Existence and static stability of a capillary free surface appearing in a dewetted Bridgman process. Part II.

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Abstract: *This paper presents six theoretical results concerning the existence and static stability of a capillary free surface appearing in a dewetted Bridgman crystal growth technique. The results are obtained in an axis-symmetric 2D model for semiconductors for which $\theta_c + \alpha_e > \pi$ (where: θ_c- wetting angle and α_e- growth angle). Numerical results are presented in case of GaSb semiconductor growth. The reported results can help, the practical crystal growers, in better understanding the dependence of the free surface shape and size on the pressure difference across the free surface and the right choice of crystal size, pressure difference and thermal conditions for the growth process.*

Key Words: *dewetted Bridgman technique, static stability, seed radius choice, GaSb growth*

1. INTRODUCTION

Dewetted Bridgman is a crystal growth technique based on the Bridgman method in which the crystal is grown detached from the ampoule wall by the free surface of a liquid bridge at the level of the liquid-solid interface. The liquid bridge is called meniscus (see Fig. 1).

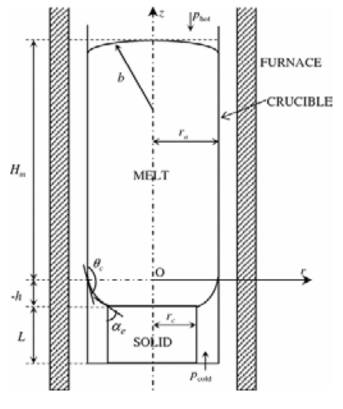

Fig. 1 Schematic dewetted Bridgman crystal growth system

Dewetting was first obtained spontaneously in space experiments during InSb Bridgman solidification performed on Skylab-NASA mission-1974 [1],[2] and subsequently in many experiments carried out in orbiting spacecraft on a wide variety of semiconductors [3]. Understanding the results obtained in microgravity opened the possibility for the dewetting growth on the Earth that can be obtained by applying a gas pressure between the cold and hot sides of the sample $\Delta P = P_{cold} - P_{hot}$ [4], [5] (Fig. 1).

Such an experimental application **is** described in [4]. On the basis of results reported by Duffar the conditions of detached solidification under controlled pressure difference were investigated by Palosz et. al in [6].

Using un-coated and coated-silica ampules they achieved detached and partially detached growth in some 20 solidification experiments.

They concluded: if $\theta_c + \alpha_e > \pi$, then steady detached growth is possible in a wide range of pressure differences; if $\theta_c + \alpha_e < \pi$, then a steady state detached growth may be expected in a narrow range only. In [7] the dependence of the meniscus shape on the pressure difference was analyzed for $\theta_c + \alpha_e < \pi$.

Paper [8] improves the theoretical part of the analysis presented in [7] also taking into account the static stability condition of the meniscus. The analysis is developed in an axis-symmetric 2D model. This paper extends the analysis developed in Part I. [8] to the case $\theta_c + \alpha_e > \pi$.

The differential equation of the meridian curve of the meniscus free surface in the coordinate system presented in Fig. 1 is given by:

$$z'' = \frac{-\rho \cdot g \cdot z + p}{\gamma}\left[1 + (z')^2\right]^{3/2} - \frac{1}{r} \cdot \left[1 + (z')^2\right] \cdot z' \quad R_c \le r \le R_a \tag{1}$$

where R_c is the crystal radius, R_a is the ampule radius and p is the pressure difference $p = \rho \cdot g \cdot H_m - \Delta P$.

The function $z(r)$ satisfying (1), has to verify also the following conditions:

$$z'(R_c) = tan((\pi/2) - \alpha_e) \quad z(R_c) = -h_c \tag{2}$$

$$z'(R_a) = tan(\theta_c - \frac{\pi}{2}) \quad z(R_a) = 0 \tag{3}$$

$$z(r) \text{ is strictly increasing on } [R_c,\ R_a] \tag{4}$$

Beside the conditions (1) - (4) function $z(r)$, describing the meridian curve, has to minimize the energy functional of the melt column behind the free surface. This functional is given by:

$$I(z) = \int_{R_c}^{R_d} \left\{\gamma \cdot \left[1 + (z')^2\right]^{1/2} - \frac{1}{2} \cdot \rho \cdot g \cdot z^2 + p \cdot z\right\} \cdot r \cdot dr \tag{5}$$

The last condition is called the static stability condition of the axis symmetric free surface. It is essential because in real world equilibrium capillary free surfaces exist only when the minimum condition is satisfied [9].

2. THEORETICAL RESULTS

Statement 1. If $\theta_c + \alpha_e > \pi$, then a necessary condition for the existence of a function $z(r)$ having the properties (1) - (4) and $z''(r) > 0$ for $r \in [R_c, R_a]$ (i.e. convex meridian curve) is that the pressure difference $p = \rho \cdot g \cdot H_m - \Delta P$ verifies the inequalities:

$$l(\varepsilon)=\gamma\cdot\frac{\theta_c+\alpha_e-\pi}{\varepsilon}\cdot sin\,\theta_c-\rho\cdot g\cdot\varepsilon\cdot tan\left(\theta_c-\frac{\pi}{2}\right)+\frac{\gamma}{R_a}\cdot cos\,\alpha_e\ \leq$$
$$p\leq\gamma\cdot\frac{\theta_c+\alpha_e-\pi}{\varepsilon}\cdot sin\,\alpha_e-\frac{\gamma}{R_a-\varepsilon}\cdot cos\,\theta_c=L(\varepsilon) \quad (6)$$

Here $\varepsilon=R_a-R_c$ = the size of the gap between the crystal and ampule walls.

