Journal of Crystal Growth 390 (2014) 80–87

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

An analysis of segregation during horizontal ribbon growth of silicon

Parthiv Daggolu, Andrew Yeckel, Jeffrey J. Derby *

Department of Chemical Engineering and Materials Science, University of Minnesota, 151 Amundson Hall, 421 Washington Avenue SE, Minneapolis, MN 55455-0132, USA

ARTICLE INFO

Article history:
Received 31 October 2013
Received in revised form
6 December 2013
Accepted 8 December 2013
Communicated by P. Rudolph
Available online 24 December 2013

Keywords:
A1. Computer simulation
A1. Convection
A1. Heat transfer
A1. Segregation
A2. Edge defined film fed growth
B2. Semiconducting silicon

ABSTRACT

A finite-element, thermal-capillary model is applied to study solute segregation in the horizontal ribbon growth of silicon. Results show a complicated redistribution of solute into the growing ribbon, with nearly constant composition in the upper portion of the crystal and high levels of solute incorporation in the lower portion. The redistribution pattern is explained by convective flow patterns and interfacial geometry in the system. Lower values of equilibrium partition coefficient and solute melt diffusivity contribute to more inhomogeneous crystal composition. Faster pull rates lead to more pronounced redistribution of solute in the crystal. Paradoxically, the inhomogeneous concentration levels in HRG ribbon may be beneficial; impurities accumulate towards a narrow bottom portion of the crystal, leaving a majority of the crystal relatively pure.

1. Introduction

Vertical ribbon growth techniques for solar silicon, such as the edge-defined film-fed growth (EFG) method, suffer from significant limitations, such as slow growth rates [1,2], high thermal stresses and buckling of crystals [3], and high concentration of carbon impurities [4] that consequently result in low solar cell efficiencies [5]. The horizontal ribbon growth (HRG) process promises to overcome these limitations. Faster growth rates may be attained by extending the solidification interface over several centimeters in length to better dissipate latent heat. Contrasting with the situation in vertical ribbon growth techniques, removing latent heat and minimizing stresses may be separated via relatively independent thermal management strategies. First, latent heat is induced to flow vertically through the sheet thickness due to the extended, nearly horizontal melt–crystal interface. Second, after-heaters may be engineered to manage thermal stresses in the ribbon exiting the growth chamber. Finally, the horizontal configuration of growth eliminates the need for graphite shaping dies, thus carbon levels can be controlled to a much greater extent than in vertical growth systems.

Bleil implemented first practical implementation of the HRG process for growing thin ribbons of ice and germanium [6,7]. Later work by Jewett et al. [8] and Kudo [9] demonstrated laboratory scale growth of silicon, both single and multi-crystalline, at growth rates as high as 41.5–85 cm/min, respectively. However, both these efforts were hindered by a host of issues that prevented stable process operation. Several early modeling efforts were aimed at addressing these challenges [10–14] but involved highly idealized assumptions.

Recently, we have developed a comprehensive thermal-capillary model to study the characteristics and underlying challenges to operation of the HRG system [15,16]. Our first study [15] demonstrated the feasibility of the process, subject to suitable heat transfer design, and revealed existence of limiting growth rates and multiple operating states due to nonlinear effects. Our second study [16] predicted the occurrence of failure events, such as bridging of crystal onto the crucible, spilling of melt from the crucible, and the undercooling at the ribbon tip, that were consistent with the major problems identified by Kudo [9]. Thus, our models validated many of the concepts arguing for the promise of HRG, while also revealing the mechanisms responsible for many instabilities that limit stable operation to relatively narrow operating windows in a parameter space.

Toward deepening our understanding of the horizontal ribbon growth process, this study aims to clarify how dopants and impurities will be redistributed into the growing ribbon. Unfortunately, to our knowledge, there has been no prior publication of segregation data for the HRG process, so we have no direct means to assess the validity of the purely theoretical results we present here. There are also no prior analyses of segregation in HRG systems. The segregation of dopants and impurities has been modeled in the past for vertical

* Corresponding author. Tel.: +1 612 625 8881.
E-mail address: derby@umn.edu (J.J. Derby).

0022-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jcrysgro.2013.12.021

EFG systems. Kalejs [17] first studied impurity redistribution during vertical silicon ribbon growth via numerical solution of the convection-diffusion equation in a geometry representative of an EFG system. Ettouney et al. [18] considered aluminum segregation during the edge-defined film-fed growth of silicon sheets via a thermal-capillary analysis similar to the approach employed here. Later analyses by Kalejs and co-workers refined the understanding of segregation in vertical growth systems [19–21]. Braescu and co-workers numerically modeled segregation occurring in thin, cylindrical rods of silicon [22] and small-diameter fibers of oxides [23] grown via EFG methods. Smirnova et al. [24] employed experiments and modeling to understand redistribution of impurities during EFG silicon crystal growth. Based on the valuable insights obtained via the prior modeling of segregation in vertical EFG processes, we believe the following study will be fruitful.

