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Vapor Crystal Growth and Characterization

ZnSe and Related II–VI Compound
Semiconductors

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For Wen-Jer Yu and Yuk Yin

Preface

With a simple processing setup, the crystal growth of physical vapor transport (PVT) transforms the original starting source material into the final form of crystal inside a closed ampoule. The vapor species are transported from the source at one end of the ampoule to form the crystal at the other end. The driving force for the transport is the pressure gradient between the source and the crystal ends created by an imposed temperature difference. Hence, the PVT process can be treated as three processes occurring in series:

- (1) The corresponding vapor species sublime from the source material at higher temperature,
- (2) The vapor species transport through the vapor phase to the crystal site at lower temperature, and
- (3) The condensation of vapor species on the crystal surface for its growth.

Besides its simplicity, crystallization by PVT has several advantages over the conventional melt growth. These advantages result mostly from (1) the lower processing temperatures, (2) the purification process associated with PVT, and (3) the improved surface morphology of the grown crystals. The high melting temperatures of the wide bandgap materials make the melt growth process very difficult to handle. For instance, in the Si–C binary system, the SiC compound melts at 2830 °C into Si-rich liquid and C solid, i.e., there is not even a stoichiometric melt of SiC to conduct melt growth at this extremely hot environment. The PVT process enables crystal growth at unique and advantageous environments than the melt growth would allow. The PVT process also acts as a purification process because of the differences in the vapor pressures of the native elements and the impurities. Additionally, most solid–vapor interfaces exhibit higher interfacial morphological stability during growth because of their low atomic roughness.

On the other hand, the main disadvantage of vapor growth techniques, compared to other growth techniques, is that the growth rates are low and inconsistent and the grown crystals are small with variable single crystal yields. To achieve a reasonable growth rate, an intrinsic requirement for the PVT process of multielements compounds is that the partial pressure of each element needs to be comparable to each

other and at least above the level of 10^{-4} atm under the growth conditions. This requirement excludes the possible PVT growth of III–V compounds because the equilibrium partial pressures of group III are usually orders of magnitude lower than those of the group V elements. It also excludes the PVT growth of any II–VI compounds consisting of oxygen and mercury due to their high pressures.

In this book, the PVT process will be focused on ZnSe-based materials, such as ZnSe, Cr- and Fe-doped ZnSe and ZnSeTe, as well as other wide bandgap II–VI compounds, such as CdTe, CdS, and ZnTe. The contents of the book are intended for the professional crystal growers, either academic researchers or commercial operators, by providing the details of the operating procedures and the theoretical bases behind them. After a short Introduction, Chap. 2 will present the fundamentals of PVT process, including partial pressure measurements and one-dimensional diffusion model for the transport of vapor species. The experimental measurements of the vapor transport rate, i.e., mass flux, as well as the heat treatments of the starting materials to maximize the mass flux for various material systems will be discussed in Chap. 3. The detailed crystal growth procedures and in situ real-time optical monitoring techniques will be given in Chap. 4. Chapters 5 and 6 will present the results of various characterization techniques, including morphology of the grown crystals, structural crystalline quality, impurity distribution, dopant levels, and optical properties. The measured results of thermal and electrical properties and the effects of post-growth annealing will be included in Chap. 7. The formulation and calculated results from two-dimensional and three-dimensional numerical simulation on the vapor transport process of ZnSe will be presented in Chap. 8.

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