

Article Title: Design of ceramic springs for use in semiconductor crystal growth in microgravity

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Abstract:

Segregation studies can be done in microgravity to reduce buoyancy driven convection and investigate diffusion-controlled growth during the growth of semiconductor crystals. During these experiments, it is necessary to prevent free surface formation in order to avoid surface tension driven convection (Marangoni convection). Semiconductor materials such as gallium arsenide and germanium shrink upon melting, so a spring is necessary to reduce the volume of the growth chamber and prevent the formation of a free surface when the sample melts. A spring used in this application must be able to withstand both the high temperature and the processing atmosphere. During the growth of gallium arsenide crystals during the GTE Labs/USAF/NASA GaAs GAS Program and during the CWRU GaAs programs aboard the First and Second United States Microgravity Laboratories, springs made of pyrolytic boron nitride (PBN) leaves were used. The mechanical properties of these PBN springs have been investigated and springs having spring constants ranging from 0.25 N/mm to 25 N/mm were measured. With this improved understanding comes the ability to design springs for more general applications, and guidelines are given for optimizing the design of PBN springs for crystal growth applications.

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81.10.M Microgravity environments for crystal growth,

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Introduction

Crystal growth studies have been done in microgravity under conditions in which buoyancy driven convection was reduced in order to study dopant distribution variations [1-5] and more general concentration variations [6-11]. In order for these studies to be effective, there must not be any other significant sources of convection, such as surface tension driven convection (Marangoni Convection). For example, Naumann [12] showed that Marangoni convection around voids could influence Bridgman crystal growth during microgravity experiments. Ostrach and co-workers [13-14] have shown that any free surface in the presence of a temperature gradient would lead to surface tension driven convection and should therefore be avoided.

For semiconductors that contract upon melting, such as gallium arsenide and germanium [15], one solution is the use of a spring to take up the change in volume. The spring must be able to withstand high temperatures and potentially reactive atmospheres such as 1500 K and an arsenic atmosphere during the processing of gallium arsenide. Metals cannot usually withstand these temperature and atmospheric requirements. Additionally, the spring must provide the necessary deflection to account for the volume contraction (10 % for gallium arsenide [15]) and provide a force that is large enough to maintain the melt contact with the container wall while small enough to not force the melt out of the container. Ideally, the force applied by the spring will be zero at full extension and increase gradually as the spring is compressed.

Both ceramic springs and graphite springs have been considered for use in past microgravity experiments. Buhl and Weiss [16] reported on a helical spring of carbon fiber reinforced carbon. This spring had a spring constant of 0.406 N/mm at room temperature and 0.525 N/mm at 1300°C. The spring constant could not be varied to meet the needs of different experiments and the spring had a total deflection of 6-10 mm. Graphite springs that have been used in past microgravity experiments have caused leakage of the melt into the spring area [11,17].

Pyrolytic boron nitride (PBN) curved leaf springs have been used in past microgravity experiments during the growth of gallium arsenide crystals on the first and second United States Microgravity Laboratories (USML-1 [1-2] and USML-2 [3-4,18]) and during the GTE Labs/USAF/NASA GaAs GAS Program [19] without causing leakage of the melt into the spring area. In these experiments, leaves cut from PBN cylinders

were stacked inside a graphite spring chamber (see Figure 1) such that the spring applied force to a graphite piston which, in turn, applied force to the sample. During USML-2, electrical contact was maintained with the sample (for current induced interface demarcation) through the graphite spring chamber.

Theoretical Background

Mechanical deformation

Figure 2 shows a schematic of a curved leaf used in a spring stack. The leaves are cut from a cylinder of radius, r , to a width, w , and depth, b , and thinned to a thickness, h . From geometry, the angular span of the curved leaf is given as

$$\theta = 2 \sin^{-1} \left(\frac{w}{2r} \right) \quad (1)$$

A model was developed previously [20] for a cylindrical section assuming that a line force is applied at the center and the edges of the curved leaf are simply supported. The expected deflection of a single leaf for a given applied load is given by

$$d = \frac{3Pr}{2Ebh^3} \left\{ -4rw + 2rw \sqrt{4 - \frac{w^2}{r^2}} + r^2 \theta + \frac{w^2}{2} \theta - r^2 \sin(\theta) \right\} \quad (2)$$

where P is the applied load, E is the appropriate elastic modulus. A predicted spring constant, k , can be determined since

$$k = \frac{P}{D} \quad (3)$$

for a general spring where D is the deflection and P is the applied load. For a stack of n leaves

$$k_p = \frac{P}{nd} \quad (4)$$

where d is the deflection of an individual leaf given in equation (2).

