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Floating Silicon Method single crystal ribbon – observations and proposed limit cycle theory

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ABSTRACT

In the Floating Silicon Method (FSM), a single-crystal Si ribbon is grown while floating on the surface of a Si melt. In this paper, we describe the phenomenology of FSM, including the observation of approximately regularly spaced "facet lines" on the ribbon surface whose orientation aligns with (111) crystal planes. Sb demarcation experiments sectioned through the thickness of the ribbon reveal that the solid/melt interface consists of dual (111) planes and that the leading edge facet growth is saccadic in nature, rather than steady-state.

To explain this behavior, we propose a heuristic solidification limit cycle theory, using a continuum level of description with anisotropic kinetics as developed by others, and generalizing the interface kinetics to include a roughening transition as well as a re-faceting mechanism that involves curvature and the Gibbs–Thomson effect.

1. Introduction

In Horizontal Ribbon Growth (HRG) [1–4] heat is removed from the free surface of a molten pool, which causes the top surface to solidify. This solid is then pulled horizontally with a velocity, u_s, such that a steady-state process is established. We have developed a specific version of HRG called the Floating Silicon Method (FSM) to grow single crystal silicon directly in a form factor suitable for high efficiency solar cells. Since the density of the solid is less that of the liquid, it floats, allowing the sheet to extend over a long length of the melt with no mechanical stress. The novelty of FSM relative to previous HRG techniques is that floating enables the creation of distinct thermal zones having sufficient separation (i.e. much greater than the crucible depth) to allow independent control and optimization of different functions, namely: solidification of the leading edge, thickness control, low-stress separation from the melt, and low-stress removal from the hot furnace (see Fig. 1). For example, the ribbon's separation from the melt at the quartz crucible wall occurs in an isothermal region (just above the melt temperature), thus avoiding both thermal stress and issues of freezing to the wall. Also, within the region between the leading edge formation and the separation at the wall, additional heaters provide the heat needed to melt back the ribbon's thickness in a controlled manner, allowing an arbitrarily thin and uniform ribbon to be pulled from the melt. In our test stand, we have been able to produce single-crystal (100) ribbons with low dislocations ($< 1E3/cm^2$), widths greater than 15 cm, pull speed greater than 2 mm/s, and thinness below 200 μm. This can all be done in a continuous manner.

Previous experimental work [3,4] has provided information such as growth rates, sheet thickness, and types of material grown (single-crystal versus multi-crystal). But heat flow for the different functions was not distinct (i.e. they did not make use of the floating nature of the ribbon), and so they were not able to achieve single crystal, wide, thin, continuous growth. Ciszek [23] observed faceted growth at the surface of a melt, but it was not pulled to form a ribbon.

In the FSM process we have found that a (111) facet forms at the leading edge of the ribbon and that the growth proceeds in a series of abrupt spurts in a saccadic process. A solidification limit cycle theory is proposed to describe this saccadic behavior. The combined facet/roughened interface kinetics of Weinstein and Brandon [5] is generalized to include a kinetic roughening transition, as well as a re-faceting mechanism that involves the curvature of the interface. Numeric estimates are included to relate this theory to observations.

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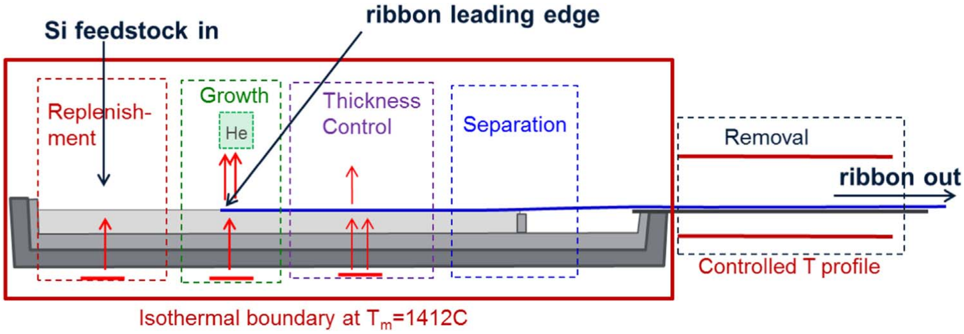

Fig. 1. Schematic depiction of the continuous FSM process. The floating ribbon enables localized heat flow zones optimized for the different functions of crystal growth.

2. Phenomenology

In FSM, ribbon growth is initiated by inserting a seed cut from a CZ (100) wafer into the furnace, floating it on the melt, and moving it such that its leading edge is within a growth zone. The growth direction is in the [011] direction, although some experiments were performed with seeds cut from a (111) wafer with a $[11\underline{2}]$ growth direction. Stable single crystal growth was achieved by using a narrow line of intense helium cooling above the melt and a heater below the quartz crucible in the growth zone. For example, in order to grow ribbons at a steady state horizontal pull speed of 1 mm/s, helium cooling with a profile peaked at approximately 100W/cm^2 and heat flow in the melt of approximately $15\ \text{W/cm}^2$ was required. Attempting to pull faster with these conditions resulted in the ribbon pulling out or becoming dendritic.