Statement 2. If $\theta_c+\alpha_e>\pi$, and $0<\varepsilon'<R_a$ then a sufficient condition for the existence of a number ε verifying $0<\varepsilon\leq\varepsilon'$ and a function $z(r)$ having the properties (1) - (4) and $z''(r)>0$ for $r\in[R_c,R_a]$ (i.e. convex meridian curve) is that the pressure difference $p=\rho\cdot g\cdot H_m-\Delta P$ verifies the inequality:

$$p>\gamma\cdot\frac{\theta_c+\alpha_e-\pi}{\varepsilon'}\cdot sin\,\alpha_e-\frac{\gamma}{R_a-\varepsilon'}\cdot cos\,\theta_c=L(\varepsilon') \quad (7)$$

Here $\varepsilon=R_a-R_c$= the size of the gap between the crystal and ampule walls.

Statement 3. If $\theta_c+\alpha_e>\pi$, and $0<\varepsilon_1<\varepsilon_2<R_a$ then a sufficient condition for the existence of a number ε verifying $\varepsilon_1<\varepsilon\leq\varepsilon_2$ and function $z(r)$ having the properties (1) - (4) and $z''(r)>0$ for $r\in[R_c,R_a]$ (i.e. convex meridian curve) is that:

$$L(\varepsilon_2)=\gamma\cdot\frac{\theta_c+\alpha_e-\pi}{\varepsilon_2}\cdot sin\,\alpha_e-\frac{\gamma}{R_a-\varepsilon_2}\cdot cos\,\theta_c$$
$$<\gamma\cdot\frac{\theta_c+\alpha_e-\pi}{\varepsilon_1}\cdot sin\,\theta_c-\rho\cdot g\cdot\varepsilon_1\cdot tan\left(\theta_c-\frac{\pi}{2}\right)+\frac{\gamma}{R_a}\cdot cos\alpha_e=l(\varepsilon_1) \quad (8)$$

and the pressure difference $p=\rho\cdot g\cdot H_m-\Delta P$ verifies the inequalities:

$$L(\varepsilon_2)<p<l(\varepsilon_1) \quad (9)$$

Here $\varepsilon=R_a-R_c$= the size of the gap between the crystal and ampule walls.

Statement 4. A sufficient condition of static stability /instability of the 2D axis symmetric capillary free surface of the meniscus which meridian curve is the function $z(r)$ having the properties (1) - (4) and $z''(r)>0$ for $r\in[R_c,R_a]$ (i.e. convex meridian curve) is that the inequalities:

$$\frac{\varepsilon}{(R_a-\varepsilon)^{1/2}}<\pi\cdot\frac{1}{R_a{}^{1/2}}\cdot\frac{\gamma^{1/2}\cdot sin^{3/2}\,\theta_c}{\rho^{1/2}\cdot g^{1/2}}\quad\text{and}\quad\frac{\varepsilon}{(R_a-\varepsilon)^{1/2}}>2\pi\cdot\frac{1}{R_a{}^{1/2}}\cdot\frac{\gamma^{1/2}\cdot sin^{3/2}\,\alpha_e}{\rho^{1/2}\cdot g^{1/2}} \quad (10)$$

hold, respectively.

The next statement is a necessary condition concerning the pressure difference for which a concave-convex (i.e. $z''(R_c)<0$ and $z''(R_a)>0$) meniscus having a gap size ε exist.

Statement 5. If $\theta_c+\alpha_e>\pi$ then a necessary condition for the existence of a function $z(r)$ having the properties(1)-(4) and $z''(R_c)<0$, $z''(R_a)>0$ is that the pressure difference $p=\rho\cdot g\cdot H_m-\Delta P$ verifies inequalities:

$$l=-\frac{\gamma}{R_a}\cdot cos\,\theta_c<p<-\frac{\gamma}{R_a-\varepsilon}\cdot cos\,\alpha_e=L(\varepsilon) \quad (11)$$

Here $\varepsilon=R_a-R_c$.

Statement 6. If $\theta_c+\alpha_e>\pi,\ \varepsilon>0$ and for p verifying (10) there exists a concave-convex meniscus on $[R_a-\varepsilon,R_a]$ then there exists ε_1 such that: $0<\varepsilon_1<\varepsilon$, in $R_c=R_a-\varepsilon_1$ condition (2) holds and the meridian curve of this meniscus on $[R_a-\varepsilon_1,R_a]$ is a convex meniscus. These statements are proven in **APPENDIX.**

3. NUMERICAL RESULTS AND COMMENTS

The values of parameters used in numerical computation for dewetted GaSb growth are the followings: $\gamma = 0.45[N \cdot m^{-1}]$; $\rho = 6060[kg \cdot m^{-3}]$; $\theta_c = 2.791[rad]$; $\alpha_e = 0.540[rad]$; $H_m = 60 \cdot 10^{-3}[m]$; $R_a = 5.5 \cdot 10^{-3}[m]$; $g = 9.81[m \cdot s^{-2}]$ and $\Delta P = P_{cold} - P_{hot} = \rho \cdot g \cdot H_m - p$.

i). Static stability and instability ranges in case of meniscus with convex meridian curve

Using Statement 4. formula (10) it is found that :if a convex meniscus having a gap size ε in the range $(0, R_a)$ exists, then for ε in the range $(0{,}1.48622406 \cdot 10^{-3})[m]$ the meniscus is static stable and for ε in the range $(3.67299713 \cdot 10^{-3}, 5.5 \cdot 10^{-3})[m]$ the meniscus is static unstable. See Fig. 2.

