RESIDUAL GAS EFFECTS ON DETACHED SOLIDIFICATION IN MICROGRAVITY

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Many microgravity directional solidification experiments yielded ingots with portions that grew without contacting the ampoule wall, leading to greatly improved crystallographic perfection [1]. Our long-term goal is to make such detached solidification reproducible, which requires a full understanding of the mechanisms underlying it. Our Moving Meniscus Model of steady-state detachment predicts that it depends strongly on the surface tension of the melt and the advancing contact angle with the ampoule wall [2-7]. Detached solidification is more likely when the contact angle for the melt on the ampoule wall is high, i.e. non-wetting. It has been claimed that impurities increase the contact angle. The objective of the current project is to determine the influence of residual gases on the surface tension and contact angle of molten semiconductors on typical ampoule materials. We are focusing on determining the influence of oxygen on the contact angle of molten InSb on clean silica ("quartz"), including the advancing and retreating contact angles in addition to the usual "equilibrium" contact angle.

We have created a gas flow system that allows us to control the oxygen partial pressure over a sessile drop of InSb on a horizontal quartz surface. The cell is slowly tilted while videotaping to reveal the contact angles on the two sides of the drop just prior to it rolling down the surface. Thus far, we have learned the following:

- Molten InSb readily forms an oxide layer in the presence of the trace amounts of oxygen found in high purity argon.
- This oxide contains a substantial amount of Ga, which presumably is a trace contaminant that is not detectable in the starting material.
- The addition of 10% hydrogen to the argon gas is sufficient to reduce the oxide and produce a clean drop.
- An infrared filter must precede the video camera in order to produce a sharp image of the drop for later image analysis.
- Tilting the surface on which the drop rests causes the two sides of the drop to display different contact angles, reflecting contact line sticking.
- Vibration strongly accelerates the approach of the drop to its final shape on a horizontal surface by helping to overcome sticking of the contact line.
- Oscillation of the drop surface due to vibration appears to increase as the surface is inclined from horizontal. Presumably, the angle at which the drop rolls down the surface is also reduced by vibration. This observation is particularly significant, as the meniscus must move along the ampoule wall during detached solidification.

Originally we had proposed to use the sessile drop technique in a closed cell, similar to that used here previously [8-10] but with the addition of a stabilized zirconia electrochemical oxygen pump and sensor. Upon thorough investigation, however, we discovered several difficulties with this approach: the operating temperature of zirconia cells is above the melting point of InSb; they are not available off-the-shelf in the form needed; and they are difficult to attach to the cell in a manner that withstand the elevated temperature required. For these reasons, we decided to flow a gas with known oxygen concentration through the cell.

Figure 1 shows a schematic diagram of the experimental apparatus. To perform an experiment, a piece of InSb was loaded into the experiment cell, which was connected to the gas supply system. The furnace was heated until the InSb melted. In early experiments, the melt appeared to be have some oxide on its surface. This oxide was slowly reduced by passing argon containing 10% hydrogen over it. In the presence of high purity argon alone, the oxide slowly reformed. Reportedly, this argon contained on the order of 1 ppm of oxygen. After cooling the furnace, the frozen drops were removed and examined by scanning electron microscopy. Some were cleaved and the cross sections viewed, as illustrated in Figure 2. Figure 3 is an energy dispersive x-ray spectrum of oxide, showing a strong Ga peak that was not present on either the starting material or on unoxidized drops. Apparently gallium was preferentially oxidized, presumably because its oxide has a higher free energy of formation (more negative) than does indium oxide.

Drops were videotaped during an experiment. Frames were later grabbed and analyzed using using HL++ 98 image analysis software. Figure 4 shows a sessile drop of unoxidized InSb on a quartz microscopic slide with 90%Ar - 10%H_2 flowing through the cell throughout the experiment. These frames show that the contact angle was relatively constant and significantly higher than the 112° measured under "static vacuum" by Harter et $al.$ [11].

In order to fully achieve the objectives of this project, we must determine the contact angle versus oxygen fugacity (or partial pressure) in the gas phase above the melt. Thus, we must know this fugacity and be able to control it. In order to vary the oxygen fugacity, we will mix argon containing a known amount of hydrogen with argon containing a known amount of oxygen. From the well-established reaction kinetics of hydrogen and oxygen, we have determined that the residence time in the experiment cell is sufficient to assure that equilibrium is reached at 530°C (see Figure 5). The equilibrium conversion can readily be calculated from the free energy of formation of water at that temperature. In order to be certain that we know the oxygen fugacity thus achieved, we are installing an oxygen sensor in the effluent gas stream.

