Low-Cost, Hands-On, Bridgman Crystal Growth Demonstrated for University Students at All Levels

Editor's Note: With this article, MRS Bulletin *is expanding Education Exchange, which formerly focused on scientific educational experiences with local schools (K–12). The department now includes articles on community and university programs. This issue's article describes a university-level experiment on Bridgman crystal growth which was demonstrated at the Materials Research Society's 1995 Fall Meeting in Boston, November 27–December 1.*

Introduction

Our simple experiment in vertical Bridgman-Stockberger (denoted as Bridgman) growth can be easily and safely performed by university students at all levels or can be done as a demonstration. Inspired by M.A. Azouni's experiment,[1] we use water for melt and ice for crystal. This system mimics semiconductors which have high conductivity melts (e.g., Si, GaAs, Te, HgCdTe). Our materials are nontoxic and the temperatures are easily accessible. We use a clear plastic tube for the crucible, mounted on an aluminum cold finger secured in a Styrofoam plug in the top of a 20 l liquid nitrogen dewar. Since crucible, solid, and melt are transparent, students can view the solidification. The interface tends to be flat. The segregation of dyes or colored salts makes a dramatic show. In a research setting, we have used the system to model the effect on interface shape of a conducting crucible wall (the solid will "climb" a conductor placed in the melt). By adding a set of thermocouples, we can study the effects of convection. As a lecture demonstration, the apparatus can be set up 10 minutes prior to starting the lecture, and 30 to 40 minutes later the show is at its height. As a laboratory experiment, it is an open-ended challenge to the students.

The students should understand the fundamentals of thermal transport phenomena and the fundamentals of directional and Bridgman solidification processes. Students would have typically gone over this material during a materials science course, an introduction to solidification processes course, introduction to metallurgy, or crystal growth techniques course. The growth interface shape and its relationship to thermophysical properties is the key part of the experiment.[2] The students should understand the basics of Bridgman solidification using an experimental model that is directly related to II-VI, III-V, and IV semiconductor melt growth such as mercury cadmium telluride, silicon, or other similar materials, to observe and understand the interface shape and its relationship to thermal transport and thermophysical properties of the solid, liquid, and crucible materials.

Theory

To understand the interface shape between the solid, liquid, and crucible wall, we refer to the thermal conditions in Bridgman growth solidification configurations. The theory proposed by T. Jasinski and A.F. Witt and later clarified by L. Holland defines the solid-liquid interface shape.[2–3] We use the solidification of water to model the Bridgman growth. For good crystallinity, a convex crystal face is required as shown by the solidification of lead. We apply Holland's theory to understand the problems of II-VI, III-V, and IV semiconductor crystal growth whose interface propagates with a concave shape.

Figure 1 illustrates a typical Bridgman solidification system. Bridgman solidification is directional crystal growth where the loaded crucible moves in the direction from the hot zone into the cold zone where the melt or liquid solidifies. The hot and cold zones are quasistatic for slow solidification. The crucible moves through the stationary furnace at a predefined velocity that defines the growth or solidification rate. Due to the change in thermal conductivity, the heat flux propagates into the cold zone, encountering thermal resistance. The corresponding heat flow diverges outward through the walls of the crucible. When the heat flux diverges, the surfaces of constant temperature, isotherms, curve up at the edges. The growth face occurs at the freezing temperature isotherm. It should be noted that crystal growth propagates perpendicular to the isotherm representing the solidification temperature.[4] The crucible walls form a thermal "short circuit" in the system.

The thermal flux and thermal gradient boundary conditions at boundaries 1, 2, and 3 (from Figure 1) defines the ruling relationship. At the crucible wall (boundaries 1 and 2), sufficiently close to the melt-solid interface, the thermal gradients obey

$$(\partial T/\partial z)_m=(\partial T/\partial z)_s \qquad (1)$$

where subscripts m and s refer to the melt and solid phase of the load, respectively. The *z*-component of the thermal flux, the thermal conductivity (k) times the thermal gradient, at the solid-melt interface (boundary 3) obeys

$$k_m(\partial T/\partial z)_m=k_s(\partial T/\partial z)_s. \qquad (2)$$

Both Equations 1 and 2 are valid only if either $k_m = k_s$ or $\partial T/\partial z = 0$ in both media. We know that k_m is not equal to k_s. So, if k_m is greater than k_s, then at the line of contact of the melt-solid interface with the crucible the heat flux is strictly hori-