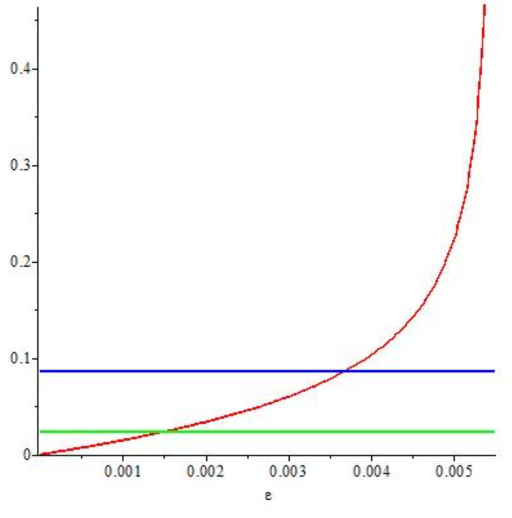

Fig. 2 Static stability and instability ranges in case of GaSb meniscus with convex meridian curve

Remark that if the gap size is in the range $(1.48622406 \cdot 10^{-3}, 3.67299713 \times 10^{-3})[m]$ there is no information concerning the static stability or instability of the meniscus having concave meridian curve (in case when the meniscus exists).

ii). Existence of static - stable meniscus with convex meridian curve

Using Statement 2 it is found that: if the pressure difference ΔP verifies inequality $\Delta P = P_{cold} - P_{hot} = \rho \cdot g \cdot H_m - p < 3566.916[Pa] - L(1.4862240629 \cdot 10^{-3})[Pa] = 3432.138[Pa]$, then for that pressure difference a static - stable meniscus having convex meridian curve is obtained, and the gap size ε of the obtained meniscus is in the range $(0{,}1.4862240629 \cdot 10^{-3})[m]$.
For instance if $\Delta P = 1345.1652[Pa]$ then a convex meridian curve is obtained for which the gap size is $\varepsilon = 1.5 \times 10^{-5}[m]$ and the meniscus height is $h_c = 3.145 \cdot 10^{-5}[m]$.

iii). Existence of a range of gap sizes for which static-stable meniscus with convex meridian curve exist

Because condition (8) from Statement 3, concerning the pressure difference, is verified for any ε verifying $1 \cdot 10^{-5} < \varepsilon < 1.970 \cdot 10^{-5}[m]$ it follows that for any gap size in the range $(1 \cdot$

$10^{-5}, 1.970 \cdot 10^{-5})[m]$, static - stable meniscus having convex meridian curve exists. (see Fig. 3).

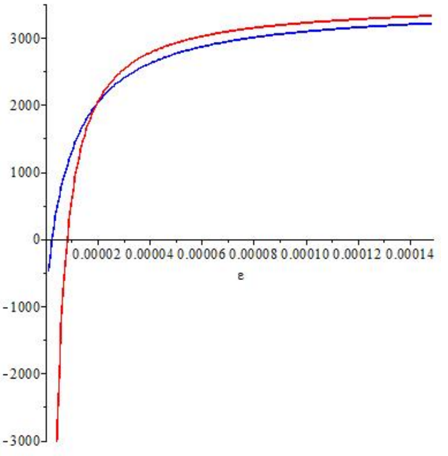

Fig. 3 Existence of convex meridian curve for $1 \cdot 10^{-5} < \varepsilon < 1.970 \cdot 10^{-5}[m]$

From the point of view of static - stability the growth can be successful in case of menisci having concave meridian curve and gape size in the range $(1 \cdot 10^{-5}, 1.970 \cdot 10^{-5})[m]$.

iv). Existence of static - stable meniscus with concave meridian curve and gap size in the range $[1.970 \cdot 10^{-5}, 1.486024269 \cdot 10^{-3})[m]$

The effective determination of a concave meridian curve, for a given gape size in the range $[1.970 \cdot 10^{-5}, 1.486024269 \cdot 10^{-3})[m]$ (if exists) can be made determining the corresponding pressure difference limits, using formula (6) Statement 1, and integrating numerically the initial value problem:

$$\begin{cases} \frac{dz}{dr} = tan\,\theta \\ \frac{d\theta}{dr} = \frac{-\rho \cdot g \cdot z + \rho \cdot g \cdot H_m - \Delta P}{\gamma} \cdot \frac{1}{cos\,\theta} - \frac{1}{r} \cdot tan\,\theta \\ z(R_a) = 0,\ \theta(R_a) = \theta_c - \frac{\pi}{2} \end{cases} \tag{12}$$

for different values of ΔP in the obtained pressure difference range. The limits of the pressure difference ΔP, computed according to formula (6), are represented in Fig. 4.

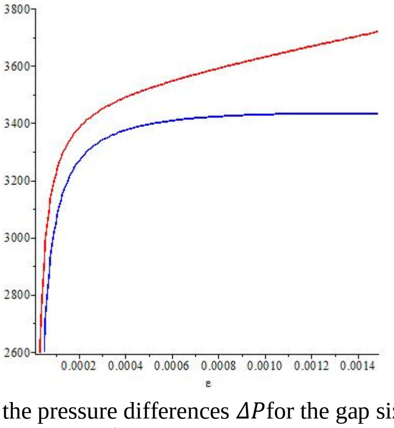

Fig. 4 Limits of the pressure differences ΔP for the gap size in the range $[1.97 \times 10^{-5},\ 1.48602426 \times 10^{-3})[m]$

The gap sizes $\varepsilon_1 = 2 \cdot 10^{-5}[m]$, $\varepsilon_2 = 5 \cdot 10^{-4}[m]$, $\varepsilon_3 = 8 \cdot 10^{-4}[m]$ belong to the above range. Computing the pressure limits, for these gap sizes the following ranges were obtained: $[l(\varepsilon_1), L(\varepsilon_1)] = [1298.718{,}2036.303][Pa]$; $[l(\varepsilon_2), L(\varepsilon_2)] = [3394.747{,}3519.472][Pa]$; $[l(\varepsilon_3), L(\varepsilon_3)] = [3422.218{,}3590.196][Pa]$.

