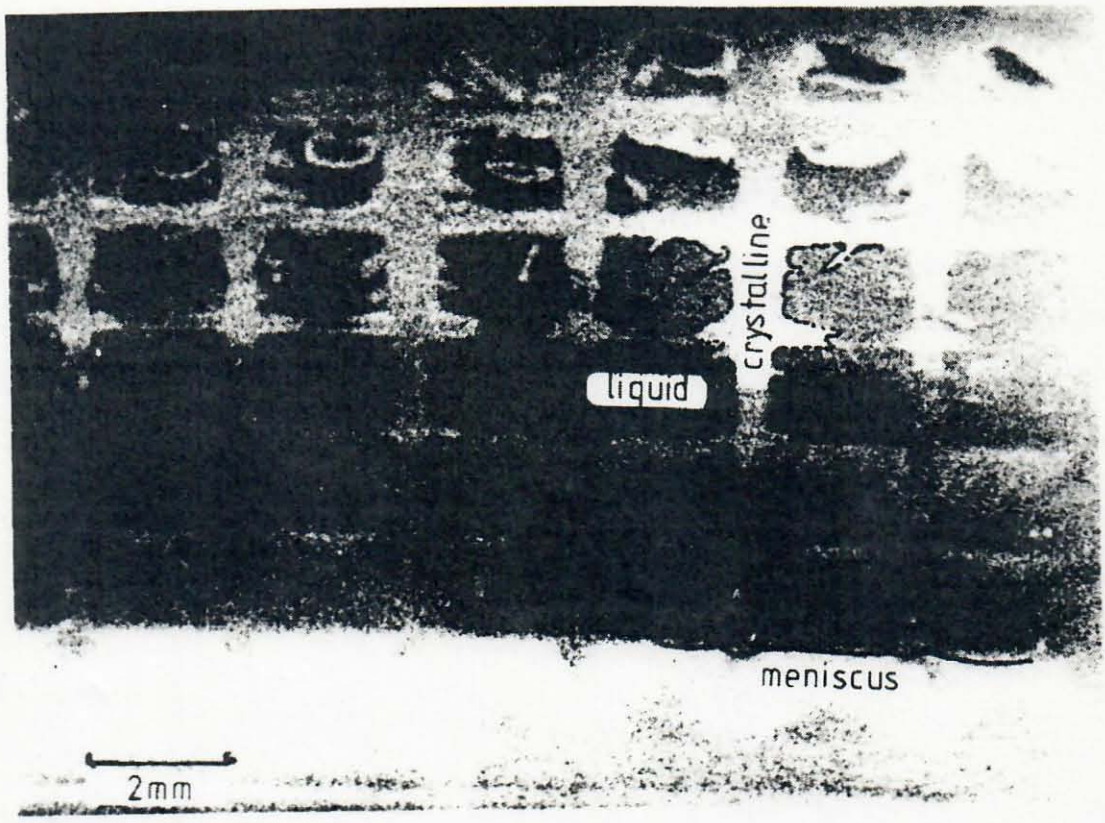

Fig. 3
In-situ photography of mesh-crystallization during withdrawal of a graphite grid.