Basic geometry gives the total height of a stack of leaves as

$$\text{stack height} = n \left\langle h + r \left\{ 1 - \cos \left(\frac{\theta}{2} \right) \right\} \right\rangle \quad (5)$$

and the deflection to flatten all of the springs as

$$d_{\text{stack}} = nr \left\{ 1 - \cos\left(\frac{\theta}{2}\right) \right\} \quad (6)$$

Generally, a spring stack should be deflected no more than 50% of this distance to prevent significant permanent deformation (i.e. delamination) of the PBN leaves.

Pyrolytic boron nitride

Pyrolytic boron nitride (PBN) is a good material to use to make curved leaf springs because it is stable at high temperatures and non-reactive in most non-oxidizing atmospheres including an arsenic atmosphere. It is also readily available in cylindrical form with various radii as vertical Bridgman crucibles (with the seedwell and taper region cut off). However, PBN is an anisotropic material so the choice of an appropriate elastic moduli to use for E in equation (2) is not trivial. PBN is a layered structure with very different properties perpendicular to the layers (in the c -direction) to those within the layers (in the a -direction). The moduli for PBN have been reported as shown in Table 1. These values were determined from a variety of methods including thermal conductivity measurements [21], ultrasonic measurements on materials of different interlayer spacing [22], calculated from thermal expansion data [23], torsional creep experiments [24], compression measurements [25-26], and ultrasonic measurements [27-28]. Deeb [27] and Kaforey *et al.* [20, 28] used mechanical deformation measurements to determine the moduli that are most applicable to the situation of interest.

Limiting case - flat plate

For a flat plate, the modulus of interest would be the shear modulus, C_{44} , which was measured using three-point bending [27-28] to be 2.60 ± 0.31 GPa.

Limiting case - half cylinder

However, for samples that are more curved, principal forces become more dominant. The effective modulus was measured for a half cylinder of PBN [20, 27] and found to be 13.42 ± 2.26 GPa.

Intermediate case – single leaves

The case of a curved leaf is intermediate between the 2 limiting cases and the effective modulus, E_{eff} was found to have a geometric dependence as follows [20]:

$$E_{eff} = E_{FP} \left[1 - \sin\left(\frac{\theta}{2}\right) \right] + E_{HC} \sin\left(\frac{\theta}{2}\right) \quad (7)$$

where E_{FP} is the modulus for the flat plate (2.60 GPa) and E_{HC} is the modulus for the half cylinder (13.42 GPa). Using this geometrical dependence, equation (2) was found to agree well with the experimental results for single leaves [20].

Intermediate case – spring stacks

Combining equations (2), (4), and (7), results in a prediction of the spring constant for a spring stack as follows:

$$k_p = \frac{2bh^3 \left\{ E_{FP} \left[1 - \sin\left(\frac{\theta}{2}\right) \right] + E_{HC} \sin\left(\frac{\theta}{2}\right) \right\}}{3rn \left\{ -4rw + 2rw \sqrt{4 - \frac{w^2}{r^2} + r^2\theta + \frac{w^2}{2}\theta - r^2 \sin(\theta)} \right\}} \quad (8)$$

