1995

NASA/ASEE SUMMER FACULTY FELLOWSHIP PROGRAM

MARSHALL SPACE FLIGHT CENTER
THE UNIVERSITY OF ALABAMA IN HUNTSVILLE

Effect of Melt-Solid Interface Shape on Lateral Compositional Distribution of Unidirectionally Solidified II-VI Semiconducting Alloys

Prepared By:	Jai-Ching Wang, Ph.D.
Academic Rank:	Associate Professor
Institution & Department:	Alabama A&M University Department of Physics
NASA/MSFC:	
Office:	Space Sciences Laboratory
Division:	Microgravity Science & Application
Branch:	Crystal Growth & Solidification Physics
MSFC Colleagues:	S. L. Lehoczky, Ph.D. C.-H. Su, Ph.D. D. C.Gillies, Ph.D. D. A. Watring Y.-G. Sha, Ph.D. F. R. Szofran, Ph.D.

INTRODUCTION

A computer code developed previously [1] has been used to simulate lateral compositional distributions for several II-VI semiconducting systems. The code is based on analytical results [2] obtained by following Coriell et al. formalism [3]. The system under study is an azimuthal symmetric cylindrical system with a curved melt-solid interface shape during an unidirectional solidification process. It is assumed that the system is under a steady state diffusion limited growth condition with a curved melt-solid interface and equation for the diffusion limited growth is

$$\nabla^2 C(r, z) + \beta \frac{\partial}{\partial z} C(r, z) = 0 . \tag{1}$$

In terms of cylindrical coordinates explicitly, the equation is expressed as

$$\frac{\partial^2}{\partial r^2} C(r, z) + \frac{1}{r}\frac{\partial}{\partial r} C(r, z) + \frac{\partial^2}{\partial z^2} C(r, z) + \beta \frac{\partial}{\partial z}(C(r, z)) = 0, \tag{2}$$

where the dimensionless solute concentration, C, has been scaled by the bulk concentration C_0, r and z are dimensionless axial and radial coordinates which have been scaled by the radius of the ampoule, R, and β=VR/D, in which V is the growth velocity, R is the sample radius and D the diffusion constant of the solute in the liquid.

The boundary conditions to be satisfied are

$$C(r, z \rightarrow \infty) = 1 , \tag{3}$$

$$\frac{\partial}{\partial r} C(r, z) = 0 \quad \text{at } r=1 \text{ and } r=0, \tag{4}$$

$$\beta (k-1) C_I(r, z) = \frac{\partial}{\partial z} C_I(r, z) - \frac{\partial}{\partial r} C_I(r, z) \frac{\partial}{\partial r} W(r) . \tag{5}$$

where k is the segregation constant, W(r) the melt-solid interface and I denotes at the melt-solid interface location.

The melt-solid interface shape can be expressed as a series of Bessel's functions,

$$W(r) = \delta + \sum_{n=1}^{\infty} \delta(n) J_0(u_n r) . \tag{6}$$

where δ is the planar interface location and $\delta(n)$'s are the coefficients for the Bessel's functions $J_0(u_n r)$ and u_n's are the zeros of $J_1(\alpha)$.

The diffusion equation, equation (2), can be solved by the separation of variables method. In the limit that dw/dr is small compared to $2k+p(n)-1$, where $p(n)$ denote $\sqrt{1+\left(\frac{2u_n}{\beta}\right)^2}$ and have large values for small β, the solution for solute concentration in the melt at coordinate (r, z) is

$$C(r, z) = 1 + \frac{1-k}{k} e^{-\beta(z-\delta)} + \sum_{n=1}^{\infty} \frac{2\beta(1-k)\delta(n)}{2k+p(n)-1} e^{-\frac{\beta}{2}[1+p(n)](z-W(r))} , \tag{7}$$

The solute concentration in the melt at the melt-solid interface is

$$C_I(r, z) = 1 + \frac{1-k}{k} e^{-\beta(W-\delta)} + \sum_{n=1}^{\infty} \frac{2\beta(1-k)\delta(n)}{2k+p(n)-1} . \tag{8}$$

The solute concentrations of the solid at the interface, $C_{SI}(r, z)=kC_I(r, z)$, is

$$C_{SI}(r, z) = k + (1-k) e^{-\beta(W-\delta)} + \sum_{n=1}^{\infty} \frac{2\beta k(1-k)\delta(n)}{2k+p(n)-1} . \tag{9}$$

For small β limit and $\beta(W-\delta)$ is small, we may expand the exponent term and obtain the solute concentration in the solid at the melt-solid interface as

$$C_{SI}(r, z) = 1 - \beta(1-k) \sum_{n=1}^{\infty} \frac{\delta(n) J_0(u_n r)}{1 + \frac{2k}{p(n)-1}} . \tag{10}$$

If $2k/[p(n)-1] << 1$, then equation (10) reduces to a simpler expression

$$C_{SI}(r, z) = 1 - \beta(1 - k)[W(r) - \delta], \tag{11}$$

i.e., the deviation of C_{SI} from unity is proportional to the deviation of interface shape from planarity. The proportional constant is the product of β and (1-k).