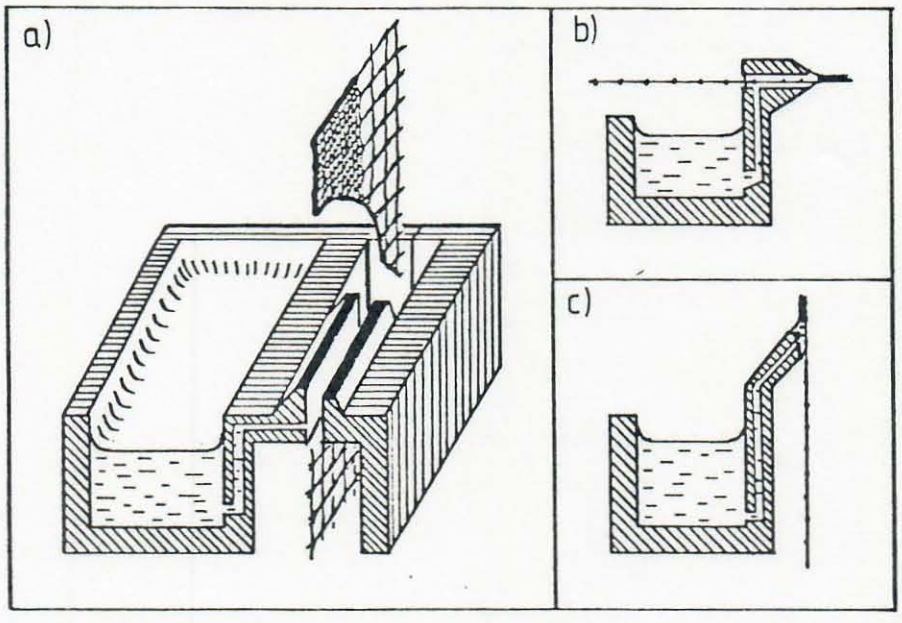

Fig. 4
Examples for slotted dies. a) shows the slotted die used in the S-Web-puller II; b)c) show two examples of slotted dies for horizontal pulling or for one-sided coating.

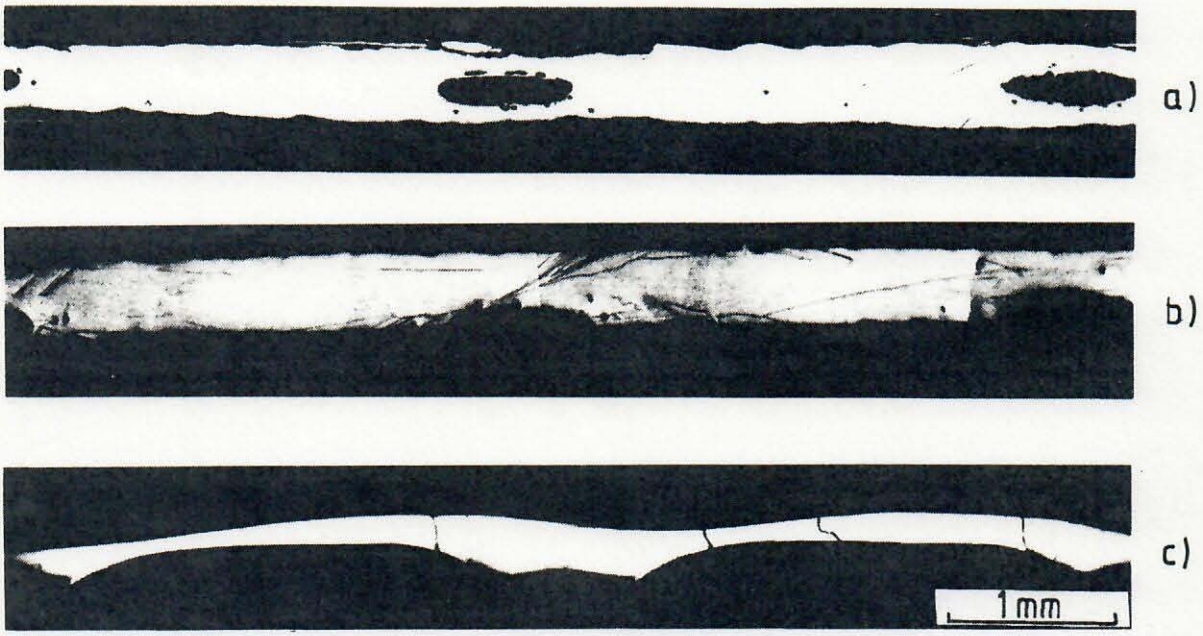

Fig. 5
Typical cross-sections of S-Web specimens obtained with a) a symmetrical slotted die; b) an asymmetrical slotted die as in Fig. 4a; and c) a one-sided die as in Fig. 4c.

