Diffusion Limited Silicon Dissolution into Germanium Melt

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Abstract. The dissolution of silicon into germanium melts has been investigated for application to solution crystal growth. Small diameter samples were processed to weaken flow structure in the melt making the transport mechanism diffusion dominated. 8mm diameter samples were processed at three different temperatures. The temperature dependence of the dissolution rate of silicon was found to be not measurably significant in the experiments presented here. The orientation of the sample, with respect to gravity, had a profound effect on the dissolution rate. A small number of 4mm diameter samples were also processed and the same effects were apparent.

1. Introduction
There has been recent interest in the silicon germanium alloy (SiₙGe₋₁ₓ) as an emerging semiconductor material since it possesses full miscibility across its composition range allowing for adjustment of the band gap and lattice parameter [1-2]. Bulk single crystals of SiₙGe₋₁ₓ have application in photodetection, photovoltaics, thermal imaging, and as a substrate for SiₙGe₋₁ₓ epitaxial layers [3]. The bulk SiₙGe₋₁ₓ substrates can be lattice-matched to the device layer, reducing strain. Among device structures of interest, the heterobipolar transistor has been most studied due to its applications in telecommunications. As for other important applications for SiₙGe₋₁ₓ, modulation doped field effect transistors and 1.3μm optoelectronics can be identified [4].

There are a number of techniques used to grow single crystal SiₙGe₋₁ₓ alloys. The Czochralski (Cz) crystal growth technique is currently the most efficient method for producing bulk SiₙGe₋₁ₓ crystals. However, since the liquidus and solidus curves in the SiₙGe₋₁ₓ phase diagram are widely separated, producing compositionally uniform material requires that silicon be replenished during growth from the melt [5]. Similarly in Bridgman growth of SiₙGe₋₁ₓ alloys, the transport of the species and the changing composition of the melt are again important for producing compositionally uniform crystals [6-7].

Silicon germanium crystals have been produced by the liquid phase diffusion (LPD) crystal growth technique [8]. This technique avoids the miscibility gap issues with melt growth. The rate limiting step in this solution growth technique is the transport of silicon to the growth interface. It has been shown that silicon transport proceeds in a diffusion dominated manner in this growth technique [9]. In order to further advance this technique, proper understanding of the transport mechanisms at work is necessary.

In previous work, dissolution has been shown to be influenced by flow structure in the germanium melt [10]. The dissolving silicon stabilizes the melt against convection in the configuration where silicon is dissolving into the melt from above. This is due to the lighter silicon reducing the density of the melt as the silicon concentration increases. This helps to weaken any convective flow structure.
However, we have seen that the weak flow structure present still has an influence on dissolution. In order to explore the diffusion behavior of silicon in the melt, we have reduced the diameter of the crucibles to 8mm in order to further weaken the flow structure in the melt.

2. Experimental Procedure

The experiments were conducted in a three zone vertical DC resistance tube furnace. An isotherm was maintained over the crucible length at temperatures of 1000°C, 1050°C or 1100°C. The isotherm is maintained within 3 degrees axially and 1 degree radially. The materials were contained in a quartz crucible. The silicon used was single crystal optical grade, 5N, material. The germanium used was 6N material. The silicon and germanium were both cleaned and etched prior to loading into the crucible. The cleaning, etching and loading took place in a clean room. Once the materials were loaded, the crucible was evacuated to approximately 1x10⁻³ Pa.

The crucible was hung in the furnace inside a quartz ampoule. It was first preheated for approximately 1 hour above the hot zone at approximately 800°C, i.e. below the melting point of Ge. This quickens the time to melt the sample and begin dissolution into the melt. To start the experiment, the crucible was dropped into the isothermal area of the furnace from the preheating position. It was allowed to remain there for the experiment time, 60 minutes. At the conclusion of this time, the crucible was pulled from the furnace and allowed to cool in air. The samples were then sectioned in half. One section was differentially etched to reveal structure.

Two different material arrangements were used. The first was a silicon source floating on top of the germanium melt. In this case the silicon source covers the melt free surface. This arrangement is similar to that used in the Liquid Phase Diffusion growth system for SiGe [8-9]. This was used for the majority of experiments. For comparison, two samples were processed at 1050°C with the silicon source at the bottom of the crucible.

3. Results

The samples processed with the silicon dissolving from the top all exhibited almost the same level of dissolution over the temperatures used. A dissolution height of around 0.5mm was measured across all samples processed as seen in figure 1. This implies that the temperature dependence of the dissolution rate and consequently the diffusion coefficient is not overly significant in this range of temperatures. It would appear from results that there is a temperature dependence but it is not resolvable with this experimental setup. The length of experiments was one hour. It is possible that a longer experiment time could allow the dependence to be better resolved.