References
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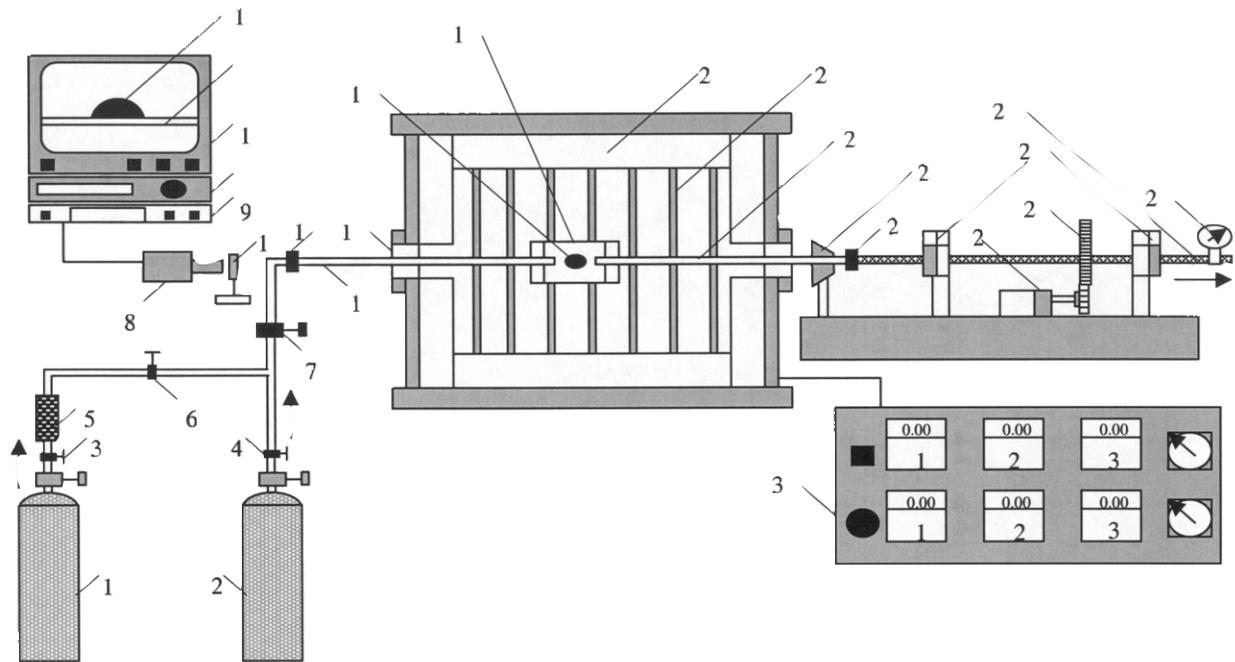
	UHP (Ultra High Purity) Argon	9. Time Code Generator	7 Borosilicate Optical Glass window	25. Bearings
2	90% Argon- 0% H_2	0: VCR	8 Indium Antimonide sessile drop	26: Motor
3	Bal Valve	1 TV	9. Quartz ampoule with a Quartz plate	27 Gear
4	Ball Valve 2	12. Quartz plate	20. Insulation	28. Aluminum tube
5	Oxisorber	13 Picture of InSb sessile drop	21 SiC Heating rods	29 Pressure Gauge
6:	Ball Valve 3	14. IR Filter	22 Quartz Gas Outlet tube	30: Temperature Controller
7	Volumetric Flow Valve	15: Swivel Fitting	23: Light Source	
8	Camera with lens	6: Quartz Gas Inlet tube	24 Quartz Metal Adapter	