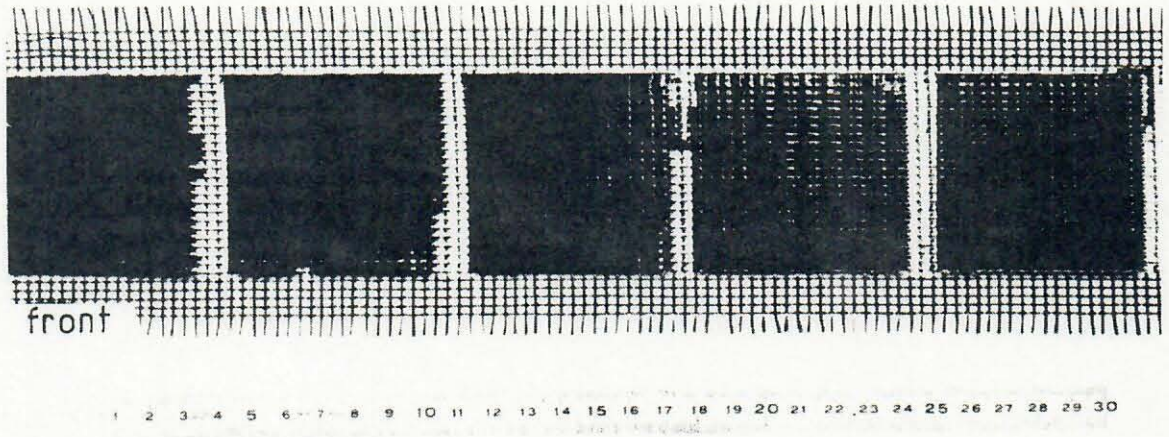

Fig. 6
Front- and back-side of part of a net coated on one side with Si.

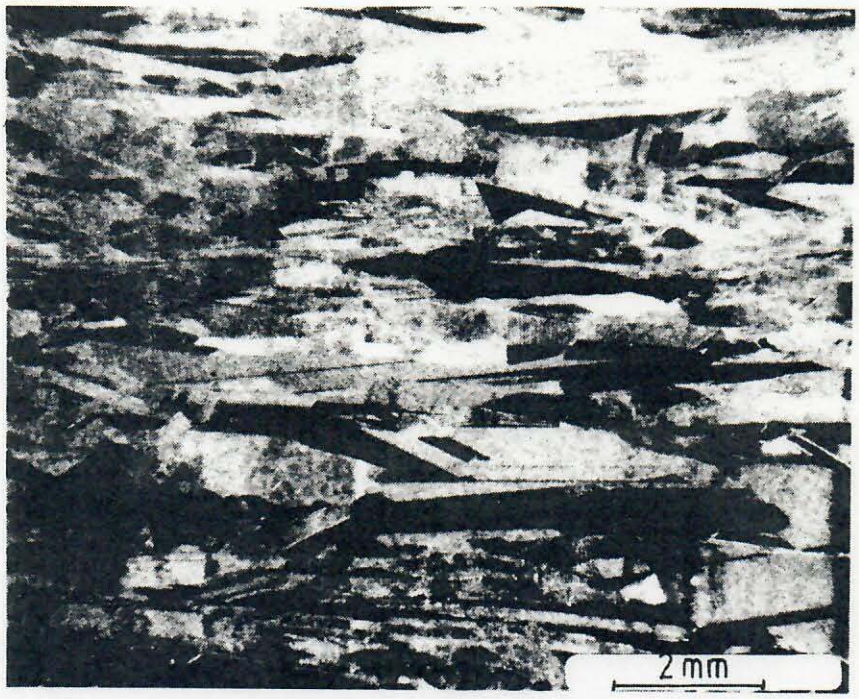

Fig. 7
Examples of carbon-filaments partially converted to SiC.

Fig. 8
As-grown surface (KOH-etched) of a horizontally pulled S-Web.