In order to find the appropriate pressure differences $\Delta P = P_{cold} - P_{hot}$, the problem (12) was solved numerically for different values of ΔP in the computed ranges. In this way it was found that the values $(\Delta P)_1$, $(\Delta P)_2$, $(\Delta P)_3$ for which the gap sizes are $\varepsilon_1 = 2 \cdot 10^{-5}[m]$, $\varepsilon_2 = 5 \cdot 10^{-4}$, $\varepsilon_3 = 8 \cdot 10^{-4}$ and $\theta(R_c) = \pi/2 - \alpha_e = 1.030\ [rad]$ are the followings: $(\Delta P)_1 = 1656.916[Pa]$, $(\Delta P)_2 = 3450.916[Pa]$ and, $(\Delta P)_3 = 3510.416[Pa]$ respectively. The shape and size of the computed menisci are represented in Fig. 5 - Fig. 7.

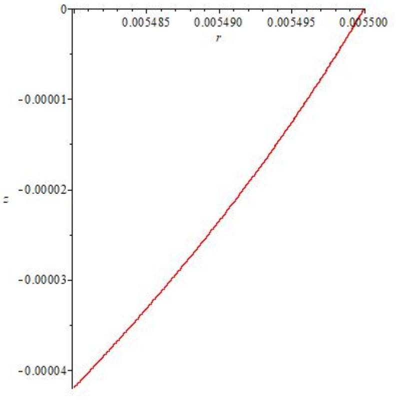

Fig. 5 $z = z(r)$; $(\Delta P)_1 = 1656.916[Pa]$
$\varepsilon_1 = 2 \cdot 10^{-5}[m]$; $R_c = 5.48 \cdot 10^{-3}[m]$;
$h_c = 4.196 \cdot 10^{-5}[m]$

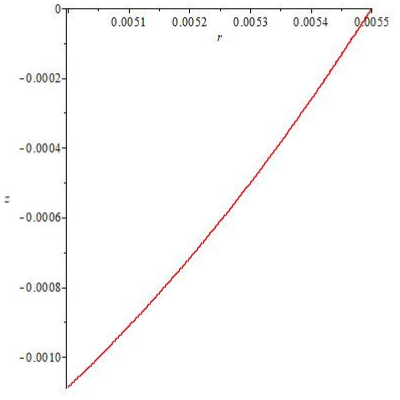

Fig. 6 $z = z(r)$; $(\Delta P)_2 = 3450.916[Pa]$
$\varepsilon_2 = 5 \cdot 10^{-4}[m]$; $R_c = 5 \cdot 10^{-3}[m]$
$h_c = 1.088 \cdot 10^{-3}[m]$

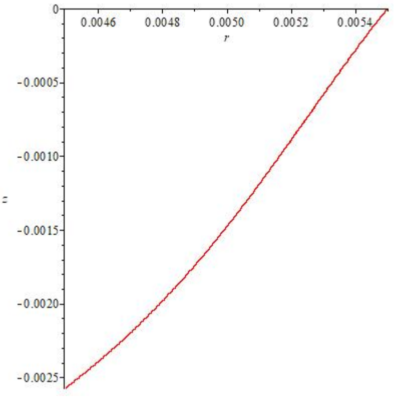

Fig. 7 $z = z(r)$; $(\Delta P)_3 = 3510.416[Pa]$; $\varepsilon_3 = 8 \cdot 10^{-4}[m]$; $R_c = 4.7 \cdot 10^{-3}[m]$;
$h_c = 1.865 \cdot 10^{-3}[m]$

It follows that the growth can be successful in the cases: gap size $\varepsilon_1 = 2 \cdot 10^{-5}[m]$, $(\Delta P)_1 = 1656.916[Pa]$, crystal radius equal to $R_c = 5.48 \cdot 10^{-3}[m]$, crystallization front height equal to $h_c = 4.196 \cdot 10^{-5}[m]$; gap size $\varepsilon_2 = 5 \cdot 10^{-4}[m]$, $(\Delta P)_2 = 3450.916[Pa]$, crystal radius equal to $R_c = 5 \cdot 10^{-3}[m]$, crystallization front height equal to $h_c = 1.088 \cdot 10^{-3}[m]$; gap size $\varepsilon_3 = 8 \cdot 10^{-4}[m]$, $(\Delta P)_3 = 3510.416[Pa]$, crystal radius equal to $R_c = 4.7 \cdot 10^{-3}[m]$, crystallization front height equal to $h_c = 1.865 \cdot 10^{-3}[m]$. Comparing the above results it is interesting to observe that for a relatively narrow range of the pressure difference ΔP i.e.

$[1656.916, 3530.216][Pa]$ it is possible to obtain a relatively large gap size range i.e. $[2 \cdot 10^{-5}, 8 \cdot 10^{-4}][m]$. It is also interesting to remark that as the gap size increases the meniscus height increases exceeding the value $1.865 \cdot 10^{-3}[m]$. This relatively high meniscus can be an explanation of the dynamic instability. But from the point of view of the static stability, the above menisci are static stable and are appropriate for the growth. Another interesting thing is that if the gap size value is $\varepsilon_3 = 8 \times 10^{-4}[m]$ but $\Delta P = 3606.916[Pa]$, then meniscus with convex-concave ($z''(R_c) > 0$, $z''(R_a) < 0$) meridian curve appears. This meridian curve is represented in Fig. 8.