Figure 1   Schematic diagram of apparatus
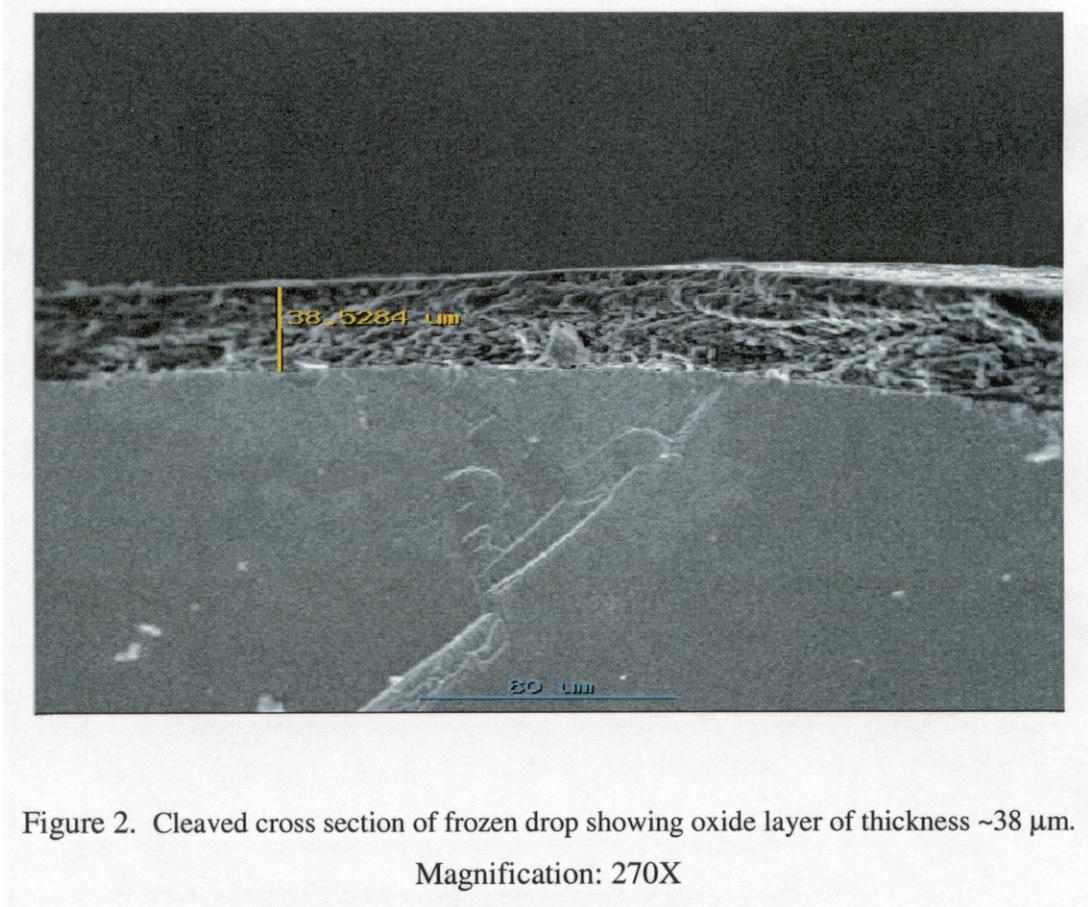
Figure 2. Cleaved cross section of frozen drop showing oxide layer of thickness ~38 μm.
Magnification: 270X
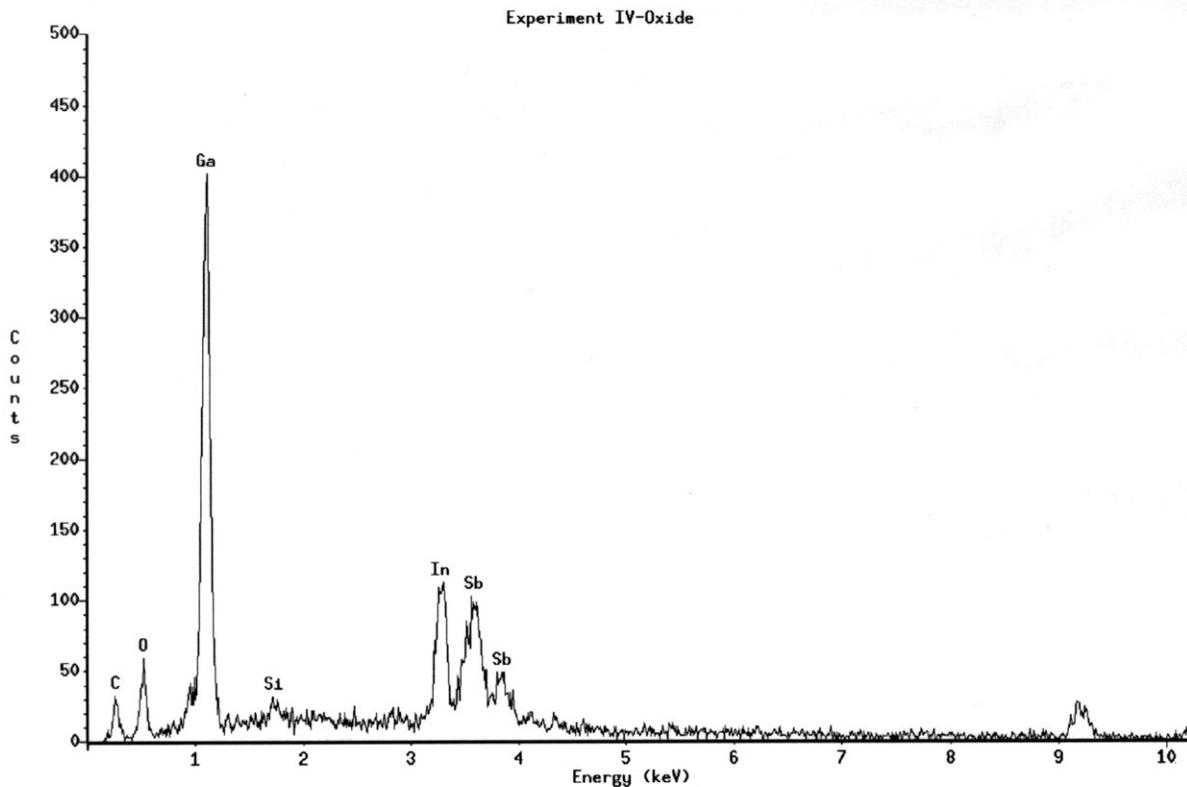
Experiment IV-Oxide