NUMERICAL CALCULATIONS AND RESULTS

We use equations (9), (10), (11) to calculate compositional distribution at the melt-solid interface for a diffusion limited growth system with a curved melt-solid interface shape for small β values. The results in Figure 1 show that equations (9) and (10) give very close answers while equation (11) over estimates the results by a few percent. Calculated lateral compositional distributions by using equation (10) for four different melt-solid interface shapes are shown in Figure 2. Scaling these compositional distributions with their interface deflections yields curves with similar shapes as shown in Figure 3. By adjusting the scaled curves they all fall on one curve, indicating that the lateral compositional distribution is proportional to melt-solid interface shape for same β and k (see Figure 4). The results agree with the simple expression equation (11) because both the conditions, β is small and $2k/[p(n)-1] << 1$, are satisfied in this study. The experimental conditions for various systems under consideration are listed in Table 1 which have β equal to 0.1455, 0.16 or 0.2667 small enough such that the analytical and approximate expression obtained above apply. In the MZT USML-1 experiments [4], the interface shapes were not radially symmetrical, therefore, the deflections of the interfaces for the right and left handed sides were measured. Table 2 is a comparison of the calculated and experimental radial segregation on MZT USML-1 experiment. The results agree reasonably well. Figure 5 shows the simulated and experimental data for MCT D4 crystal grown under axial 50 kG magnetic field [5]. The experimental data agree quite well with the theoretical results indicating that the convection in the melt during the growth has been reduced by the magnetic field. Figure 6 gives the simulated and experimental data for MCT D6 crystal grown without magnetic field [5]. Due to larger convective fluid flow in the melt during crystal growth in D6 experiment compared to that of D4 experiment, D6 crystal has larger deflection of melt-solid interface shape. The simulated results show that the composition distribution scales with melt-solid interface shape, but with larger discrepancies between the two curves at the edges. This is due to the contribution from the convective fluid flow in the melt. The simulated data and the experimental data for MZT B16-4 crystal are shown in Figure 7. The disagreement between theory and experiment in MCT D6 and MZT B16-4 experiments are also believed to be due to contributions from convective fluid flow [6]. Figure 8 shows the simulated and experimental data for MCT USMP-2 space flight crystal [7] grown in space. The two curves have significant mismatches at the edges. Which was believed to be contributed by the residual transverse microgravity.

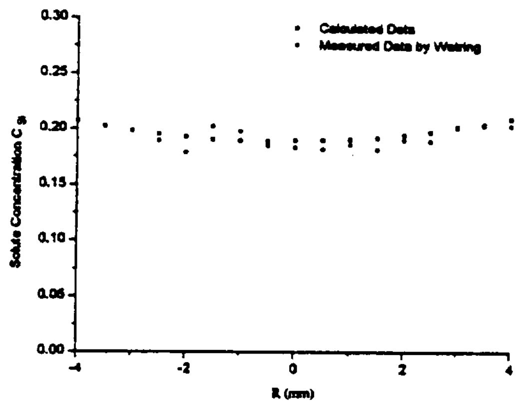

Figure 5. Calculated and measured data of MCT D4 crystal with 50 KG magnetic field

