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Influence of contact angle, growth angle and melt surface tension on detached solidification of InSb

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Abstract

We extended the previous analysis of detached solidification of InSb based on the moving meniscus model. We found that for steady detached solidification to occur in a sealed ampoule in zero gravity, it is necessary for the growth angle to exceed a critical value, the contact angle for the melt on the ampoule wall to exceed a critical value, and the melt-gas surface tension to be below a critical value. These critical values would depend on the material properties and the growth parameters. For the conditions examined here, the sum of the growth angle and the contact angle must exceed approximately 130°, which is significantly less than required if both ends of the ampoule are open.

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1. Introduction

Directional solidification in microgravity has often led to ingots with sections that grew with little or no contact with the ampoule wall. We call this phenomenon "detached solidification". The many experimental observations were recently reviewed in detail, with 136 references to microgravity results [1]. Several different types of detachment were distinguished, ranging from isolated bubbles on the wall to an hour-glass shaped solid. The data did not support any conclusion about the type of material most likely to yield detachment or the best gas pressure to use when sealing the growth ampoule. The experimental observations did indicate that it is desirable to use a low freezing rate and an ampoule that the solid does not strongly adhere to. When detachment occurred, crystallographic perfection was greatly enhanced. Dislocation densities were typically reduced by two orders of magnitude, often with complete cessation of nucleation of new grains and twins. In semiconductors, charge carrier mobility was greatly increased, presumably as a consequence of the lower defect density. Sometimes there was evidence of Marangoni convection, and sometimes there was not. Possible reasons for the erratic results of flight experiments are discussed in Ref. [1].

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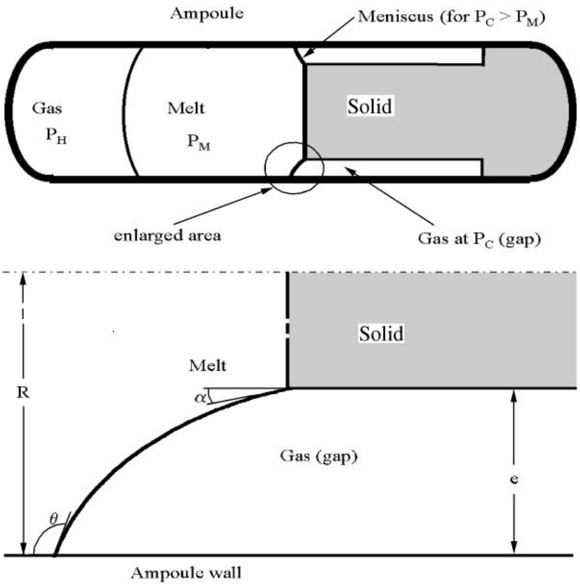

Fig. 1. The moving meniscus model for detached solidification. Gas dissolves in the melt, is segregated out by the freezing solid, and is liberated at the meniscus to fill the gap. A volatile species may fill the same role.

Proposed mechanisms for detached solidification were reviewed in Refs. [2,3]. For many years, it was commonly thought that the detached solid must have solidified from a melt that was not in contact with the ampoule wall, i.e. that the solid took the same shape as the melt from which it froze. A combination of experiments and theory showed that it is not possible to have a cylindrical melt without the constraint of an ampoule wall. Consequently, in 1995 Regel and Wilcox proposed the moving meniscus model for detached solidification [2]. As shown in Fig. 1, the melt remains in contact with the ampoule wall. There is a gap between the solid and the wall. A meniscus connects the melt at the wall with the edge of the freezing interface. As freezing progresses, this meniscus moves along the wall. When both ends of the ampoule are sealed, a volatile species must fill the gap in order to provide a pressure difference across the curved meniscus. Generally speaking, this volatile species is residual gas that dissolved in the melt and is rejected by the growing solid.

In 1997, three papers from our group were published on numerical simulation of the moving meniscus model [4–6]. These analyses used the properties of indium antimonide, which has frequently demonstrated detached solidification in microgravity. It was necessary to assume values for the solubility of gas in the melt and in the solid, as no data could be located. The relationship between growth angle, contact angle and gap width was that appropriate for an ampoule diameter much larger than the gap width. At steady state, the flux of gas across the meniscus and into the gap must be sufficient to maintain the pressure difference due to curvature of the meniscus. These analyses were concerned largely with determining this flux.

