

Geometrical aspects of solid solution separation by evaporation-condensation driven in a closed system by a small temperature difference

A. Szczerbakow*

Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, pl-02-668 Warszawa, Poland

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Evaporation-condensation driven in a closed system by a small temperature difference has demonstrated its ability to deliver semiconducting IV-VI and II-VI solid solution crystals of highest compositional uniformity. Geometrical aspects of solution component distribution emerging in the crystals grown in the near equilibrium evaporation/condensation systems are considered in this paper. The conclusion is drawn that no increase in the range of compositional variations with increase in the crystal size is to be anticipated.

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1 Introduction

The process of self-selecting vapour growth (SSVG) is marked by the ability to produce high quality monocrystals of semiconducting solid solutions belonging to the IV-VI and II-VI types. The structural quality achieved in SSVG depends especially on the specific control of the temperature field in the growth furnaces [1], while the uniform distribution of solution components is due to the almost isothermal character of the growth ampoule. Although a high level of uniformity was achieved for numerous solid solution systems, the question emerges, whether the compositional uniformity can be maintained at the crystal sizes above 15 mm, and whether the efforts to construct apparatus for the SSVG-type growth of essentially larger crystals are justified. The experimentally confirmed uniformity of the solid solution crystals remaining below 15 mm in size does not seem to cause doubts.

2 Interpretation of the separation effects

In the cases of small temperature differences, separation of a uniform solid solution in a closed system has essentially different character from that observed in the simple, “differential” distillation, where large temperature differences are employed. It should be recalled that the separation effect in the simple distillation originates from practically equilibrium composition of the vapours above the source liquid solution (owing to fast mixing in the liquid) with rapid condensation of these vapours. In the almost isothermal process of crystal growth, the relations are different. The process is marked by a high degree of reversibility in the closed space, and the mass transport is strongly influenced by the tendency to maximise the entropy by the creation of uniform solution, while the only thermodynamic force able to cause compositional variations is generated by

* Corresponding author: e-mail: szczzer@ifpan.edu.pl

the temperature difference of a few degrees – required to achieve satisfactory crystal growth rates. The second law of thermodynamics leads to the simple conclusion that under fully isothermal conditions no spontaneous separation of a solution (including a solid one) occurs, while the maximum separation caused by an "almost negligible" temperature difference was the subject of theoretical estimation [2]. Nevertheless, the above statements do not provide sufficient basis for conclusions concerning the geometrical distribution of solution components.

Characteristics of the effects determining the near equilibrium evaporation-condensation procedure should be preceded by description of the separation types, for which non-equilibrium conditions of large temperature differences are deliberately employed. Under these conditions, unidirectional vapour flows from the evaporation zone to the condensation zone determine the process. In the case of negligible mixing in the source, the so-called "flash evaporation" takes place, where the vapour composition is the same, as the composition of the evaporated solid solution. As a consequence, congruent evaporation as well as congruent mass transport are imposed by extremely non-equilibrium conditions, while the condensation can be performed in a smaller distance from reversibility (with small temperature gradients in the condensation zone) to cause "geometrical fractionation", where the fractions are continuously collected in the sections of different temperatures. This is principally different from "fractionation in time" – typical for the simple distillation of liquids, where the fractions are subsequently collected in the same cooler. In respect of the constant compositions of the mass currents, as well as of the "geometrical fractionation", some analogy for the case of negligible mixing in the solid source can be found in the continuous, "integral" distillation of liquids. More complex effects emerge, when efficient mixing in the source takes place – for instance owing to the local mass currents of recrystallisation via the vapour phase. Mixing in the source material is unavoidably accompanied by enrichment of the vapours transported to the condensation zone with the more volatile component; consequently, enrichment of the source with the less volatile component progresses, and this leads to variability in the vapour composition. One can observe that the growing mixing efficiency in the solid source brings the character of mass transport closer to that typical for simple, "differential" distillation of liquids. If rapid cooling is applied, the compositional variations of the vapours during the process are "frozen" in the condensed solid in the form of variations along the path of condensation front.

In the case of a closed, near isothermal evaporation-condensation system, similar reversibility of the solid-vapour transitions and also comparable mixing efficiency in the solid phase can be assumed for the whole process space. To describe a real system, two extreme models should be separately considered: of fast mixing and of negligible mixing in the solid phase. For very efficient mixing, the problem of non-uniformity disappears, since then the solution components become uniformly distributed after completion of the material transport. Negligible mixing causes more complex character of the system and an analogy for it – also in the mathematical description – can be found in the single-pass zone melting performed with a short molten zone [3]. In the latter case, the molten zone achieves the status of compositional equilibrium with the solid phase at the very beginning of the process; next the compositional variations in the middle period remain negligible. The content of the molten zone, which is enriched with the component that lowers the melting point, crystallises at the end. The single-pass zone melting results in distinct compositional changes limited to the end fragments of the produced bar, while the sizes of the areas with changed compositions are growing functions of the molten zone size. Then, the composition of the starting solid solution is reproduced to a high degree in the main part of the bar and this is practically independent from its length. In a closed sublimation-condensation system, capacity of the vapour phase is incomparably smaller, than that of any molten zone; thus the areas of changed compositions can be estimated small enough to be diffused during the main period of the process. Even at the beginning and at the end of the procedure, the compositional differences between the front surfaces of the evaporated material and that condensed obey the limits determined by small temperature differences [2] – whatever the mixing intensity in the solid. It should be added for completeness, that under the conditions of small supersaturation, energetical barriers of the phase transitions solid-vapour and vapour-solid may cause a very small separation effect of different kind, where slight enrichment of the condensing material with the less volatile solution component is not excluded [4].

3 Conclusion

A practical evaporation-condensation system can be considered as an intermediate form between the cases of slow and fast mixing in both the source and the product, where each case is marked by very small, final separation effect. Enrichment of the first portion of the deposited material with the more volatile component is probable, but the final effect can be expected to be negligible. However, if the “vapour transport resistance” becomes insignificant for the process, and the phase transition barrier dominates, very small enrichment of the initially condensing material with the less volatile component may occur. No premise appears to anticipate increase of compositional differences in a closed, near isothermal evaporation-condensation system of crystal growth as a result of growing sizes of the produced crystals. On the contrary, limited differences extended along larger sizes can be expected to lead to smaller compositional gradients.

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