SUMMARY REPORT

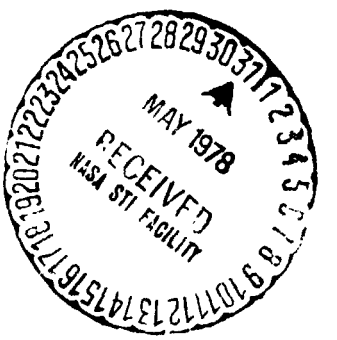
for the Period

April 1977 - March 1978

GROWTH OF SINGLE CRYSTALS BY VAPOR TRANSPORT IN ZERO-GRAVITY ENVIRONMENT (GROUND-BASED EXPERIMENTS)

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NUMBER NAS8-26146



by

Heribert Wiedemeier

Professor of Physical Chemistry

Rensselaer Polytechnic Institute

Troy, New York

April 1978

(NASA-CR-150680) GROWTH OF SINGLE CRYSTALS BY VAPOR TRANSPORT IN ZERO-GRAVITY ENVIRONMENT, GROUND-BASED EXPERIMENTS Summary Report, Apr. 1977 - Mar. 1978 (Rensselaer Polytechnic Inst., Troy, N. Y.) G3/12

N78-23116

Unclas 16708

NASA Contract
NAS8-26146

I. INTRODUCTION

The research performed under this contract is concerned with the investigation of mass and heat transfer phenomena associated with the growth of single crystals by chemical vapor transport reactions. In this technique, a gaseous transport agent reacts with the solid source material to form exclusively gaseous products. The gas phase species migrate from the source to the condensation zone of the closed reaction ampoule where the reverse reaction occurs with formation of single crystals. The necessary concentration gradient is achieved by means of a temperature gradient.

The materials presently under investigation include IV-VI and related compounds with interesting structural and electronic properties. The choice of these systems for ground-based transport studies is twofold. Firstly, their crystallographic structures and thermodynamic-kinetic properties cover a wide range. Secondly, developments in the area of device oriented applications indicate the potential use of these systems, in particular as components in alloy-type semiconductors. Systematic studies of these materials will establish the feasibility of different classes of electronic materials for crystal growth from the vapor phase on earth and in space.

The results of our Skylab and ASTP experiments on binary and mixed Ge-chalcogenides demonstrated distinctly improved crystal quality and considerably greater mass transport rates in micro-gravity than expected for a diffusion controlled vapor transport process. These observations have focused increasing attention in our laboratory on the continued

investigation of the thermodynamic properties of solid-gas phase reactions and their effects on mass transport. The results of simultaneous fluid-dynamic studies on the systems employed for the Skylab and ASTP experiments will be reported separately. The present report is concerned with the investigation of "forward" and "reverse" transport phenomena in the SnS_2-SnI_4-iodine system.

The combined effort will lead to a conclusive interpretation of previous space experiments and will produce fundamental data which are important for the design and evaluation of future vapor phase crystal growth studies in micro-gravity environment.

II. SUMMARY OF RECENT PROGRESS

In order to investigate gas phase transport phenomena based on diffusive and/or convective flow, the composition of the gas phase in terms of species and their partial pressures must be accurately known. This applies to the interpretation of experimental mass transport data as well as to the evaluation of fluid-dynamic properties. In connection with transport studies on the SnS_2-SnI_4-iodine system, it was observed that SnS_2 can be transported in the forward (high to low temperature) and reverse (low to high temperature) direction. The existence of both transport modes has a significant effect on gas motion and, thus, on the observed net transport rates. This situation is even more complicated by the fact that SnS_2 may undergo decomposition depending upon the experimental parameters of the transport experiments. This report is concerned with studies to predict the net mass transport direction in

a multi-component, multi-reaction system. This is based on quantitative Knudsen-type vaporization studies, on mass transport experiments and on detailed thermodynamic calculations of gas phase compositions.