Initially, it was found that Marangoni convection introduces vigorous convection near the meniscus and significantly alters the local concentration field [4]. However, Marangoni convection has only a small influence on the gas flux into the gap [4]. Consequently, it was ignored in subsequent analyses. When the other parameters were held constant, it was found that there is a residual gas pressure below which steady-state detachment cannot occur. This prediction cannot be compared with published experimental results [1] because several mechanisms lead to development of a significant gas pressure even in ampoules that have been sealed under high vacuum [7–9].

It was also found that there is a freezing rate above which detachment does not occur [4]. This result does agree with the experimental observations that low freezing rates favor detachment [1]. It comes about because the "diffusion layer" is increasingly compressed against the freezing interface as the freezing rate is increased. Eventually this causes diffusion of gas out of the gap for that part of the meniscus far from the freezing interface, thereby leading to a maximum in total gas flux versus freezing rate.

In Ref. [5], the stability of steady-state detachment was examined. The shape of the meniscus is a destabilizing influence, as with diameter control in Czochralski growth. While a flux of gas into the gap is necessary for detachment to continue, it does not appreciably stabilize the process. Heat transfer does stabilize detachment, again similarly to the stabilization of diameter in Czochralski growth.

In Ref. [6] the influence of gravity was examined. The presence of a hydrostatic head increases the required gas flux into the gap. On earth, buoyancy-driven convection, although weak in vertical Bridgman growth, generally mixes the melt sufficiently to reduce the gas flux into the gap. It is for these two reasons that detached solidification is rare on earth. Rare, but not impossible, as shown by a serendipitous result on germanium [10–12]. Convection increases the flux of gas into the gap if it is gentle and directed radially outward along the freezing interface. In vertical Bridgman growth such convection is expected for a slightly convex interface shape, as observed in Refs. [10–12].

Duffar [13] generalized the equation relating meniscus shape to gap width for any ampoule radius at zero gravity. He also pointed out that detachment can be obtained for an ampoule open at both ends if the sum of the growth angle and melt contact angle are sufficiently large, 180° in the limit of a very large ampoule diameter.

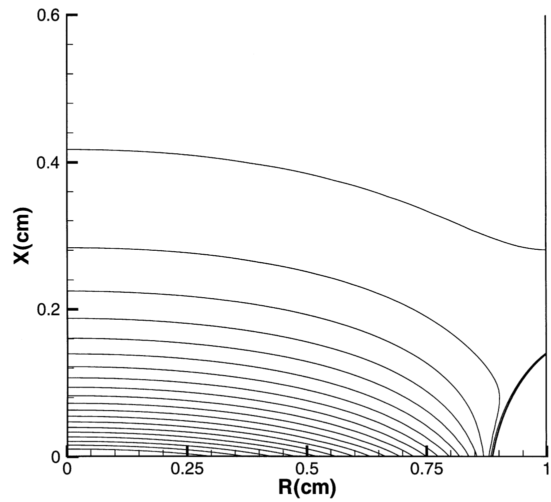

Fig. 2. The concentration field of dissolved gas in the melt for a gap width e of 0.12 cm, contact angle θ of 115°, and growth angle α of 15°. The curves are lines of constant concentration, with 2×10^{-8} mol/m^3 between lines.

2. Method

Here, we utilized the previous method [4] to perform parametric analyses of the influence on detachment of the contact angle of the melt on the ampoule wall, the growth angle, and the melt-gas surface tension. The assumptions and the values chosen for the other operating parameters and physical properties were the same as in Ref. [4], i.e. the properties of InSb, zero gravity, steady state, a gap width e much less than the ampoule radius R, no Marangoni convection (zero stress along the meniscus), slip for a short distance near the meniscus-ampoule contact line, the end of the melt far from the freezing interface, saturation of the melt with dissolved gas, constant average temperature of the gas in the gap, constant gap width versus distance along the solid, and ideal gas behavior within the gap. The following values were used as the basic state: freezing rate $V_c = 1.0\times10^{-4}$ m/s, diffusion coefficient $D = 10^{-9}$ m^2/s, growth angle $\alpha = 25°$, contact angle $\theta = 112°$, melt-gas surface tension $\sigma = 0.43$ N/m, residual gas pressure above the melt $P_H = 100$ Pa with a solubility in the melt of 0.16 mol m^{-3} Pa^{-1}, average temperature of the gas in the gap = 800 K, solubility of gas in the melt at the meniscus of 0.13 mol m^{-3} Pa^{-1}, kinematic viscosity of the melt equal to 3.6×10^{-7} m^2/s, segregation coefficient of dissolved gas at the freezing interface equal to 0.03.