The behavior of spring stacks as a function of radius, width, thickness, number of leaves, and temperature were experimentally tested [27,29] and compared to the predicted spring constants from equation (8). Thickness was found to have the greatest impact on the spring constant. Temperature was not found to have a significant effect. Thus, measurements made at room temperature were determined to be statistically equivalent to values at processing temperatures (not statistically different at a 95% confidence level). The predicted values were found to be a lower bound on the measured values with the majority of the measured values falling within one order of magnitude larger than the predictions. For taller stacks, it was experimentally observed that the applied force was not distributed evenly throughout the stack. That is, only a portion of the stack of leaves was compressed evenly. This was believed to be due to significant interaction between the spring stack and the wall of the spring chamber. For leaves with a higher degree of curvature, it was again observed that the applied force was not distributed evenly throughout the stack. This was believed to

be due to a higher probability of slipping of leaves relative to one another and a higher probability of having a leaf stick against the spring chamber wall. When using equation (8) in the design of springs, it is recommended that conditions be chosen such that predicted spring constants provide a force that is no larger than half of the force necessary to cause the melt to leak out of the growth chamber.

Design guidelines

The force necessary to keep the melt in contact with the container wall and prevent formation of a free surface could be calculated from viscosity data using the equation

$$F = \eta A \frac{v}{l} \quad (9)$$

where η is viscosity, A is area, and v/l is strain rate. For materials like gallium arsenide that have viscosity values similar to that of water [30], an extremely small force is sufficient to generate an appreciable strain rate. Thus, the minimum force necessary is approximately zero for most materials.

Similarly, the force that will cause the melt to be forced out of the growth chamber should also be calculated or measured. The most common place for leakage to occur has been between the piston and the spring chamber. Assuming that leakage would occur there, and if the surface tension of the melt and the contact angle of the melt with the spring chamber/piston material are known, the force can be calculated as follows. The force on the melt at the gap between the piston and the spring chamber due to surface tension, F_{ST} , is

$$F_{ST} = L \gamma_{LV} \cos \Theta \quad (10)$$

where L is the total length of line contact, which is the sum of the line contact between the melt and the piston and between the melt and the spring chamber, γ_{LV} is the surface tension between the melt and the atmosphere, and Θ is the contact angle between the melt and the spring chamber/piston material. For a non-wetting material, $\Theta > 90^\circ$, this provides a force that opposes leaking. This force acts on the area of the gap between the piston and the spring chamber, A_{gap} , creating a pressure. In order for leakage to occur, a pressure must be applied to the melt that is larger than this opposing pressure. The spring applies a force to the melt that acts on the area of the piston, A_{piston} . Thus, the force of the spring that would balance the force due to surface tension is

$$F = F_{ST} \frac{A_{piston}}{A_{gap}} \quad (11)$$

Ideally, an applied force should be determined which is intermediate to the two limits on the force. Whenever possible, a spring should be designed such that the maximum predicted force applied by the spring at the maximum compression distance, D , is not more than one-half of the force needed to cause leakage ($P \leq 2F$). This compensates for any potential increase in the spring constant that temporarily results from interactions with the chamber walls. Once the desired maximum applied load, P , and maximum deflection, D , are known, this determines a range of acceptable spring constants from equation (3).

Given a desired spring constant, k_p , equations (8) and (1) result in a family of solutions (in w , r , h , and n) that yield the correct spring constant. In order to determine the optimal solution from the available family of solutions, the following general guidelines are provided.

Generally, the largest width possible within the geometric limits of the container size is the best width to use. The spring chamber must have a wall thickness that will not fracture during machining or processing. Also, it is necessary to make sure that the width of a deflected spring is not larger than the interior width of the spring chamber. As a rule of thumb, the difference between the width of a leaf and the width of the spring chamber should be 10 percent of the width of a leaf.

The radius is bounded by the limits of the cylinders that can be fabricated. Thus, 10 cm is a reasonable limit for the largest practical radius. In general, it is best if the angular span of a curved leaf, θ (equation (1)), is not larger than 30° to prevent undo slippage of stacked leaves and to prevent excessive sticking to the edges of the leaves in the spring chamber wall. Thus the range of radii available is bounded by the curvature limit on the lower end, and the maximum practical fabrication limit on the upper end.

Remembering that it is best if a spring is only compressed to 50% of the deflection to flatten the leaves, the number of leaves needed to give the necessary deflection can then be calculated from equation (6).