Column	: JEOL,Pioneer		
Take-off angle	: 30	Accelerating voltage	: 15
Acquisition type	: eds	Magnification	: 1300
Creation time	: 2001/12/14 1:46	Charge	: 13
Livetime	: 13	Beam current	: 1
Deadtime	: 4.49	Beam spot size	: 0
Channels	: 1024	Beam location	: 0.0
Channel width	: 10	Working distance	: 15
Detector type	: Silicon/Lithium	Stage X	: 0
Window type	: norvar	Stage Y	: 0
Window thickness	: 0.3	Stage Z	: 0
Coating material	: Al	Stage tilt	: 0
Coating thickness	: 0.04	Stage rotation	: 0
Contact material	: Au	Contamination material	: none
Contact thickness	: 0.02	Contamination thickness	: 0
Crystal thickness	: 3		

File name :

Notes:

       Fri Dec 14 01:46:12 2001

       Experiment IV-Oxide

       Livetime : 13.0 Sec.
       Technique: Least Squares Fit

       Elements Present:
           C(6), O(8), Ga(31), Si(14), In(49),
           Sb(51)

Energy (keV)	Intensity (counts)	Elements Present
0.267	183	C Ka
0.523	337	O Ka

Figure 3. Energy-dispersive x-ray spectrum of oxidized InSb drop.
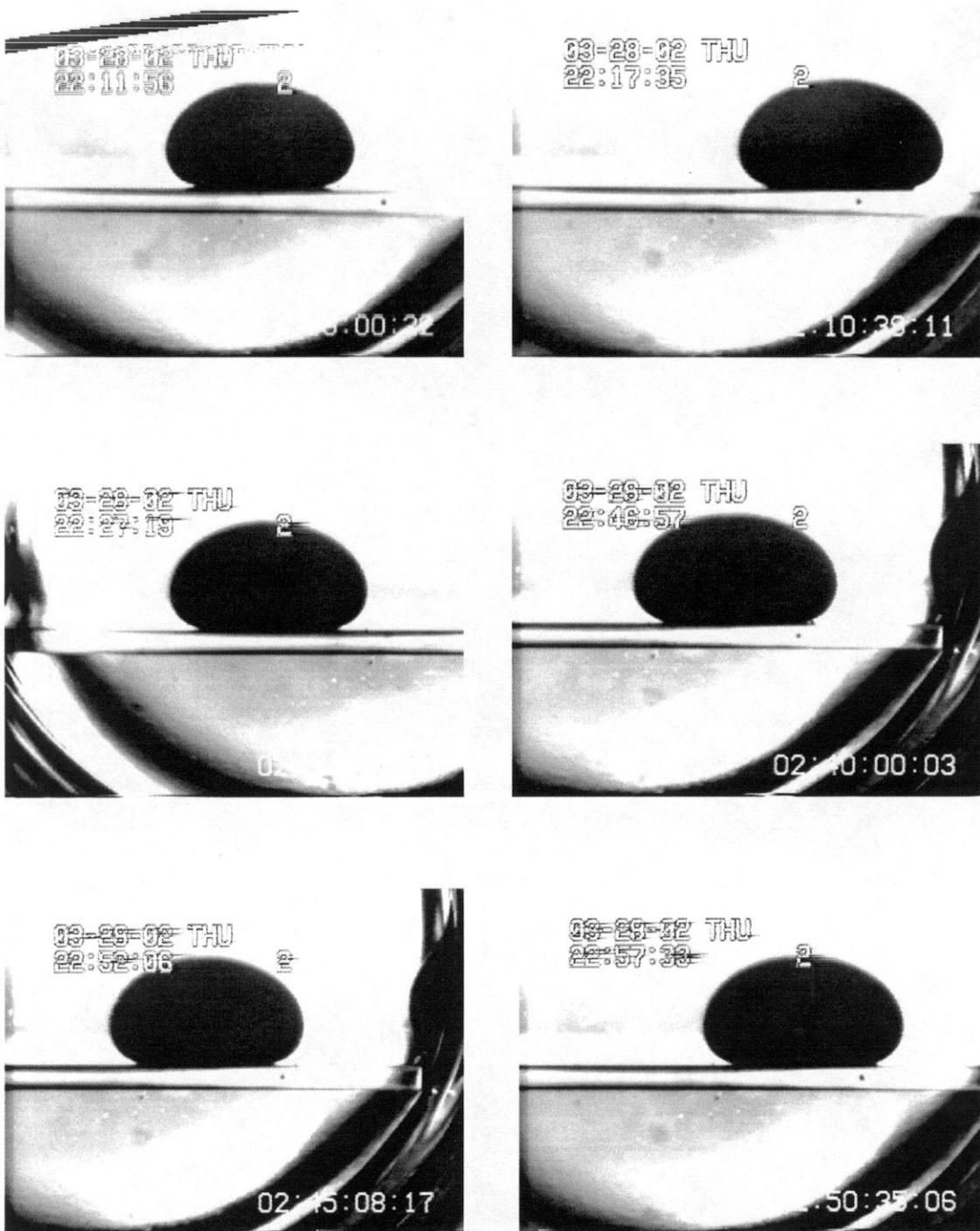
Figure 4. Sessile drop during an experiment in the presence of 90%Ar-10%H$_2$.
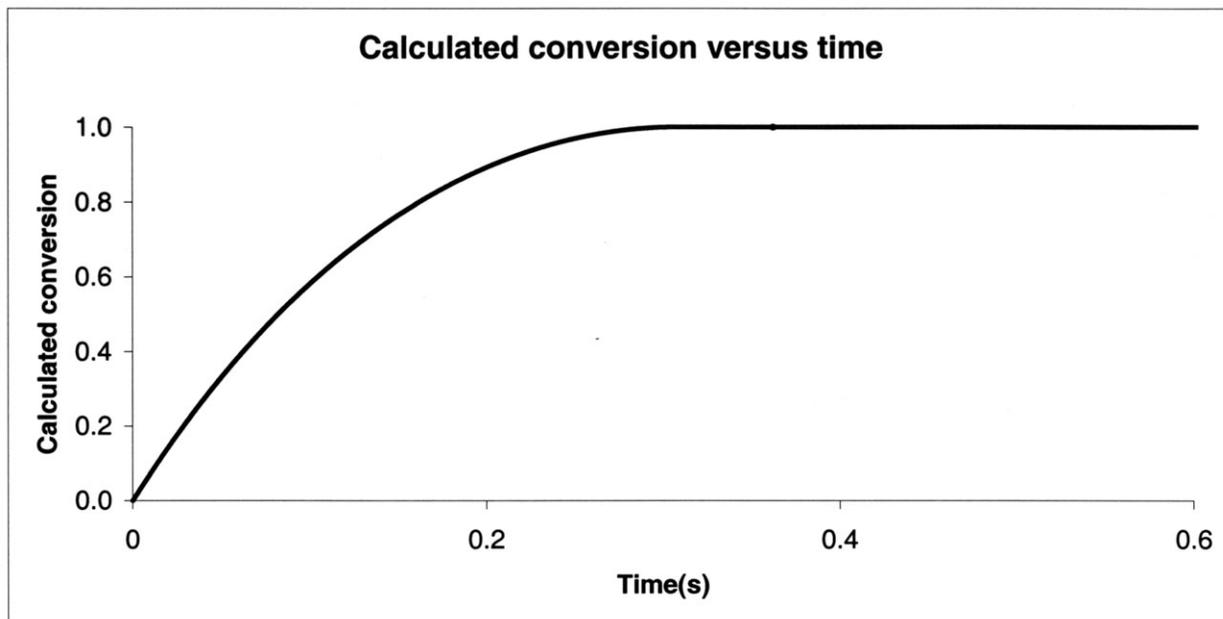
Figure 5. Calculated conversion of hydrogen to water by reaction with oxygen at 530°C. The residence time in the experiment cell is 2.4 s.