In this procedure [4], first the gap width is assumed, giving the meniscus shape and the required pressure change across it. The velocity field in the melt is calculated numerically. The concentration field is calculated, from which the gas flux into the gap is found. This yields a new value for the gap width. For the same assumed gap width, this process is repeated for several values of the parameter being varied, e.g. contact angle. The calculated gap width is plotted versus this parameter. The value of the parameter for which the calculated gap width equals the assumed gap width is the correct value of the parameter for this gap width. This process is repeated for other assumed gap widths, finally yielding gap width versus the value of the parameter under investigation.

3. Results

Fig. 2 shows the concentration field of dissolved gas throughout the melt for one set of conditions. Rejection of dissolved gas by the freezing interface increases its concentration there. The flux of gas

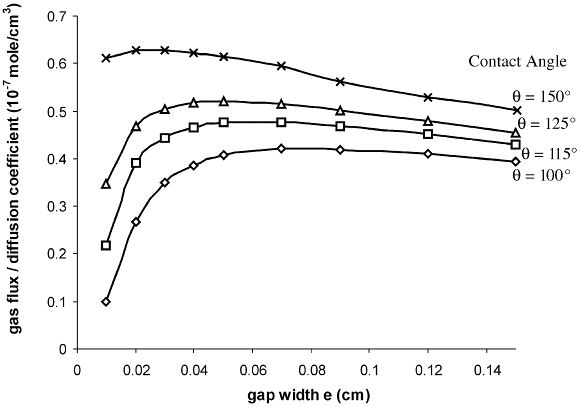

Fig. 3. Dependence of the molar gas flux on the gap width e and the contact angle θ.

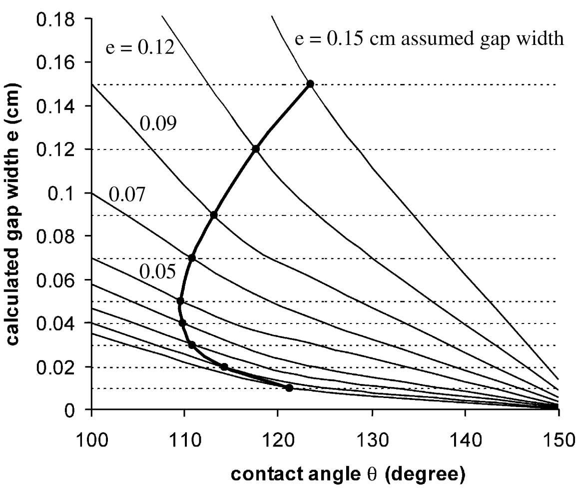

Fig. 4. Dependence of the steady-state gap width e on the contact angle θ. From bottom to top, the assumed gap widths for the curves are 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.09, 0.12 and 0.15 cm. A correct value is where the assumed gap width equals the calculated gap width, i.e. the intersection of the curve with the horizontal line for the same value of gap width.

into the meniscus lowers the gas concentration there. The consequence is that the concentration is a maximum at the freezing interface at the ampoule centerline. If the concentration at the meniscus near the ampoule wall is below the equilibrium value for the gas pressure in the gap, there will be a flux of gas back into the melt.

Fig. 3 shows the dependence of the total integrated gas flux on gap width e for different values of

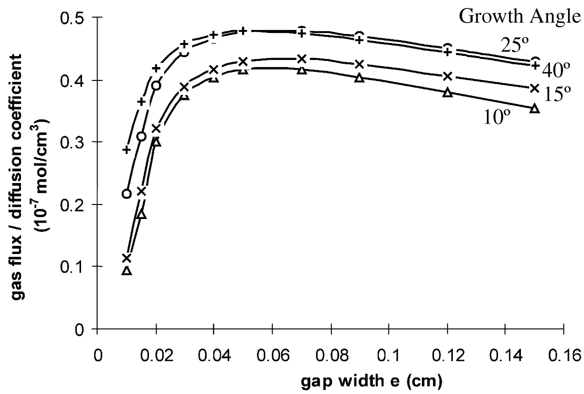

Fig. 5. Dependence of the molar gas flux on the gap width and the growth angle α.

the contact angle θ. For small e, the flux increases with e, because of the increase in the length of the meniscus through which the dissolved gas can diffuse. With continued increases in e, the meniscus near the wall moves farther from the freezing interface and eventually contacts melt where the dissolved gas concentration is below equilibrium with the gas in the gap. Thus out-diffusion occurs over this part of the meniscus to lower the total integrated flux. The net result is a maximum in total flux versus gap width. For the same gap width, increasing the contact angle increases the total flux into the gap, again because of the interaction of the meniscus shape with the concentration field.