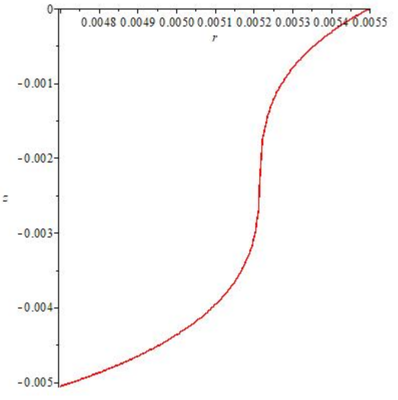

Fig. 8 $z = z(r)$; $\Delta P = 3606.916[Pa]$ $\varepsilon_3 = 8 \times 10^{-4}[m]$;$R_c = 4.7 \times 10^{-3}[m]$; $h = 5.059 \times 10^{-3}[m]$

v). Existence of meniscus with concave - convex meridian curve

Statements 5 and 6 concern general conditions for the existence and property of static meniscus with convex concave meridian curve. For the gap size in the range $(1 \times 10^{-6},\ 5 \times 10^{-3})[m]$**,** the computed pressure difference limits ΔP versus gape size for convex-concave meridian curve are presented in Fig. 9. Fig. 9a shows that for the gap size in the range $[1 \times 10^{-6}, 4.77 \times 10^{-4})[m]$ there is no way to obtain concave-convex meridian curve. Fig. 9b and Fig. 9c show that for the gap size in the range $[4.47 \times 10^{-4},\ 5.5 \times 10^{-3})[m]$ the necessary condition (10) for the existence of a meniscus having concave-convex meridian curve is verified.

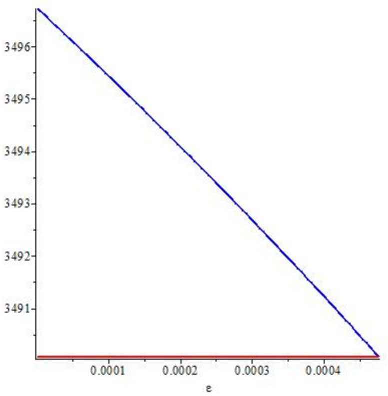

Fig. 9a gap size in the range $[4.47 \times 10^{-4}, 1.1 \times 10^{-3})[m]$.

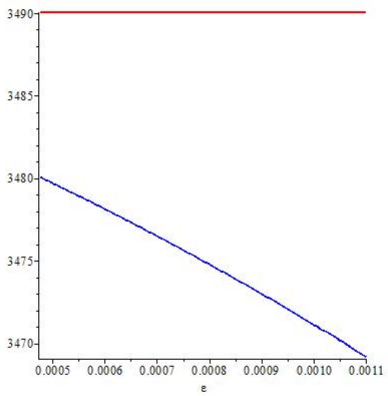

Fig. 9b gap size in the range $[1 \times 10^{-6}, 4.77 \times 10^{-4})[m]$

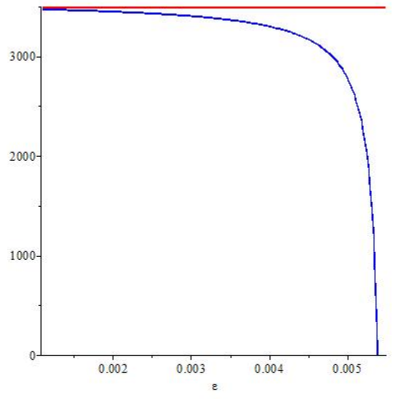

Fig. 9c gap size in the range
$[1.1 \times 10^{-3}, 5.5 \times 10^{-3})[m]$

For the gap sizes in the range $[5 \times 10^{-4},\ 5 \times 10^{-3})[m]$ the upper limit of the pressure difference ΔP is $\Delta P = 3490.074[Pa]$ and the lower limit of the pressure differences ΔPvaries in the range $\Delta P \in [2794.978, 3489.722][Pa]$. For the gap sizes $\varepsilon_4 = 5 \cdot 10^{-4}[m]$; $\varepsilon_5 = 1 \cdot 10^{-3}[m]$; $\varepsilon_6 = 1.1 \cdot 10^{-3}[m]$; $\varepsilon_7 = 1.5 \cdot 10^{-3}[m]$; $\varepsilon_8 = 2.5 \cdot 10^{-3}[m]$; $\varepsilon_9 = 3 \cdot 10^{-3}[m]$; $\varepsilon_{10} = 3.5 \cdot 10^{-3}[m]$; $\varepsilon_{11} = 4.5 \cdot 10^{-3}[m]$; $\varepsilon_{12} = 5 \cdot 10^{-3}[m]$; $\varepsilon_{13} = 5.4 \times 10^{-3}[m]$; solving (12) in the corresponding pressure difference ranges computation shows that there is no meniscus with concave-convex meridian curve.