The practical range on thickness, h , is bounded by the limits of the cylinders that can be fabricated. Springs thinner than 0.025 cm (0.010") will break upon compression and the manufacture of PBN cylinders thicker than 0.127 cm (0.050") is not recommended since residual strain can lead to delamination. Equation (8) can then be used to calculate a value for h that gives the desired k_p , using the previously chosen values for r ,

n , and $w = b$. Cylinders can be ordered with the desired thickness or thinned to the desired thickness using a razor blade to separate between pyrolytic layers.

Equation (5) can then be used to calculate the total stack height to make sure that it fits within the geometrical constraints of the system. If the solution is not acceptable, r , h , and n can be changed and this procedure iterated until an optimal solution is found which meets the geometric constraints and the performance requirements.

Once an optimal solution has been determined, leaves can be cut, cleaned, stacked, cycled and measured to confirm the design before it is used in a crystal growth application (for more detail, see Kaforey *et al.* [29] or Deeb [27]). Spring stacks have been found to have reproducible force versus deflection behavior after they have been cycled two times [27,29]. Thus, it is recommended that a spring be stacked, cycled 2 times to the deflection that will be seen in the desired application, and the actual resulting force measured before loading into a system for processing in microgravity.

Example

To illustrate this spring design process, consider the growth of a 2 cm diameter crystal of gallium arsenide where 10 cm of the crystal will be melted and regrown. Assume that PBN leaves will be used in a graphite spring chamber with a graphite piston. The shrinkage for gallium arsenide is approximately 10 % upon melting, so the spring must be able to travel 1 cm.

The dimensions of the spring chamber and piston must be known before the maximum acceptable force can be determined. The diameter of the crystal is 2 cm, and a reasonable wall thickness for the spring chamber is 0.05 cm. This results in a corner to corner distance of 1.9 cm, and a side length of 1.34 cm. Thus, the interior dimension of the spring chamber will be set at 1.34 cm. Assuming a gap between the piston and the spring chamber of 0.03 cm results in a square piston dimension of 1.28 cm. Knowing the surface tension for molten gallium arsenide (in an arsenic atmosphere) is $\gamma = 460 \text{ dyn/cm} = 0.0046 \text{ N/cm}$ [30], and using the contact angle for molten gallium arsenide in contact with carbon coated quartz at 1260 °C of 105° [30] as an approximation, the maximum limit on the applied force can be calculated. Equations (10) and (11) yield values of $F_{ST} = -0.012 \text{ N}$ for the force opposing leakage and $F = 0.13 \text{ N}$ for the spring force which would be expected

to cause leakage. Remembering that it is preferable to have a maximum predicted applied load that is less than one-half of the force necessary to cause leakage, a value of $P = 0.13 \text{ N} / 2 = 0.06 \text{ N}$ can be used with equation (3) and a maximum deflection of 1 cm, to yield a maximum spring constant of $k = 0.06 \text{ N/cm} = 0.6 \text{ N/mm}$.

Allowing 10 % room for the leaves to widen upon compression, the leaf width is 1.2 cm. A value of $r = 4 \text{ cm}$ is chosen because this is close to a standard vertical Bridgman crucible size and therefore readily available. This yields a value for θ of 19° that is less than the upper limit of 30° . Using equation (6) and a deflection of 2 times the desired travel for the spring or $d_{stack} = 2 \text{ cm}$, yields a value of $n = 45$ springs. A value for h is selected as 0.04 cm since experience has shown that this is easily obtainable. Equation (8) can then be used to calculate the predicted spring constant, remembering that $b = w$. This yields a value of $k_p = 0.17 \text{ N/mm}$. This is less than the maximum desired k_p of 0.6 N/mm so this is acceptable.

Finally, the total stack height must be calculated using equation (5). This yields a stack height of 3.8 cm that is within the system requirements so this solution meets the design performance criteria.

Conclusions

Curved leaves of PBN can be effectively tailored through the control of the geometry of individual curved leaves (that is, the leaf width, w , radius of curvature, r , depth, $b=w$, and thickness, h) to provide desired spring constants varying from 0.1 to 25 N/mm. By stacking individual leaves, springs can be designed to provide a desired deflection distance. By considering the appropriate limits on the individual leaves, the geometrical limits of the particular application, and the force constraints due to the materials of interest, springs can be designed to give optimal behavior for use in crystal growth experiments.