This result is quite distinct from the expectation from previous HRG work, where the solidification is described by a "growth wedge" [5,6–13], in which the leading end of the ribbon tapers to zero thickness forming a shallow growth angle. The interface is assumed to be atomically roughened, remaining at the equilibrium melt temperature, with growth velocity determined solely by heat flow, so that one should be able to pull ribbon at arbitrarily fast speeds with a low intensity, broad, heat removal source, with the thickness of the ribbon getting arbitrarily smaller as one pulls faster without limit.

Another feature of ribbons grown with FSM is the presence of "facet lines" on the top surface (Fig. 2). For a (100) ribbon, the top surface is generally in the [100] crystal direction, yet is not itself a facet. The top surface is rather the wake of the leading edge as it freezes, and is in a certain sense a "fossil record" of the leading edge freezing process. Ridges or facet lines run laterally across the ribbon, perpendicular to the growth direction, with roughly regular spacing of approximately 10 μm, ending at the ribbon edges caused by the tapering off of the cooling gas jet towards the sides. The side effects regions are still single crystal, i.e. one finds that there are no grain boundaries or twins. On closer inspection, side effects consist of the mitered joining of angled facet lines. In the case of (100) ribbons pulled in the [110] direction, these mitered joints are at 90°, whereas for (111) ribbons pulled in the [112] direction, the mitered angles are at 120°.

A more detailed study of the top surface morphology was accomplished using a Keyence confocal microscope (Fig. 3a). This revealed a surface profile resembling a rounded saw tooth with peak to valley amplitude generally between 0.05 and 0.5 μm; the lines being a visual effect of the saw tooth peaks and valleys. This pattern also exhibits a random element; while the saw teeth generally alternate up and down, at times there may be 2 or more ups or downs in a row. We believe that this is due to the random sampling of the relatively slow melt surface waves by the very fast saccadic facet layering (as will be discussed later in this paper). It should be noted that in solar cell manufacturing, the KOH texturization etch (which is generally >10 um) will eliminate the facet lines, and the side-effects can be melted back while the ribbon is floating in the melt, so that a ribbon will be able to be used as-grown, without additional surface processing steps.

The direction of these facet lines on the ribbon surface can be related to the diamond cubic crystal structure of silicon with space group Fd3m. In the case of a (100) ribbon being grown in the [011] direction, there are 8 possible {111} planes that can intersect the surface as shown in Fig. 4a. $\{111\}=(111), (\underline{1}11), (1\underline{1}1), (11\underline{1}), (\underline{11}1), (\underline{1}1\underline{1}), (1\underline{11}), (\underline{111})$, where we are using underlining to indicate a negative Miller index. The intersection of either the (111) or $(\underline{1}11)$ planes with the top surface (100) plane forms a line that is perpendicular to the pull direction, corresponding to the facet lines across the width of the ribbon. If the leading edge of the ribbon were indeed a (111) facet, it would form an "acute" 54.7° angle with the top surface, while a $(\underline{1}11)$ leading edge would form an

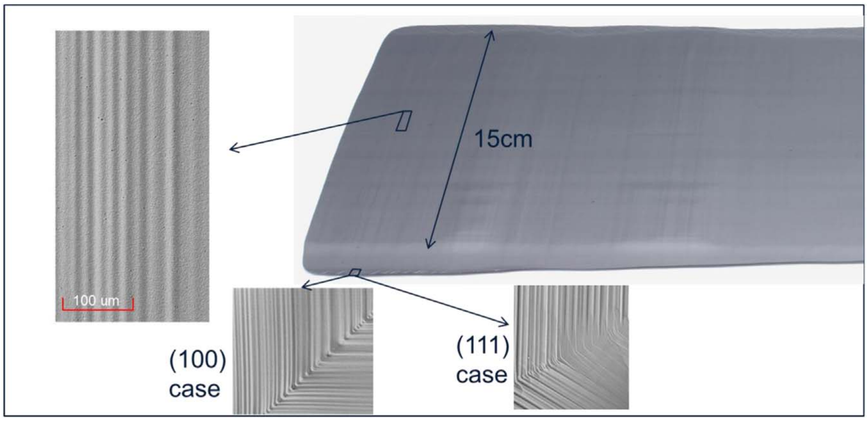

Fig. 2. Picture of typical top surface of FSM ribbons, with micrographs of the transverse facet lines and "side effects" for both (100) and (111) cases.