4. CONCLUSIONS

1. The six theoretical results provide information concerning the existence, stability/and instability of convex meniscus as well as the existence of convex-concave menisci in terms of the gap size. This information is new and can help the crystal size choice as well the thermal conditions preparations for a dewetted Bridgman process.
2. The numerical results show that in case of GaSb semiconductor when O_2 is introduced in the ampule and the apparent wetting angle is high the theoretical results are effective and from the static stability point of view reveal interesting facts.
The growth can be successful for pressure differences in the range $1656.916[Pa], 3510.416[Pa]$; (cases presented in Fig. 5-Fig. 7) and we suspect that is not successful for $\Delta P = 3606.916[Pa]$ (case presented in Fig. 8)

5. APPENDIX

Proof of the Statement 1

Let $\theta_c + \alpha_e > \pi$, $R_c = R_a - \varepsilon$, and $z(r)$ defined for $r \in [R_c,\ R_a]$ which verifies (1)-(4) and $z''(r) > 0$. The function defined as:
$\theta(r) = \arctan z'(r)$ for $r \in [R_c, R_a]$ verifies $\theta'(r) = \frac{-\rho \cdot g \cdot z(r) + p}{\gamma} \cdot \frac{1}{\cos(\theta(r))} - \frac{1}{r} \cdot \tan(\theta(r))$ and the boundary conditions: $\theta(R_a) = \theta_c - \pi/2$, $\theta(R_c) = \pi/2 - \alpha_e$.
Hence, by the mean value theorem, there exists $r' \in [R_c, R_a]$ such that the following equality holds: $p = \gamma \cdot \frac{\theta_c + \alpha_e - \pi}{R_a - R_c} \cdot \cos\theta(r') + \rho \cdot g \cdot z(r') + \frac{\gamma}{r'} \cdot \sin(\theta(r'))$.

On the other hand, inequality $z"(r) > 0$ implies that the function $z'(r)$ is strictly increasing and by consequence the function $\theta(r)$ is strictly increasing. Therefore, the following inequalities hold:
$\frac{\pi}{2} - \alpha_e < \theta(r') < \theta_c - \pi/2$; $sin\,\theta_c \le cos\,\theta\,(r') \le sin\,\alpha_e$; $-cos\,\alpha_e \le sin\,\theta\,(r') \le cos\,\theta_c$;
$-\rho \cdot g \cdot \varepsilon \cdot tan(\theta_c - \frac{\pi}{2}) \le \rho \cdot g \cdot z(r') \le -\rho \cdot g \cdot (R_a - r') \cdot tan(\frac{\pi}{2} - \alpha_e) \le 0$.
Hence inequality (6) is obtained.

Proof of the Statement 2. Consider function $z(r)$ which verifies (1) , (3). Denote by I the maximal interval on which the function $z(r)$ exists and by $\theta(r)$ the function defined by $\theta(r) = arctan\, z\,'(r)$. This function verifies $\theta'(r) = \frac{-\rho \cdot g \cdot z(r) + p}{\gamma} \cdot \frac{1}{cos(\theta(r))} - \frac{1}{r} \cdot tan(\,\theta(r))$. Because $z"(R_a) = \frac{\theta'(R_a)}{cos^2\,\theta(R_a)} = \frac{1}{cos^3\,\theta(R_a)} \cdot [\frac{p}{\gamma} - \frac{sin\,\theta(R_a)}{R_a}] > \frac{1}{cos^3\,\theta(R_a)}[\frac{\theta_c + \alpha_e - \pi}{\varepsilon'} \cdot sin\,\theta_c - \frac{1}{R_a - \varepsilon} \cdot cos\,\theta_c - \frac{1}{R_a} \cdot cos\,\theta_c] > 0$; $z'(R_a) = tan(\,\theta_c - \frac{\pi}{2}) > 0$ and $z'(R_a) > tan(\frac{\pi}{2} - \alpha_e)$;
there exists $r' \in I$, $0 < r' < R_a$ such that for any r which verifies $r' \le r \le R_a$ the following inequalities hold: $z"(r) > 0$; $z'(r) < tan(\,\theta_c - \frac{\pi}{2})$ and $z'(r) > tan(\frac{\pi}{2} - \alpha_e)$. Let r_* be the infimum of the set of numbers r' for which the above conditions hold, $r_* = inf\{r'\}$.
Remark that for $r_* + 0$ the following inequalities hold: $z(r_* + 0) \le z(r) < 0$ for any r which verify $r_* \le r < R_a$, $-(R_a - r_*) \cdot tan(\,\theta_c - \frac{\pi}{2}) \le z(r_* + 0) \le -(R_a - r_*) \cdot tan(\frac{\pi}{2} - \alpha_e)$.
Now we will show that $\varepsilon = (R_a - r_*) \le \varepsilon'$ and $z'(r_* + 0) = tan(\frac{\pi}{2} - \alpha_e)$.
For showing inequality $\varepsilon = (R_a - r_*) \le \varepsilon'$ assumes the contrary i.e. $\varepsilon = (R_a - r_*) > \varepsilon'$. Under this hypothesis for some $r' \in (R_a - \varepsilon, R_a)$ the following relations hold:

$$\theta(R_a - \varepsilon') - \theta(R_a) = -\theta'(r') \cdot \varepsilon' = \frac{1}{cos\,\theta(r')} \cdot \left[-\frac{p}{\gamma} + \frac{\rho \cdot g \cdot z(r')}{\gamma} + \frac{1}{r'} \cdot sin\,\theta\left(r'\right)\right] \cdot \varepsilon' < 0$$

$$\varepsilon' \cdot \frac{1}{cos\,\theta(r')} \cdot \left[-\frac{\theta_c + \alpha_e - \pi}{\varepsilon'} \cdot sin\,\alpha_e + \frac{1}{R_a - \varepsilon'} \cdot cos\,\theta_c + \frac{\rho \cdot g \cdot z(r')}{\gamma} + \frac{1}{r'} \cdot sin\,\theta\left(r'\right)\right] < \pi - \theta_c - \alpha_e.$$