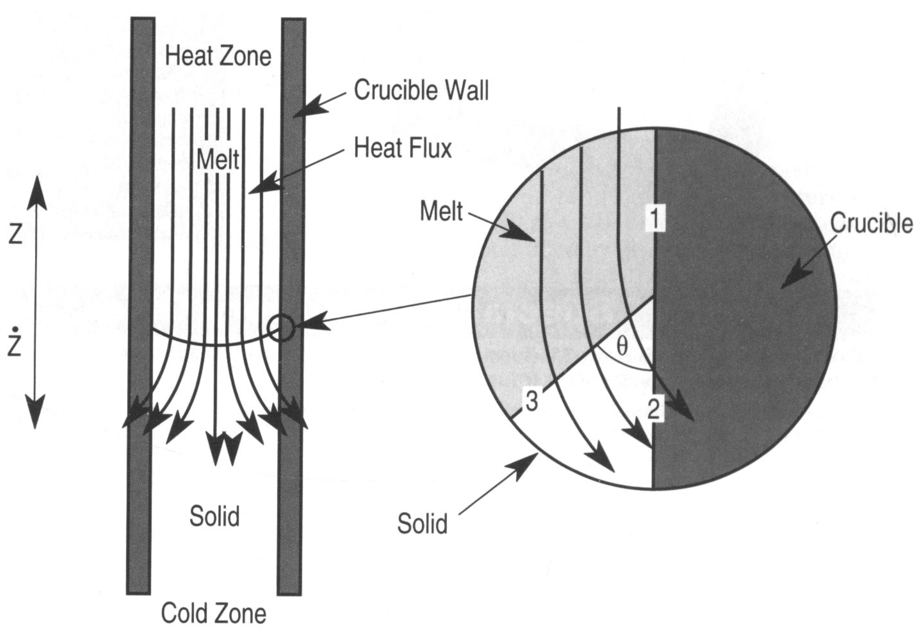

Figure 1. Steady-State Bridgman Model Schematic.

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zontal, into the crucible wall ($q = 0°$). Similarly, if k_m is less than k_s, as in the case with a metal, then the interface turns down at the edge, and $q = 180°$.

Experimental Equipment

We use the following experimental equipment to construct the modified Azouni[1] experiment:

1. Plexiglas crucible (25 mm inner diameter approximately 600 mm in length);
2. aluminum alloy cold finger (25 mm diameter, with o-ring, that fits into the Plexiglas crucible);
3. liquid nitrogen dewar (20 l) or other cryogenic source;
4. Styrofoam dewar-cold finger adapter 2 $^{7}/_{16}$ in. outer diameter (anything that would secure the cold finger in the dewar would be acceptable);
5. de-ionized water;
6. aluminum welding rod (3.175 mm or $^{1}/_{8}$ in.);
7. a meter stick or other measuring device; and
8. a stopwatch.

We purchase the Plexiglas crucible from a local plastics retailer. The Plexiglas tube typically costs less than $10 and we can sometimes get it for free as remnant stock. Through a machine shop at the university, we construct the 1-in. cylindrical aluminum stock. We can find a nitrogen dewar in the physics department and de-ionized water in the chemistry department. Using a lathe and knife, we cut the Styrofoam adapter into form from commonly available packing block material.

Experiment

First, we explain to the students the precautions needed when using nitrogen, and we make sure the laboratory has proper ventilation. The interface shape experiment involves eight steps:

1. Insert the cold finger into the dewar adapter.[5]
2. Slip the transparent crucible over the cold finger until it fits over the o-ring. The meter stick does not need to be affixed to the crucible.
3. Fill the crucible with de-ionized water.
4. Insert the cold finger, crucible, and adapter assembly into the liquid nitrogen dewar or other available cryogenic source and note the starting time in a data sheet.
5. Upon solidification of the water, note the morphology of the ice. Take measurements of the ice growth length each minute after the ice has fully solidified past the cold finger, noticing the interface shape at the wall of the crucible. Observe whether the ice grows with a concave or convex interface; predict whether liquid water has a larger thermal conductivity than solid water; whether the solid or liquid has a greater density; whether a relationship exists between the density and the thermal conductivity of the solid and melt material. Consider the packing fractions for the different states of matter.
6. Insert an aluminum or other metallic rod into the crucible after the ice has solidified past the cold finger and let the rod rest on the ice. Note what happens at the point of contact between the metallic rod and ice and the interface shape as the water solidifies up the metallic rod. Again, predict whether liquid water has a larger thermal conductivity than solid water and question whether this result agrees with the conclusion from Step 5.
7. Stop the experiment or demonstration after 30 minutes. Remove the cold finger, crucible, and adapter assembly from the liquid nitrogen dewar, and cap the dewar.
8. Let the students, then, answer all questions given in the preparation steps and complete their data sheets. They plot the growth rate as a function of time.

Education Exchange highlights experiences of scientists and engineers with local schools (K–12), community programs, and university programs, along with helpful hints and resources. If you would like to share your own involvement in science education, contact *MRS Bulletin*, Materials Research Society, 9800 McKnight Road, Pittsburgh, PA 15237-6006; fax 412-367-4373; e-mail Bulletin@mrs.org.

Conclusion

Transparency, a prominent characteristic of pure water, gives this demonstration experiment a unique attraction for the participant. Some of us had worked with semiconductor crystal growth for years without ever having seen a real growth face in action. The excitement of "seeing and believing" is infectious. We owe the genius of using water as a model material to Azouni of the CNRS in France. The pace of the growth is perfect, as there is plenty of suspense and time for discussion, but nevertheless enough action to keep up the interest. We have run this demonstration at various conferences and in classrooms and invariably lively discussion results with many suggestions for improvements and extensions. At another level, it validates the theory of Jasinski and Witt beyond question. The references cited give the background in easily understandable form, and will give ideas for further development.

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1. M.A. Azouni, *J. Cryst. Growth* **42** (1977) p. 405.
2. L.R. Holland, *J. Cryst. Growth* **96** (1989) p. 577.
3. T. Jasinski and A.F. Witt, *J. Cryst. Growth* **71** (1985) p. 295.
4. W. Kurz and D. J. Fisher, *Fundamentals of Solidification*, 3rd. ed., (Trans Tech Publications, 1989).
5. Contact the authors for fabrication drawings for the aluminum cold finger, dewar adapter, and crucible assembly.

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