Our modeling approach is outlined in the following section, followed by a discussion of several representative cases. We find that the unusual geometry of the HRG system, in particular its extended solidification interface, leads to unexpected concentration profiles in the ribbon. We find that solute redistribution in this system is quite inhomogeneous; however, the particular segregation profiles arising in HRG may be beneficial.

2. Thermal-capillary, species segregation model

We have developed a two-dimensional, thermal-capillary model that rigorously solves for mass, momentum, and energy conservation while simultaneously accounting for capillary physics of the menisci, solidification at the interface, and self-consistent determination of ribbon thickness. Detailed discussion of this model is presented in [15,25]. A brief recap of the model is presented below, followed by a description of how segregation is computed.

A schematic representation of the HRG system is depicted in the upper portion of Fig. 1, showing the melt–crystal–crucible domains, arrangement of heating and cooling mechanisms, and other model details. The heat transfer between the system and the surrounding furnace is represented by radiation to specified ambient temperature profiles. In addition, convective cooling by a gas jet is applied at the leading edge of the ribbon. Driving forces for flow include buoyancy through the bulk and Marangoni forces along the menisci. For simulations of steady operating states of this system, we specify a make-up flow through the bottom of the crucible to keep the upper surface of the melt at a prescribed level. Details of this implementation are provided in [15].

The domain shapes are determined by the solution of moving boundaries in the problem, namely the solidification interface, the upper and lower menisci, and the thickness of the ribbon. At the solidification interface, which divides the melt and crystal domain, the temperature field is continuous, the difference in heat flux between melt and crystal is balanced with the latent-heat release, and its shape is tracked by following the melting-point isotherm. The shapes of the two melt-gas interfaces, namely the upper and lower menisci, are determined via a normal force balance between capillary and fluid forces. The lower meniscus is pinned to the crucible while the upper meniscus is allowed to slide along the crucible wall as melt level varies, maintaining a contact angle of $\theta_C = 90^\circ$. At the triple phase lines (TPL), where the melt connects to the crystal, a growth angle of $\theta_g = 11^\circ$ is always maintained, which determines the location of these points and the ribbon thickness. Useful discussions of the physics associated with this growth angle can be found in [26–29].

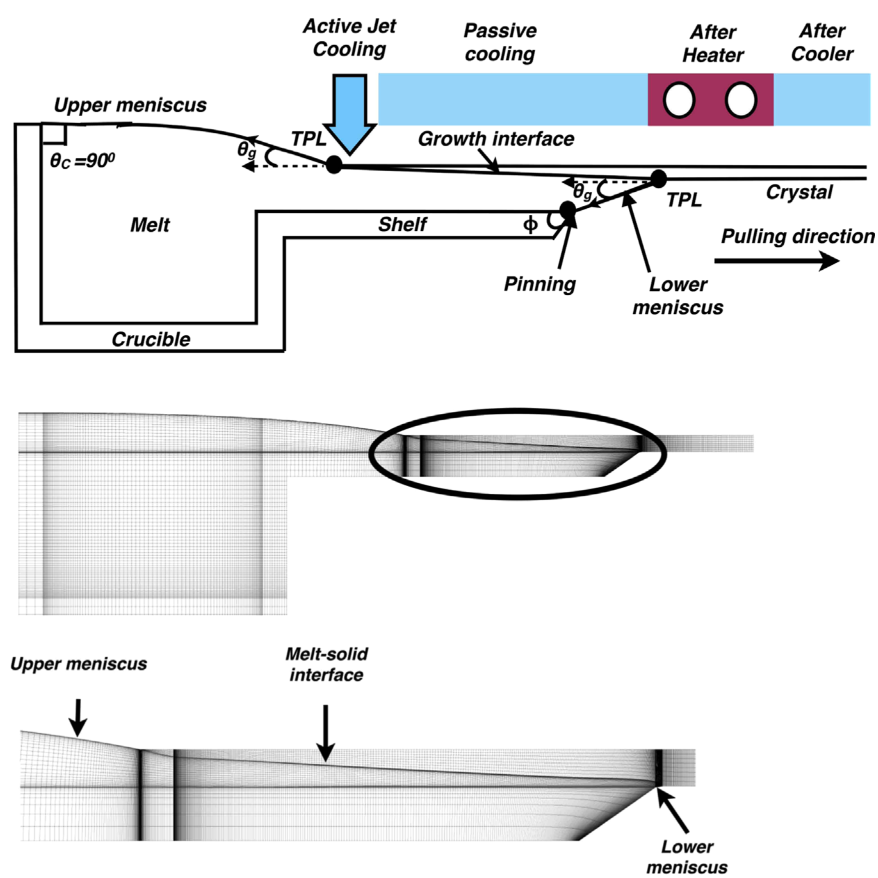

Fig. 1. Above: schematic of HRG system showing the domains of melt, crystal and crucible, along with the shape of extended growth interface and pulling direction. Below: example of finite-element mesh showing geometry of a steady-state solution. Lower image is an expanded view of the mesh near the growing ribbon.