Hence $\theta\left(R_a - \varepsilon'\right) < \frac{\pi}{2} - \alpha_e$ what is impossible according to the definition of r_*.
In order to show that $z'(r_* + 0) = tan(\frac{\pi}{2} - \alpha_e)$ we remark that from the definition of r_* it follows that in r_* one of the following three equalities holds: $z"(r_* + 0) = 0$ or $z'(r_* + 0) = tan(\,\theta_c - \frac{\pi}{2})$, or $z'(r_* + 0) = tan(\frac{\pi}{2} - \alpha_e)$. Since $z'(r_* + 0) \le z'(r) < tan(\,\theta_c - \frac{\pi}{2})$ for $r \in (r_* + 0, R_a)$ equality $z'(r_* + 0) = tan(\,\theta_c - \frac{\pi}{2})$ is impossible. It follows that at r_* only one of the following two equalities holds $z"(r_* + 0) = 0$ or $z'(r_* + 0) = tan(\frac{\pi}{2} - \alpha_e)$.
Now we will show that the equality $z"(r_* + 0) = 0$ is impossible. For that assume the contrary, that is $z"(r_* + 0) = 0$. Hence: $p = \rho \cdot g \cdot z(r_* + 0) + \frac{\gamma}{r_*} \cdot sin\,\theta\,(r_* + 0) < \frac{\gamma}{r_*} \cdot sin\,\theta\,(r_* + 0) < \frac{\gamma}{R_a - \varepsilon} \cdot sin(\,\theta_c - \frac{\pi}{2}) < \frac{\gamma}{R_a - \varepsilon'} \cdot sin(\,\theta_c - \frac{\pi}{2}) = -\frac{\gamma}{R_a - \varepsilon'} \cdot cos\,\theta_c$ and that is impossible. Therefore in r_* equality $z'(r_* + 0) = tan(\frac{\pi}{2} - \alpha_e)$ holds.

Proof of the Statement 3. According to the Statement 2 for any p which verifies inequality $p > L(\varepsilon_2)$ there exists a number ε having the property $0 < \varepsilon < \varepsilon_2$ and function $z(r)$ having the properties (1) - (4) and $z"(r) > 0$ for $r \in [R_c, R_a]$ with$R_c = R_a - \varepsilon$. Assume now that p verifies also the inequality $l(\varepsilon_1) < p$ and shows that $\varepsilon_1 < \varepsilon$. Assuming the contrary i.e. $\varepsilon < \varepsilon_1$ it is easy to show that the following inequality holds: $p < \gamma \cdot \frac{\theta_c + \alpha_e - \pi}{\varepsilon} \cdot sin\theta_c -$

$\rho \cdot g \cdot \varepsilon_1 \cdot \tan(\theta_c - \pi/2) + \frac{\gamma}{R_a} \cdot \cos\alpha_e$ which is in contradiction with the left hand side of the inequality (6) appearing in Statement 1.

Proof of the Statement 4.

Since (1) is the Euler equation ([9] Chapter 2) for the free energy functional (5), in this case it is sufficient to investigate the Legendre and Jacobi conditions ([9] Chapter 8).

To this end, consider function:

$$F(z, z', r) = \left\{\gamma \cdot [1 + (z')^2]^{1/2} - \frac{1}{2} \cdot \rho \cdot g \cdot z^2 + p \cdot z\right\} \cdot r$$

and remark that the Legendre condition $\frac{\partial^2 F}{\partial z'^2} > 0$ reduces to the inequality:

$$r \cdot \gamma [1 + (z')^2]^{-3/2} > 0$$

which is verified. The Jacobi equation

$$[\frac{\partial^2 F}{\partial z^2} - \frac{d}{dr}(\frac{\partial^2 F}{\partial z \partial z'})] \cdot \eta - \frac{d}{dr}[\frac{\partial^2 F}{\partial z'^2} \cdot \eta'] = 0$$

in this case becomes

$$\frac{d}{dr}(\frac{r \cdot \gamma}{[1 + (z')^2]^{3/2}} \cdot \eta') + \rho \cdot g \cdot r \cdot \eta = 0$$

i). For obtaining the stability result, remark that for the coefficients of the Jacobi equation the following inequalities hold:

$$\frac{r \cdot \gamma}{[1+(z')^2]^{3/2}} \geq (R_a - \varepsilon) \cdot \gamma \cdot \sin^3\theta_c \qquad \rho \cdot g \cdot r \leq \rho \cdot g \cdot R_a$$

Therefore, equation

$$\frac{d}{dr}((R_a - \varepsilon) \cdot \gamma \cdot \sin^3\theta_c \cdot \varsigma') + \rho \cdot g \cdot R_a \cdot \varsigma = 0$$

is a "Sturm type upper bound" ([9] Chapter 11) for the Jacobi equation. An arbitrary solution of the above "Sturm type upper bound equation" is given by $\varsigma(r) = A \cdot sin(\omega \cdot r + \phi)$.

