CONVECTIVE AND MORPHOLOGICAL INSTABILITY IN VAPOR CRYSTAL GROWTH †

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ABSTRACT

Theoretical and experimental work on the fluid dynamics of physical vapor transport is reported. It is shown that diffusion in viscous interaction with container walls leads to concentration gradients normal to the main transport direction. Consequently any convection threshold is removed. This coupling with convective instabilities makes the theoretical interpretation of earthbound (anisotropic) morphological stability studies on vapor-solid interfaces intractable. Hence low-gravity experiments are suggested that will allow for the establishment of morphological stability criteria under diffusion controlled conditions.

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INTRODUCTION

Crystallization from vapors has gained ever increasing importance in materials preparation and solid state device production. Vapor-to-solid processes have various advantages [1] over, say, crystallization from melts. These advantages result mostly from (i) the lower temperatures involved, and (ii) the fact that vapor-solid interfaces, due to their low atomic roughness [2] exhibit considerable morphological (i.e. interfacial shape) stability during growth.

Most solid state devices utilize extensive properties of solids, i.e. properties that have been obtained through the introduction of impurities ("dopants") into the solid, typically during its growth. The performance of devices depends often strongly on the compositional homogeneity and structural perfection of the solid. These, in turn, depend to a large extent upon the mass and heat transfer conditions in the vicinity of the solid-nutrient (vapor) interface during growth. Steady non-uniform, and in particular nonsteady transport [3-5] can result in inhomogeneities that severely limit device performance. Hence a quantitative understanding of the transport mechanisms that prevail in vapor-solid processes under physical and chemical conditions relevant to materials preparation is of great technological importance.

The transport conditions that are characteristic for vapor crystal growth and, hence, the required transport models are unusually complex. The presence of numerous chemical species demands multicomponent concentration diffusion treatments. Displacement flows ("streaming") due to changes in the number of vapor molecules during interfacial reactions must be accounted for. The steep temperature and concentration gradients often employed lead readily to nonsteady, oscillatory convective phenomena. Further complications arise in various semiconductor production processes where vapor (gas) mixtures of components with strongly differing molecular weight are used. Then thermal (Soret) diffusion must be taken into account. Radiative heat transfer is often significant or even dominant. These complex conditions are further aggravated by the complicated geometries and boundary conditions encountered in practice--conditions which have typically not been considered yet in the fluid dynamics literature. Consequently, with a few exceptions, the current understanding of the transport that prevails in crystal growth from vapors is rather limited and mostly of a qualitative nature.

In order to obtain guidance for advantageous design and control of (vapor-solid) crystal growth processes, three (coupled) questions must be addressed; viz,

(1) What are the critical (boundary) conditions that lead to time dependent (oscillatory, "turbulent") heat and mass transport?,

(2) To what extent does the uniformity of (steady) transport depend on practical boundary conditions?,

(3) What limits the stability of a certain interfacial shape, i.e., how fast can a crystal be grown without developing morphological instabilities--which, in turn, lead to inhomogeneities in the solid even if the transport in the bulk nutrient were steady and uniform--? This question is of particular importance in vapor crystal growth where one encounters often very low growth rates.

The author and his co-workers have begun experimental and theoretical investigations on various simplified model configurations towards the clarification of the first two questions. For a review of these efforts see [1].

In the following we will outline some selected results. Then we will briefly discuss the current state of understanding of morphological stability in vapor growth and point out the necessity for further work in these areas. The selection of topics is oriented on the great potential of a low-gravity environment for the clarification of these fundamentally and practically important questions.

DIFFUSIVE-CONVECTIVE TRANSPORT

To date most analyses of transport in closed tube systems have not accounted for the viscous fluid dynamics of the transport flows. One of the reasons is that at the typical flow velocities (Reynolds numbers) neither creeping flow nor boundary layer approximations can yield significant insight. Existing treatments of diffusion-governed mass transport in closed vapor growth systems are exclusively formulated as one-dimensional problems (see summary in [1]).

In order to investigate the effect of viscous interaction of the transport flows with the container walls we have numerically modeled the physical vapor transport of a component A through an inert gas B in vertical cylindrical ampoules. The full fluid dynamic treatment [6-8] shows that the "no-slip condition" (mass average velocity zero on walls) has considerable consequences:

(1) In constrast to the one-dimensional treatments, where the inert component B is considered stagnant, B is found to recirculate even in the absence of gravity.