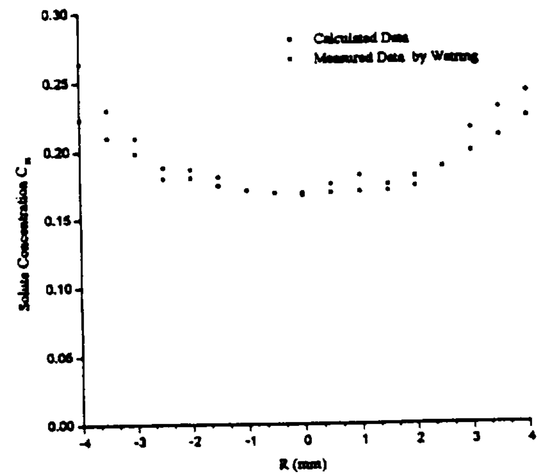

Figure 6. Calculated and measured data of MCT D6 crystal without magnetic field

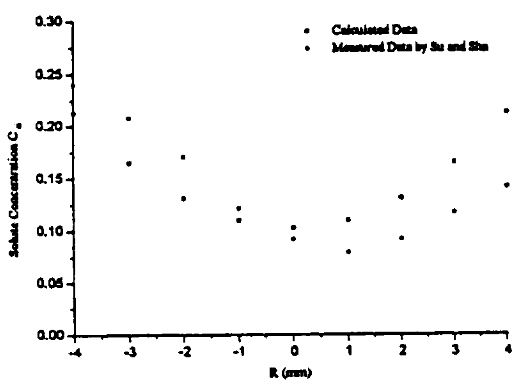

Figure 7. Calculated and measured data of MZT B6-4 ground based crystal. Deflections are 1.086 & 1.091 on left and right hand sides of the crystal.

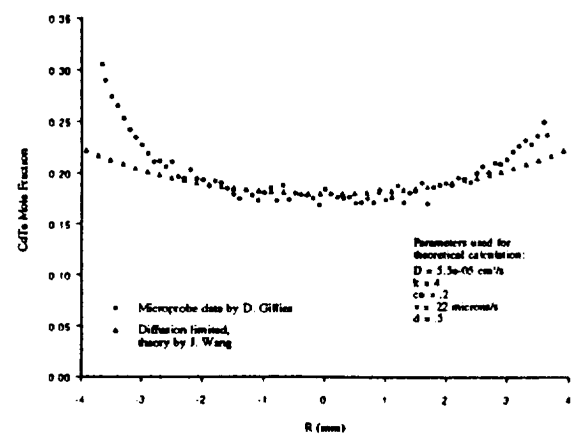

Figure 8. MCT-27Q, Flight Sample Composition across x-Diameter

Table 1: Ampoule Data

Ampoule I.D.	C_0	V (cm/s)	k	D (cm^2/s)	R (cm)	β=VR/D	Deflection Δ
MCT D4	0.2	2x10-5	4	5.5x10-5	0.4	0.1455	0.275
MCT D6	0.2	2x10-5	4	5.5x10-5	0.4	0.1455	0.8125
MZT USML-1	0.16	4x10-6	4	6x10-6	0.4	0.2667	R-0.5 L-0.225
MZT B16-4	0.16	4x10-6	4	6x10-6	0.4	0.2667	R-1.091 L-1.086
MCT USMP-2	0.2	2.2x10-5	4	5.5x10-5	0.4	0.16	0.5

Table 2: Measured and simulated lateral compositional deviations of MZT USML-1 space flight experimental data

Measured	Calculated
$\Delta C_1/C_0=0.40$	$\Delta C_1/C_0=0.375$
$\Delta C_2/C_0=0.18$	$\Delta C_2/C_0=0.153$

REFERENCES

[1] Wang, J. C., "Numerical Formulation of compositional Segregation at Curved Solid-Liquid Interface during Steady State Solidification Process", NASA CR 196533, ed. by Freeman, M., Chappell, C. R., Six, F. and Karr, G. R., Oct. 1994

[2] Wang, J. C., "Investigation of compositional Segregation During Unidirectional Solidification of Solid Solution Semiconducting Alloy", NASA CR 162051, ed. by Karr, G. R., Barfield J., and Kent, M., pXLI1-20, Aug. 1982

[3] Coriell, S. R., F. Boisvert, R. G. Rehm, and R.F. Sekerka, "Lateral Solute Segregation During Unidirectional Solidification of a binary Alloy with a Curved Solid-Liquid Interface", Journal of Crystal Growth 54, 167, 1981

[4] Lehoczky, S. L., F. R. Szofran, D. C. Gillies, S. D. Cobb, C. H. Su, Y. G. Sha, R. N. Andrews, "Crystal Growth of Selected II-VI Semiconducting Alloys by Directional Solidification," NASA CP-3272 Volume I 163-222, May 1994

[5] Watring, D. A., "The Effects of Vertical Magnetic Fields on Segregation in HgCdTe," Presented Second International Conference on Solidification and Gravity Miskole-Lillafured, Hungary, April 25-28,1995

[6] Capper, P., C. L. Jones, E. J. Pearce and M. J. T. Quelch, "Growth of $Cd_xHg_{1-x}Te$: Comparison of Some Properties with the Predictions of two Melt Growth Models", Journal of Crystal Growth 62, 487, 1983

[7] Lehoczky, S. L., F. R. Szofran, and D. C. Gillies, "Growth of Solid Solution Single Crystals", to be published in Launch+1 Year Science Review of USMP-2, 1995