Here A and ϕ are arbitrary real constants and $\omega^2 = \frac{\rho \cdot g}{\gamma \cdot sin^3\theta_c} \cdot \frac{R_a}{R_a - \varepsilon}$. The half period of any non-zero solution $\varsigma(r)$ is $\frac{\pi}{\omega} = \pi \cdot \frac{\gamma^{1/2} \cdot sin^{3/2}\theta_c}{\rho^{1/2} \cdot g^{1/2}} \cdot \frac{(R_a - \varepsilon)^{1/2}}{R_a{}^{1/2}}$. If the half period is more than $R_a - R_c = \varepsilon$ then any non-zero solution $\varsigma(r)$ vanishes at most once on the interval $[R_c, R_a]$. In other words if the following inequality holds

$$\pi \cdot \frac{\gamma^{1/2} \cdot sin^{3/2}\theta_c}{\rho^{1/2} \cdot g^{1/2}} \cdot \frac{(R_a - \varepsilon)^{1/2}}{R_a{}^{1/2}} > \varepsilon \quad \text{or} \quad \frac{\varepsilon}{(R_a - \varepsilon)^{1/2}} < \pi \cdot \frac{1}{R_a{}^{1/2}} \cdot \frac{\gamma^{1/2} \cdot sin^{\frac{3}{2}}\theta_c}{\rho^{1/2} \cdot g^{1/2}}$$

then any non-zero solution $\varsigma(r)$ vanishes at most once on the interval $[R_c, R_a]$. Hence, according to [9] Chapter 11, the solution $\eta(r)$ of Jacobi equation which verifies $\eta(R_a) = 0$ and $\eta'(R_a) = 1$, has only one zero on the interval $[R_c, R_a]$. This means that the Jacobi condition for weak minimum is verified [9].

ii). For obtaining the instability result, remark that for the coefficients of the Jacobi equation the following inequalities hold:

$$\frac{r \cdot \gamma}{[1+(z')^2]^{3/2}} \leq R_a \cdot \gamma \cdot cos^3(\frac{\pi}{2} - \alpha_e) \quad \text{and} \quad \rho \cdot g \cdot r \geq \rho \cdot g \cdot (R_a - \varepsilon).$$

Therefore, the equation

$$\frac{d}{dr}(R_a \cdot \gamma \cdot sin^3\alpha_e \cdot \xi') + \rho \cdot g \cdot (R_a - \varepsilon) \cdot \xi = 0$$

is a "Sturm type lower bound equation" ([9] Chap. 11) for the Jacobi equation. An arbitrary solution of the above "Sturm type lower bound equation" is given by

$$\xi(r) = A \cdot sin(\omega \cdot r + \phi)$$

Here A and ϕ are arbitrary real constants and $\omega^2 = \frac{\rho \cdot g \cdot (R_a - \varepsilon)}{R_a \cdot \gamma \cdot sin^3 \alpha_e}$. The period of any non-zero solution $\xi(r)$ is $\frac{2 \cdot \pi}{\omega} = 2 \cdot \pi \cdot \frac{\gamma^{1/2} \cdot sin^{3/2} \alpha_e}{\rho^{1/2} \cdot g^{1/2}} \cdot \frac{(R_a - \varepsilon)^{1/2}}{R_a{}^{1/2}}$. If the period is less than $R_a - R_c$ then any non-zero solution $\xi(r)$ vanishes at least twice on the interval $[R_c, R_a]$. In other words, if the following inequality hold:

$$2 \cdot \pi \cdot \frac{\gamma^{1/2} \cdot sin^{3/2} \alpha_e}{\rho^{1/2} \cdot g^{1/2}} \cdot \frac{(R_a - \varepsilon)^{1/2}}{R_a{}^{1/2}} < \varepsilon \quad \text{or} \quad \frac{\varepsilon}{(R_a - \varepsilon)^{1/2}} > 2 \cdot \pi \cdot \frac{1}{R_a{}^{1/2}} \cdot \frac{\gamma^{1/2} \cdot sin^{3/2} \alpha_e}{\rho^{1/2} \cdot g^{1/2}}$$

then any non-zero solution $\xi(r)$ vanishes at least twice on the interval $[R_c, R_a]$. Hence, according to [9] Chapter 11, that solution $\eta(r)$ of Jacobi equation which satisfies $\eta(R_a) = 0$ and $\eta'(R_a) = 1$ vanishes at least twice on the interval $[R_c, R_a]$. This means that the Jacobi condition for weak minimum is not satisfied [9].

Proof of the Statement 5. Using equation (1) it is easy to see that condition $z''(R_a) > 0$ implies inequality $-\frac{\gamma}{R_a} \cdot cos\, \theta_c < p$. For the left-hand side of (10) remark that condition $z''(R_c) < 0$ implies that $p < \frac{\gamma}{R_a - \varepsilon} \cdot cos\, \alpha_e$.

Proof of the Statement 6. Since $z''(R_c) < 0$ it follows that $\theta(r) < \theta(R_a - \varepsilon)$ for $r > R_a - \varepsilon$, r sufficiently close to $R_a - \varepsilon$ i.e. $\theta(r) < \frac{\pi}{2} - \alpha_e$. Due to the fact that $\theta(R_a) = \theta_c - \frac{\pi}{2} > \frac{\pi}{2} - \alpha_e$ it follows that there exist $r_* \in (R_a - \varepsilon, R_a)$ such that $\theta(r_*) = \frac{\pi}{2} - \alpha_e$. So for $\varepsilon_1 = R_a - r_*$ we have $\theta(R_a - \varepsilon_1) = \frac{\pi}{2} - \alpha_e$.

The static instability of the convex-concave meniscus is a consequence of the inequality:

$$\int_{R_c}^{R_a} \left\{ \gamma \cdot [1 + (z')^2]^{1/2} - \frac{1}{2} \cdot \rho \cdot g \cdot z^2 + p \cdot z \right\} \cdot r \cdot dr > \int_{r^*}^{R_a} \left\{ \gamma \cdot [1 + (z')^2]^{1/2} - \frac{1}{2} \cdot \rho \cdot g \cdot z^2 + p \cdot z \right\} \cdot r \cdot dr$$

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