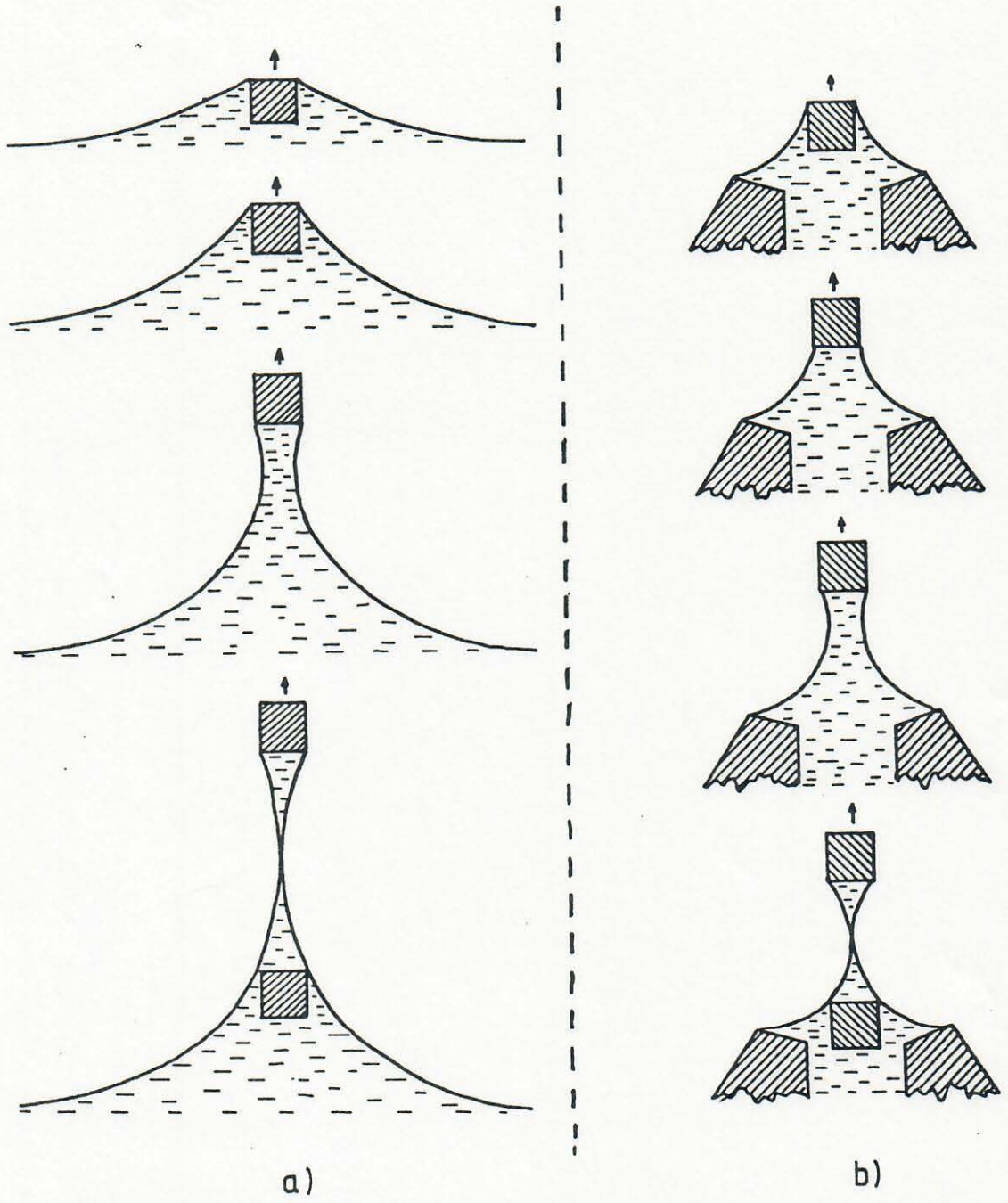

Fig. 9
Successive stages of filling the meshes of an idealized net (rectangular cross-section) with liquid Si for the case of pulling the net through a free surface (9a) or through a slotted die (9b).