Springs made from curved leaves of PBN have been used effectively in past experiments in microgravity for particular geometrical constraints. Now, the knowledge has been gained to design springs for various geometrical constraints with a good *a priori* prediction of the upper bound of the spring constant. This enables the design of springs that will not force leakage of the melt out of the desired region of the system.

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Figure Captions

Figure 1. Schematic for ampoule designs for USML-1 and USML-2 gallium arsenide growth experiments using PBN springs.

Figure 2. Schematic of a curved leaf (a) end view of cylinder and (b) cylindrical section including variables r (radius), w (width), b (depth), h (thickness) and θ (angular span of a leaf).

Tables

Table 1. Elastic moduli for PBN, values given in GPa.

C_{11}	C_{33}	C_{12}	C_{13}	C_{44}	$E_{//a}$	$E_{//c}$	Ref.
				2.52 1.54			Duclaux <i>et al.</i> [21]
750	18.7	150					Jager [22]
830	29.5	13	50	0			Kelly [23]
			7.8				Pezzotti [24]
					22	4.76	Advanced Ceramics[25]
					19.6	6.9	Archer [26]
	10.33			3.85 2.6			Kaforey <i>et al.</i> & Deeb [27-28]

Figures

Figure 1. Schematic for ampoule designs for USML-1 and USML-2 gallium arsenide growth experiments using PBN springs.

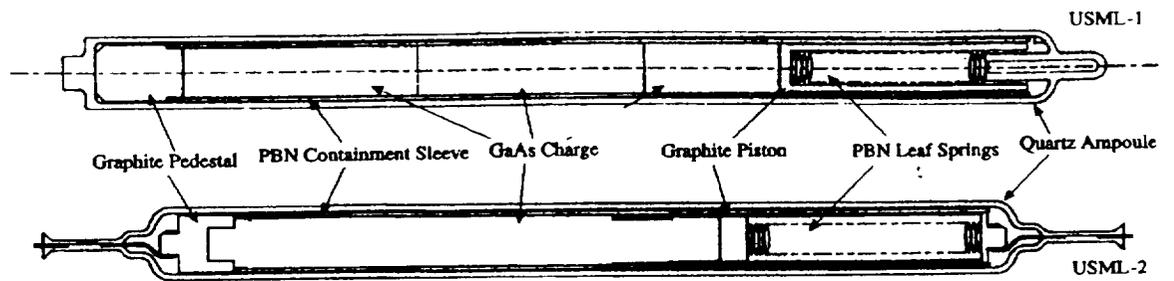
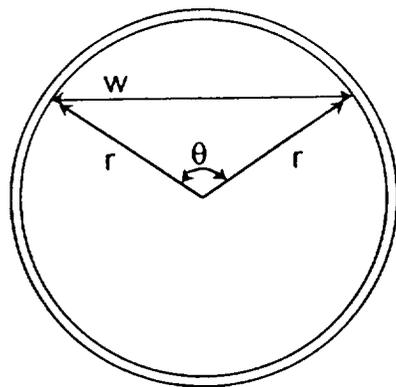
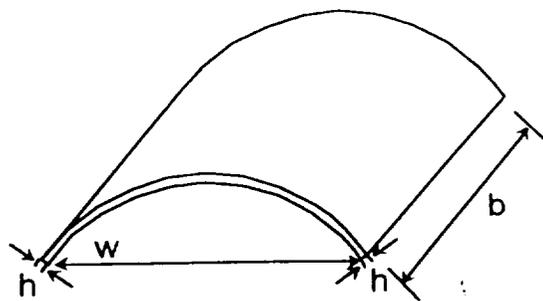


Figure 2. Schematic of a curved leaf (a) end view of cylinder and (b) cylindrical section including variables r (radius), w (width), b (depth), h (thickness) and θ (angular span of a leaf).



(a)



(b)