Investigation of "Contactless" Crystal Growth by Physical Vapor Transport

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The subject of the research is to investigate the process of crystal growth by Physical Vapor Transport (PVT) of binary and ternary/doped II-VI and IV-VI materials. Two specific crystal growth configurations are the focus of the investigation. The first configuration, the so called 'contactless' growth technique, allows for growing large crystals without contact with the side walls of the ampoule. The second ampoule geometry uses different thermal screens to control the shape of the crystal-vapor interface. Another feature of the latter design is an application of silica frits used to accomplish a given growth rate under the same thermal conditions but different pressure inside the ampoule.

'Contactless' PVT technique limits the contact of the crystal to the seed/pedestal part of the system by maintaining a narrow, free space between the crystal and the side wall of the ampoule. Such growth conditions reduce the major source of strains which form in the crystals during post-growth cool-down as a result of sticking of the crystal to the ampoule wall, combined with a difference in thermal expansion coefficients of the two materials. A contact of the growing crystal with the ampoule wall may also contribute to a formation of defects during growth. As shown by the results of Dr. Larson's experiments on directional solidification of cadmium-zinc telluride in microgravity (the First United States Microgravity Laboratory (USML-1) mission), the above factors may be critical for a formation of dislocations and stacking faults in the crystals. 'Contactless' technique allows for studying the gravity-dependent phenomena (convection in the vapor phase, weight of the crystal) without interfering effect of the ampoule wall on the growth and post-growth processes.

The second configuration of the PVT systems was designed to achieve crystal growth with a flat crystal-vapor interface. Different thermal properties of the crystal and the ampoule materials, as well as an inherent (in growth ampoules) non-uniform exposure of different parts of the system to the external thermal field lead to development of non-planar interfaces between the crystal/source and the vapor phase. This phenomenon makes the geometry of the vapor phase in the ampoule different from a simple, cylindrical shape of the enclosure. The more complex the geometry of the vapor phase volume, the more complex is the mass flow in the ampoule. Thus, a potential gravity-dependent convective motion of the fluid is complicated by geometry-generated, gravity-independent mass flow contributions. Under these conditions, a meaningful interpretation of some experimental results, particularly of gravity-dependent convective contributions, may become difficult or even impossible. By an appropriate design of the growth ampoule, particularly by using thermal screens, the temperature field inside the system may be modified and the shape of the crystal-vapor interface maintained flat for a required period of time. The shape of the opposite end of the vapor phase cavity can be controlled by using a glass frit. Additional function of the frit is to modify (reduce) the growth rate in the system. In particular, the frit can adjust the growth rate such that, under identical thermal conditions, the same average growth rate can be achieved for different total pressure conditions. This would allow the most direct comparison of the effect of the Grashof number (by a change in the gas density) on convective phenomena.

Our research program includes: (1) numerical modeling of mass flow processes in the above described growth ampoule configurations; (2) thermochemical modeling and experimental studies on mass transport of ternary IV-VI compounds (which are our candidate materials for the investigated growth systems); (3) studies on the optimum preparation of the source materials with respect to their stoichiometry and generation of residual gases under actual growth conditions; and, (4) growth and characterization of the crystals obtained using the above described growth configurations.

Numerical modeling of the growth systems was based on commercial CFD-ACE code developed by Computational Fluid Dynamics Research Corporation. Modeling of thermal field in 'contactless' configuration was done, and the effect of the ampoule geometry, material thermal properties, crystal length, and furnace temperature profile on the growth conditions was assessed. In particular, it was found that, for CdTe and PbTe, both narrow and wide ampoules facilitate parasitic nucleation, leading to termination of 'contactless' growth conditions; the best results may be expected for ampoules of about 25 mm in diameter.

A thermochemical model of the mass transport in Pb(Te, Se) PVT system has been developed. Both lead telluride and lead selenide vaporize congruently and therefore, unlike in case of II-VI compounds, an excess of either of the constituent elements practically does not affect the composition of the deposited material. Relatively small differences in equilibrium partial pressures of PbTe and PbSe may lead to only small compositional non-uniformity of the grown crystals. Experimental results confirm these predictions. It was also found that uniform composition of the crystals can be accomplished by using a compact solid instead of a powdered source.

The growth rate was found to be diffusion limited and dependent on the material preparation procedures. High reproducibility of the vapor stoichiometry can be achieved by using a small (a few milligrams) excess of lead in the source region. Lead has a relatively low equilibrium pressure and, thus, has a limited effect on the mass transport conditions. However, even a small excess of chalcogenide that may be present in the source may drastically reduce mass transport rate in the system. Excess lead acts as a getter for those chalcogenide species.

The main factor which may limit mass transport and crystal growth in our systems is a presence of residual gases in the ampoule. The gases can evolve from the ampoule itself, or can be generated from the residual impurities in the source material. We have done extensive studies on the subject. The amount and composition of the gases evolved from silica glass and their dependence on the heat treatment conditions have been determined. The gases present in crystal growth ampoules have also been investigated. It was found that the major component of the gas released from the most commonly used brands of fused silica glass is hydrogen. The gas generated by the source material is usually dominated by carbon oxides, apparently formed from residual amounts of oxides and graphite in the system. Relatively large amounts of oxide impurities are reflected in the presence of carbon dioxide and/or water in the residual gas, and can serve as a test of the material purity. With a proper chemical and thermal treatment of the source material the amount of residual gases can be significantly reduced and the crystal growth rate considerably increased.

A number of experiments on growth of CdTe and (Cd,Zn)Te single crystals in 'contactless' growth configuration have been performed. It was found that both compositional non-uniformity as well as a contact with fused silica surfaces introduce strains in the crystals. The cooling rate was found to have a distinct effect on a distribution of dislocations in the grown material.