In Fig. 4, each thin line gives calculated e versus contact angle θ for a particular assumed value of e. The correct gap width is where the calculated e equals the assumed e, i.e. the intersection of the horizontal dashed line with the thin curved line. The heavy line connecting all these intersections describes the relationship between steady state gap width and contact angle. Note that there is a critical contact angle, here about 110°, below which steady detached solidification is not possible under these conditions.

Fig. 5 presents similar results for the influence of growth angle α, with the contact angle θ held constant at 115°. For fixed gap width, there is a maximum in integrated gas flux at a particular growth angle, again reflecting the interaction between the meniscus shape and the concentration field. Fig. 6 shows that there is a minimum growth angle,

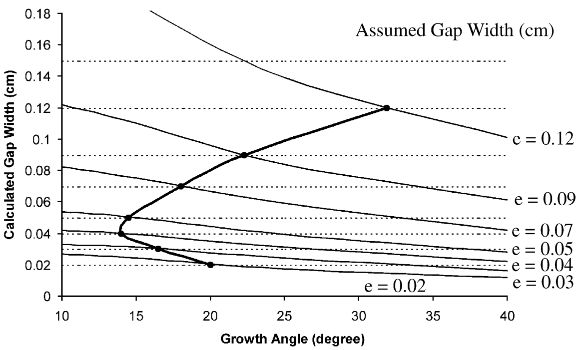

Fig. 6. Dependence of the steady-state gap width on the growth angle α. A correct value is where the assumed gap width equals the calculated gap width, i.e. the intersection of the curve with the horizontal line for the same value of gap width.

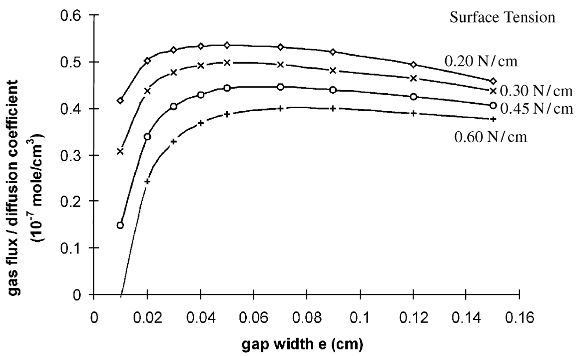

Fig. 7. Dependence of the molar gas flux on the gap width e and the surface tension σ of the melt.

here about 14°, below which steady detached solidification is not possible.

Fig. 7 shows the influence of surface tension σ with a fixed growth angle $\alpha = 25°$ and contact angle $\theta = 115°$. For fixed gap width, the integrated gas flux decreases with increasing surface tension. Fig. 8 shows that the melt-gas surface tension must be below a critical value in order to achieve detached solidification.

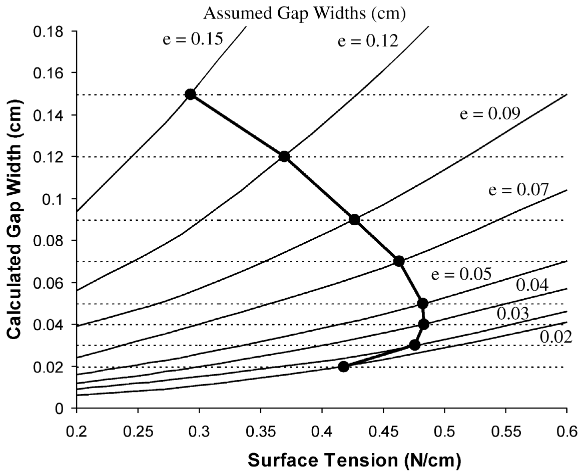

Fig. 8. Dependence of the steady-state gap width on the surface tension of the melt. A correct value is where the assumed gap width equals the calculated gap width, i.e. the intersection of the curve with the horizontal line for the same value of gap width.

4. Conclusions

Steady-state detached solidification is possible only if the growth angle α and contact angle θ are sufficiently large and the surface tension σ is sufficiently small. The critical values for these parameters will depend on the values of the operating parameters and the other material properties. We note that the present critical values yield $\alpha + \theta \approx 135°$ for $\alpha = 25°$ and $\alpha + \theta \approx 129°$ for $\theta = 115°$. These are to be compared to the value $\alpha + \theta = 180°$ for $e \ll R$ with the ampoule open at both ends so that the pressure in the gap is the same as at the other end of the ampoule [13]. Thus, we see that gas transport into a sealed gap significantly reduces the growth angle and the contact angle required to achieve detached solidification.

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