II.1. Vaporization Properties of SnS_2

Before reliable transport experiments could be performed, the stability range of SnS_2 had to be established. Based on mass spectrometric studies. SnS_2 decomposes measurably at temperatures above about 350°C according to the reaction

$$2\ SnS_2(s) = Sn_2S_3(s) + \tfrac{1}{2}\ S_2(g)\ . \qquad (1)$$

Higher molecular species were below the detection limits of the instrument. Quantitative Knudsen-type mass-loss measurements employing automatic vacuum micro-balance techniques in the temperature range 350° - 500°C yielded absolute partial pressures of S_2 for reaction (1) to be in the range 10^{-7} - 10^{-4} atm.

Similar mass spectrometric and micro-balance mass-loss measurements established the decomposition and absolute partial pressures for Sn_2S_3 according to the reaction

$$Sn_2S_3(s) = 2\ SnS(s) + \tfrac{1}{2}\ S_2(g)\ . \qquad (2)$$

In the temperature interval 400°C - 525°C, the partial pressures of S_2 range from about 5×10^{-7} to 10^{-4} atm.

The final decomposition product sublimes congruently according to the reaction

$$SnS(s) = SnS(g) \quad . \qquad (3)$$

The absolute partial pressures of SnS(g) at temperatures between about 475° and 650°C are in the range 10^{-8} to 10^{-4} atm.

These studies also yielded values for the heats of formation and absolute entropies for $SnS_2(s)$, $Sn_2S_3(s)$ and SnS(s) to be used for thermodynamic calculations of the transport studies. In order to maintain stable SnS_2 as source material in the transport experiments, the S_2-partial pressures produced by the transport reactions must be greater than the equilibrium constant of reaction (1). Under these conditions, reaction (1) cannot occur and, consequently, reactions (2) and (3) are also suppressed. The minimum amount of SnI_4 or iodine required to yield partial pressure of S_2 equal to or greater than K_p of reaction (1) is based on thermodynamic calculations discussed below.

II.2. Mass Transport Rate Studies on SnS_2

Mass transport rate studies on SnS_2 were performed in three different temperature gradients employing SnI_4 and elemental iodine, respectively, as initial transport agents.

In the temperature interval 375° - 450°C and with SnI_4 added initially, SnS_2 is transported from high to low and from low to high temperature. At low pressures of SnI_4 ($\sim 10^{-4}$ atm) reverse transport predominates ($T_1 \rightarrow T_2$) and at higher pressures forward transport ($T_2 \rightarrow T_1$) occurs ($T_2 \leftarrow T_1$). Based on the predominant reaction

$$SnS_2(s) + SnI_4(g) = 2\ SnI_2(g) + S_2(g)\ , \qquad (4)$$

only the forward transport of this system is consistent with the endothermic nature (ΔH positive) of reaction (4). In the temperature gradients 525° → 450°C and 650° → 550°C, forward transport ($T_2 \rightarrow T_1$) is observed for all pressures of SnI_4. When elemental iodine is used as initial transport agent in the gradient 375° → 450°C, SnS_2 is transported from low to high temperature. These observations cannot be explained by the analogous reaction

$$SnS_2(s) + 2\ I_2(g) = SnI_4(g) + S_2(g)\ , \qquad (5)$$

whose ΔH predicts forward transport under these conditions. These discrepancies indicate the importance of other transport reactions and of higher molecular species. The results of the above experimental transport studies in terms of flux versus pressure are based on a large number of individual experiments for each temperature gradient covering pressure ranges between about 10^{-5} and 1.5 atm and yielded reproducible data within ± 15% error limits.