(2) The mere diffusive-advective mass flux (zero gravity) is accompanied by radial concentration gradients. Due to viscous interactions, component A is transported with some preference in the core region, whereas B tends to accumulate at larger radii.

(3) Convection (buoyancy-driven) fluid motion occurs without threshold due to gravitational interaction with the diffusion-induced (horizontal) density gradients (a new insight into the convective stability of multi-component fluid columns).

Another result that is relevant here stems from our experimental studies of convective instabilities in closed vertical cylinders [9,10]. Measurements of the critical Rayleigh numbers for the onset of various convection modes showed that thermal (Soret) diffusion, in contrast to widespread belief, can play a decisive role in the transport of vapors in ampoules. Drastic convective destabilization and, hence, changes in the concentration distribution was observed in binary gas mixtures.

MORPHOLOGICAL STABILITY

The morphological stability of a growing cyrstal depends on the growth mechanism which in turn is a consequence of the atomic structure of the interface. Rather isotropic growth, i.e., adjustment of the interface to the geometry of the mass and heat transfer field will occur when the interface is atomically rough [2] as in many melt growth systems. Isotropic (one-dimensional) morphological stability theory [11-13] predicts the critical concentration and temperature gradients, normal to a planar interface at which (in practice always present) shape perturbations can grow. Under subcritical conditions all (small amplitude) perturbations in the interface shape decay and the original planar form is restored. Interfacial breakdown conditions and spatial periodicity of perturbation features observed in crystal growth from melts support isotropic morphological stability rather well. One should mention, however, that few experiments have yet been characterized sufficiently to allow for an evaluation of the "fine-structure" of the various theoretical models. Most recently it has been recognized that in certain parameter regimes there is a strong coupling between morphological and fluid dynamics instabilities [14]. Convective instability (from melt density gradients close to the interface, dominantly due to solute rejection) may considerably lower the critical growth rate predicted from merely diffussive transport.

Solid-vapor interfaces, due to their low atomic roughness, grow dominantly by (anisotropic) layer spreading. Adatoms have to diffuse on the average over distances of many lattice constants before they become incorporated into the lattice. Macroscopically this is reflected in the occurance of facets. Faceted growth is considerably less responsive to the mass and heat transfer geometry in the fluid than isotropic growth.

In spite of the pronounced kinetics anisotropy, efforts were made to describe morphological stability in vapor growth, in analogy to melt growth, with an isotropic model [15,16]. This constitutional supersaturation concept (CSS) has been employed in various theoretical papers on vapor crystal growth [17,18,19]. However, the only experiment that seemed to verify CSS quantitatively [16] was shown by our group to be in error by one order of magnitude [20]. Other experiments [17,18] agreed with CSS only to within a factor of 2-3. Vapor solid interfaces, are generally found to be more stable than the isotropic CSS predicts.

Anisotropic morphological stability theory [21-23] has been advanced to a point where interfacial breakdown can be predicted in (faceted) solution and vapor growth if (i) certain interfacial kinetics parameters are known and (ii) transport is diffusive from a <u>homogeneous bulk nutrient</u>. The predicted trends [21-23] are well confirmed experimentally. There are, however, no adequately characterized (vapor) growth experiments that allow for a quantitative comparison with anisotropic morphological stability theory.

SUGGESTED WORK IN LOW-GRAVITY ENVIRONMENT

Much more work on transport dynamics and morphological stability is needed for a better understanding of vapor crystal growth. Much of this work can be performed under 1-g conditions. The investigative possibilities on earth are still far from being fully exploited. However, a low gravity environment offers fascinating possibilities which, even when taking the drastically higher research costs into account, would result in considerable higher efficiency in accquiring the badly needed insights.

In particular, earthbound vapor-solid morphological stability studies that can be theoretically evaluated will be impractical in the foreseeable future. The anisotropic interface kinetics complicates the problem to an extent where externally imposed temperature and concentration gradients parallel to the interface make a theoretical description mathematically intractable. Meaningful morphological stability studies require relatively large dimensions of the interface (centimeters) in order to observe theoretically expected periodicities in the developing instabilities. Hence, in order to avoid signficiant diffusion-induced gradients normal to the main transport direction (i.e., radially in an ampoule) walls must be widely spaced from the growing interface. This, however leads to convectively unstable ampoule dimensions and pronounced convection-induced concentration non-uniformities in the (bulk) vapor.