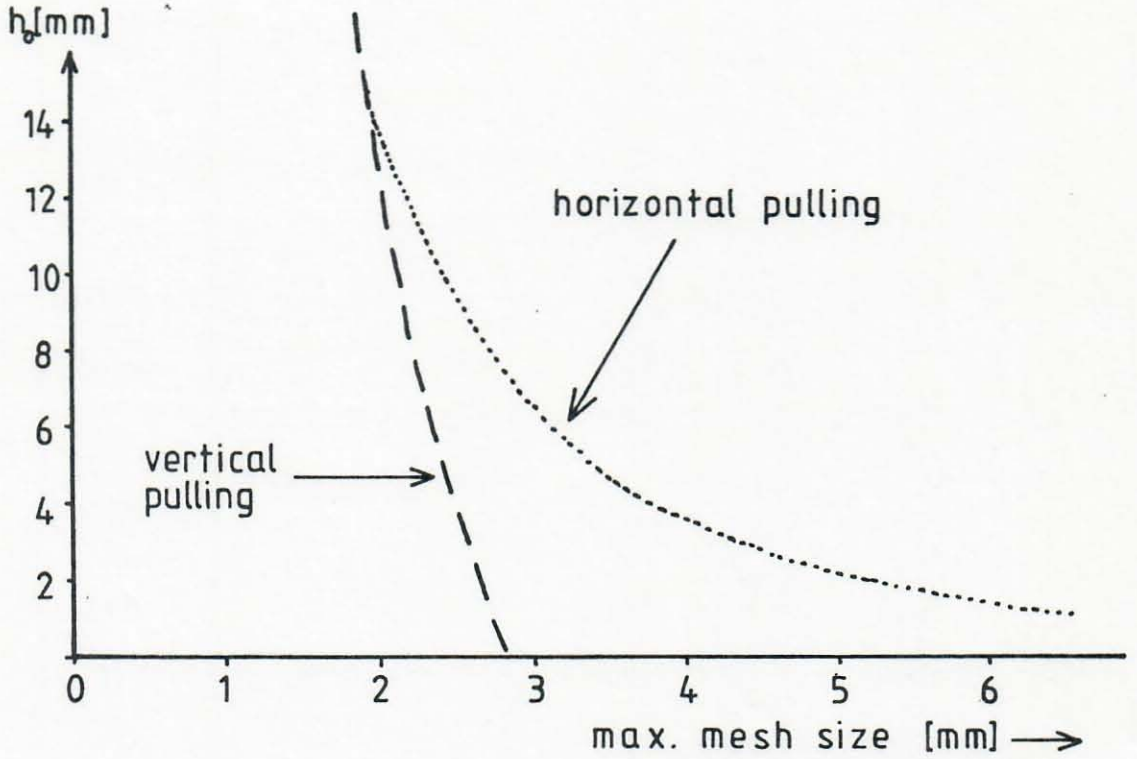

Fig. 10
Maximum mesh sizes for vertical and horizontal pulling for an idealized net with a "thickness" of 0.5 mm.

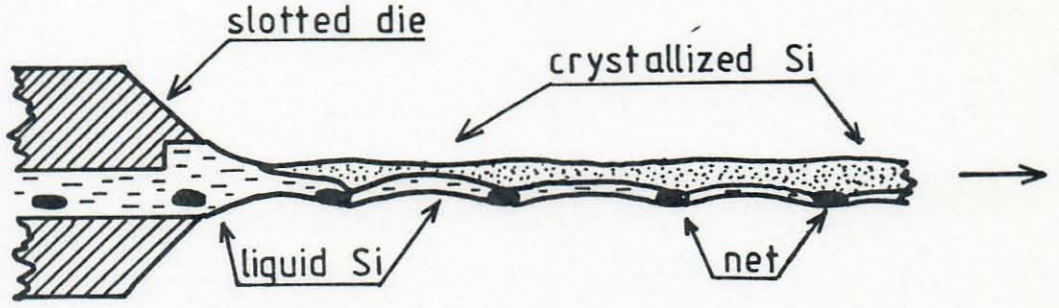

Fig. 11
Proposed geometry for high pulling speed.

DISCUSSION

KALEJS: Where are the advantages in your technique over the better-known vertical-pull techniques of the silicon-on-ceramic (SOC) that was done at Honeywell and the ribbon-against-drop (RAD) process that is being done in France?