In previous work, these types of experiments were conducted in a 25mm diameter crucible [10]. The experiments were run for shorter periods of time and only at 1100°C. In those experiments the dissolution height was up to 1mm. This highlights the increased mixing present in the melt with the larger diameter due to the contribution of stronger convection in the melt [11]. The decreased diameter crucibles used in the current experiment work do help to weaken convection in the melt. Experiments on 4mm and 2mm diameter crucibles were performed with little success as surface tension often prevented the silicon from fully wetting with the melt and voids formed separating the melt into segments. The crucible would require modification so pressure could be exerted to ensure proper wetting between all elements.

Numerical modelling did not show significant change in flow structure between the 8mm and smaller diameter crucibles. As seen in figure 2, the composition profiles after the one hour experiment time are virtually identical. The flow structure was computed with the effects of solutal buoyancy and similar weak flow is present in both crucibles. All numerical work was completed using the commercial ANSYS CFX package.
Figure 1. Plot of dissolution height of processed samples versus temperature. The lack of differential between temperatures with respect to error is apparent.

Figure 2. Computed concentration profiles for dissolution experiments. The solid line is for an 8mm diameter crucible and the dotted line is for a 4mm diameter crucible. Little difference in the computed concentration profiles is visible. The experiment conditions are 1000°C for one hour. The diffusion coefficient was 2.8x10⁻⁸ m²/s

The samples processed with the silicon at the bottom of the melt exhibited a drastically different result. In the cases of a ten minute and thirty minute experiment times, the silicon source material is completely dissolved. This is dissolution of 5mm of silicon. As can be seen in figure 3, no silicon is visible in the sample with the silicon dissolving from the bottom while most of the seed remains when the silicon is dissolving from the top. This is dramatically faster transport than what was seen in the opposite orientation of the dissolution interface. This highlights the significant effect of gravity (convection) on the dissolution process.
Figure 3. On the left is a sample processed with the silicon dissolving from the bottom. There is no silicon source material left. The needle structure apparent over the cross section is indicative of the presence of silicon in the material. The sample on the right is the top of a sample processed at 1100°C with the silicon dissolving from the top. The darker material is the left over silicon source material. A small amount of the needle structure is apparent around the dissolution interface.

In previous results, a difference in transport rates between orientations was observed similar to that seen here but not as dramatic [10-11]. A key difference in this set of experiments is that the ratio of germanium to silicon was increased. Therefore from the previous work, the dissolution of silicon from the bottom of the melt was limited by the saturation of the germanium melt with silicon. The rate at which silicon dissolves in this configuration seems limited only by the saturation level of the melt. Enough silicon is used in the experiment to fully saturate the melt. The approximate composition of the melt at saturation at 1000°C is 18% silicon by mole. As the melt approaches this threshold, the transport away from the dissolution interface will slow and therefore the dissolution rate will slow.

The longer column of germanium was used so that useful composition information could be later extracted to directly estimate the diffusion coefficient. However, due to the low concentration of silicon present in the melt there is significant expansion of the melt during solidification. The presence of silicon in the melt reduces the amount the melt expands on solidification. Due to this expansion during quenching, the melt column is significantly disturbed by cracking and leaking. This unfortunately makes it impossible to reliably correlate the position in the column to a composition. The use of shear cell would seem necessary to extract this type of information accurately.
4. Conclusions
Dissolving silicon into a germanium melt in an 8mm crucible resulted in a more diffusion dominated process than previously observed. However, we were unable to observe any temperature dependence of the dissolution height. This indicates that the dissolution rate and therefore the diffusion coefficient are not significantly affected by temperature over the range of temperatures examined here. In addition, it was noted that the flow structure with the silicon dissolving from the bottom is extremely strong leading to extremely fast dissolution when compared to the opposite orientation.

5. References
[1] Kasper E 1995 J. Crystal Growth 150 921
[2] Seidenberg P 1997 Facets: New perspectives on the history of semiconductors ed A Goldstein and W Aspray (New Brunswick:IEEE Press) pp 36
[3] Usami N, Kitamura M, Obara K, Nose Y, Shishido T and Nakajima K 2005 J. Crystal Growth 284 57
[4] Schuppen A and Dietrich H 1995 J. Crystal Growth 157 207
[5] Yonenaga I 2005 J. Crystal Growth 275 91
[6] Volz M P, Schweizer M, Kaiser N, Cobb S D, Vujisic L, Motakef S and Szofran F G 2002 J. Crystal Growth 237 1844
[7] Volz M P, Walker J S, Schweizer M, Cobb S D, Szofran F R, 2005 J. Crystal Growth 282 305
[8] Yildiz M, Dost S and Lent B 2005 J. Crystal Growth 280 151
[9] Yildiz M and Dost S 2005 Int. J. Engng. Sci. 43 1059
[10] Armour N, Dost S and Lent B 2007 J. Crystal Growth 299 227
[11] Armour N and Dost S 2007 J. Crystal Growth 306 200

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