Therefore it is proposed that morphological stability experiments on optimally chosen vapor-solid interfaces (with and without Soret diffusion) be conducted in the Fluid Experiment System. As a "fringe benefit" of these investigations some clarification could be obtained on the concentration profiles which, as our modeling suggests, are introduced by mere diffusion in viscous interaction with container walls, a topic of great general fluid dynamic interest.

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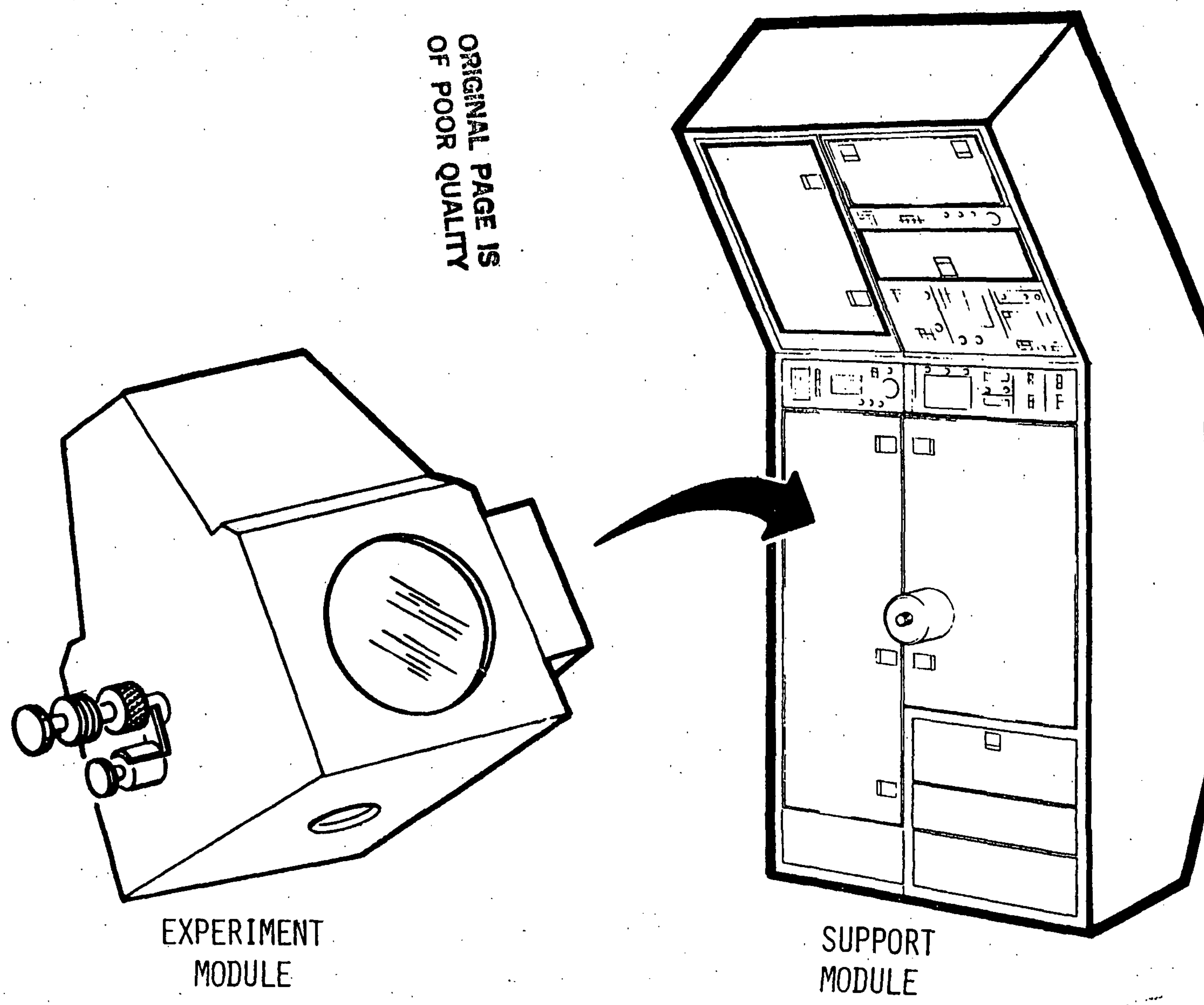

Figure 1. Experiment Module and Support Module Exteriors for FES
(Cell is representative of the Lal Radial Growth Experiment)