II.3. Thermodynamic Calculations and the Hypothetical Pressure P*

Detailed thermodynamic calculations for the temperature gradient 375° - 450°C for reactions (4) and (5) and for the dissociation of iodine and the association reactions of sulfur yielded partial pressures for the species SnI_4, SnI_2, I_2, I, S_2, S_5, S_6, S_7 and S_8. The concentration of other species is negligible. These calculations were performed for different total pressures ranging from 10^{-5} to 1 atm. The

relative importance of the various species is pressure dependent and confirms that reaction (4) is dominant at all pressures when SnI_4 is added initially. The observation of reverse transport at low pressures is due to kinetic limitations of reaction (4) and the simultaneous occurrence of other reactions. This is based on the pressure dependence of the ratio $P(I_2)/P(SnI_4)$ which is a maximum at low pressures and decreases with increasing total pressure. Thus, at very low pressures, the SnS_2-SnI_4 system behaves as if elemental iodine was added initially. With increasing SnI_4 pressure, kinetic limitations are reduced and the system transports as predicted by the thermodynamic properties of reaction (4). If reaction (5) is expressed in terms of the higher molecular sulfur species

$$SnS_2(s) + 2\ I_2(g) = SnI_4(g) + 2/i\ S_i(g)\ , \qquad (5')$$

where i = 5,6,7, or 8, the exothermic nature (ΔH negative) of reaction (5') is consistent with reverse transport when iodine is added initially. These calculations indicate that the higher molecular species are important for the net mass transport of sulfur.

In order to generalize the above observed forward and reverse transport phenomena for this system, the concept of the hypothetical pressure P* of SnS_2 is employed. In the absence of kinetic limitations, the net transport direction can be predicted based on the hypothetical pressure P* of SnS_2, defined as the "solubility" of SnS_2 in the gas phase as a result of transport reactions. This leads to the definition of ΔP^* given by the equation

$$\Delta P^* = P^*(SnS_2)_{T_2} - P^*(SnS_2)_{T_1} , \qquad (6)$$

where $T_2 > T_1$. The solubility of SnS_2 is represented by the sum of the sulfur partial pressures in terms of S_2 molecules,

$$P^*(SnS_2) = P(S_2) + 5/2\ P(S_5) + 3\ P(S_6) + 7/2\ P(S_7) + 4\ P(S_8). \qquad (7)$$

The partial pressures are calculated at T_2 and T_1 based on the above indicated reactions. The quantity ΔP^* is calculated for different temperature gradients as a function of total pressure of the system. When ΔP^* is positive, forward transport ($T_2 \rightarrow T_1$) is dominant. For negative values of ΔP^*, net reverse transport will occur. The presence of both forward and reverse transport implies the existence of an inversion temperature at which the "solubility" of the solid is a minimum. Calculations of ΔP^* as a function of pressure reveal that the inversion pressure (change in transport direction) occurs at higher total pressures with increasing temperature. These calculations are consistent with present observations and previous studies on the SnS_2-SnI_4-iodine system.

The combined experimental and theoretical studies demonstrate that the net transport direction of a multi-component multi-reaction system can be reliably predicted. This is based on a thorough experimental approach and quantitative thermodynamic computations. Since "reverse" transport phenomena are most likely more frequent than presently known, the above results are of basic scientific and of practical importance for the prediction of the transport direction and for the optimization of crystal growth conditions. The above studies are being prepared for publication.

NASA Contract
NAS8-26146

III. DIRECTION OF CONTINUED RESEARCH

The major directions of continued research on crystal growth by chemical vapor transport under this contract are as follows:

1. Further applications of thermodynamic aspects to generalize transport behavior and to predict the inversion temperature of systems.

2. Continued investigations of fluid-dynamic properties of transport systems, including temperature measurements inside ampoules and the effect of orientation with respect to the gravity vector on flux. (Progress in this area will be reported separately).

3. Continued growth rate studies to differentiate between the effects of gas motion (convection) and growth mechanism on crystal morphology. Correlation between growth rates and bonding for different crystallographic orientations.

The combined results of this research program are of practical importance for the space processing of single crystals of preselected orientation and growth velocity.

NASA Contract
NAS8-26146

STATEMENT OF FUNDING STATUS

A. Expenditures to Date:
03-09-78

1.	Personnel	
	Salaries and Wages (including overhead and fringe benefits)	$ 221,743.09
2.	Supplies and Expenses	21,498.40
3.	Special Equipment	8,033.11
4.	Travel	5,051.17
	TOTAL	$ 256,325.77

B. Funds Required for Completion:

Unexpended balance of budget

C. Problem Areas:

None