Alloy Phase Diagrams for III-P Semiconductor Crystal Growth

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ABSTRACT

Bulk crystals of III-V ternary and quaternary semiconductors with tunable band gaps and lattice constants are attractive for numerous electronic and optoelectronic applications. In particular, the ternary $Ga_xIn_{1-x}P$ has a band gap range of 1.351 - 2.261 eV, which corresponds to wavelengths in the near infrared to green range of the electromagnetic spectrum, and lattice constant ranging of 5.4512 - 5.8688 Å. This makes it attractive for applications such as a high energy junction in multi-junction photovoltaics, terahetrtz emission, and as a substrate for yellow, amber, orange, and red AlGaInP LEDs.

However, bulk growth of $Ga_xIn_{1-x}P$ ternary III-V semiconductor crystals using elemental Ga-In-P melts or pseudo-binary GaP-InP melts is significantly challenging due to the high vapor pressure of phosphorus at the typical growth temperatures, the large variation in the lattice constant of the constituent binaries, and the slow growth rates necessary in order to avoid the formation of cracks, dislocations, and multiphase inhomogeneities. Lowering the growth temperature is desirable such that the vapor pressure of phosphorus can be more easily managed. Low growth temperatures can be achieved by using gallium or indium rich solutions, as is currently used for liquid phase epitaxy. However, this approach is less attractive for growing bulk crystals due to numerous experimental difficulties such as high segregation of gallium in indium as well as sticking of the growth solution to the crucible wall and to the grown crystal, making crystal extraction without causing damage challenging.

The objective of this research is to establish the conditions required for the growth of uniform composition bulk crystals of $Ga_xIn_{1-x}P$ at any desired composition from a stoichiometric $Ga_xIn_{1-x}P_ySb_{1-y}$ quaternary melt, as well as conditions for compositional grading from a binary III-V material seed. Due to large number of conditions of melt composition and temperature that are possible, trial and error experimentation to determine said condition would be time consuming and costly. To reduce the amount of experimentation that must be done equilibrium phase diagram are constructed using the CALPHAD method. Calculations are performed using Gibbs free energy minimization software commercially available from Thermo-Calc Software, Inc., and databases containing thermochemical data on binary III-V material systems. Diagrams were calculated for temperatures between 530 °C and 1475 °C, thus providing coverage of the entire temperature range where both a segregated liquid and solid phase exist and liquid phase

solution growth is possible. Data from these phase diagrams were used to establish conditions of temperature and melt composition for growth of any solid composition of $Ga_xIn1\text{-}xP$, as well as theoretical Scheil solidification profiles for various starting charge compositions. Additionally, equilibrium phase data was used to create models for rates at which the depleted phosphide components (GaP and InP) must be replenished in the melt solution in order to grow bulk crystals of uniform axial compositions. It was also determined from the Scheil solidification curves that it is theoretically possible for self-grading of the solid composition to occur followed by growth of a solid with uniform axial composition simply by cooling a system with sufficiently high atom fractions of phosphorus and sufficiently low atom fractions of gallium.

Experiments were carried out to test conditions for growth given by the phase diagrams, as well as validate the Scheil solidification profiles and the possibility of compositional grading to high-GaP compositions through feed of GaP. Growth of different $Ga_xIn_{1-x}P$ compositions from this melt and compositional grading toward high-GaP compositions was demonstrated to feasible. In addition, the extent of the solubility of GaP and InP as well as their low diffusion rates in InSb was demonstrated. Finally, high sensitivity of the solid composition to small changes in the melt composition was demonstrated for conditions where the atom fraction of gallium was higher than that of phosphorus in melt, with the effect increasing the further the growth temperature was below the equilibrium melting temperature of InP.