GRABMAIER: The processing and the growth are very easy. At the moment we make plates up to 10 centimeters. When we grow vertically at high speeds, we have difficulties coating the mesh.

SCHWUTTKE: The major disadvantage, if you work with silicon-on-ceramic, is how you make a contact on the back. In this particular case you have no problem in making your contact on the back.

KALEJS: I think we should ask Dr. Belouet why he doesn't grow one meter per minute.

BELOUET: I don't really think we can pull at one meter per minute in our process as it is now. In the vertical system that we have, the pulling rate is close to 15 centimeters per minute with a practical thickness.

KALEJS: [Directed to Belouet] So you believe that one meter per minute in your technique is not possible?

BELOUET: As it is now, no. If they (the S-web) want to make a smooth growth, they are in our situation and will have the same pulling rate.

KALEJS: That is the question I was asking--in order to go to one meter per minute in whatever vertical method, you have roughly the same problems with coating the substrate.

BELOUET: Yes.

KALEJS: In the horizontal mode, what do you see different in the crystal morphology at high speeds when the S-web is there? Do you see any differences in morphology from the vertical mode as you increase the speed and keep the net covered?

GRABMAIER: No, but I think it is much easier to grow horizontally than vertically. We can use larger meshes and therefore we need less carbon material. Carbon fiber material is expensive. One square meter costs around $10.

KALEJS: Have you actually grown at 20 centimeters per minute horizontally?

GRABMAIER: No. We are developing that now.

C. K. CHEN: What is the minimum diameter of the carbon fibers that you can use?

GRABMAIER: One filament has a thickness around 7 to 8 μm.

JEWETT: Are you going to be limited in your device quality by the mesh that you use?

GRABMAIER: Maybe. The problem develops when the fibers break, and hook to the surface.

SCHWUTTKE: How good are the cells? What is the average efficiency?

GRABMAIER: This cell has a 7% efficiency with the grid. If you remove the grid, you get a higher efficiency.

BELOUET: Are your silicon carbide contacts ohmic?

GRABMAIER: Yes.

LOUET: We always found the contrary.

GRABMAIER: Our idea was to incorporate the carbon fiber net in the back contact and we succeeded.

BELOUET: Regarding your concept of the combination of the LASS technique and the S-web, if you pull very fast, I don't see how the crystallinity will not be affected by the mesh and second, the active surface will be quite decreased at those high speeds.

GRABMAIER: I think the combination of LASS with a net is much better than the LASS is now because you will have fewer problems with the temperature, with thickness, with width and a better potential for the production line.

CISZEK: In the work that Jeff Hurd and I reported at the 14th Photovoltaic Specialists Conference in 1980 on a similar technique that we called Contiguous Capillary Coating, we observed a dendritic structure in the meshes as we tried to grow fast. Do you see also a dendritic morphology inside the meshes at your high growth speeds?

GRABMAIER: Sometimes, yes.

SUREK: This is more in the way of a comment and it may answer Dr. Kalejs's and Dr. Belouet's concern. You are decoupling the growth problem from the liquid attachment problem to the web, so the potential advantage of the technique is that you are really dragging the liquid away from the main melt source and crystallizing in a completely different environment, which you can control separately, unlike in LASS or RAD or SOC. So in principle there is decoupling of the wetting of the web and the crystallization that gives you flexibility, and even at higher growth rates you don't have to have dendritic growth, necessarily, because you can control your freezing over a much larger area. You can have a 4-meter-long cooling furnace to control the crystallization of the liquid over the web?

WARGO: I would like to reinforce what Tom Surek just said. That is absolutely true, and I see that as a major advantage of the technique. But if you are growing at faster speeds and you don't get complete filling of the mesh, it seems to me you also showed a technique where you can do

single-sided addition of silicon. Have you thought of a two-step process where in the first run you fill the web and in the second run you do a single sided addition of silicon on top of that filled web?

GRABMAIER: We tried it but we still have more development work left to do.