JOURNAL OF MATERIALS SCIENCE 25 (1990) 589–594

Residual gases in HgI_2 crystal growth ampoules

J. LASKOWSKI, M. OLĘDZKA, J. PRZYŁUSKI
Warsaw University of Technology, Institute of Inorganic Technology ul. Noakowskiego 3, PL-00664 Warszawa, Poland

Gases evolve in sealed borosilicate glass ampoules containing HgI_2, which influence the crystallization of HgI_2. It was found by mass spectroscopy that they are mainly H_2, H_2O, CH_4, CO, CO_2 and NO. The composition of gases depended on the mode of HgI_2 preparation. The amount of gases evolved covered the range $(2–12) \times 10^{-7}$ mol/g HgI_2. The HgI_2 vapour transport rate in ampoules containing different samples of mercuric iodide was measured. Other ampoules filled with HgI_2 were degassed and preheated in various ways which influenced the HgI_2 crystallization rate. On the basis of the experiments carried out a procedure was elaborated permitting a 35-fold increase of the HgI_2 vapour transport rate under identical thermal conditions.

1. Introduction

Gases present in sealed crystal growth containers and not introduced there purposely are called residual gases. They can originate from the walls of the ampoule, starting material for crystal growth or vacuum system atmosphere. Sometimes permeation of gases through the container's walls must be also considered [1].

Water vapour and carbon dioxide were evolved from glass baked in vacuo. The gas evolution reaches a maximum at about 570 K for borosilicate glass [1]. In [2–4] traces of water vapour were observed in sealed silica ampoules. Detailed studies were carried out by Murray *et al.* [5]. They observed the evolution first of all hydrogen from fused quartz ampoules and also of CO_2, CO, H_2O, N_2, O_2, SO_2, H_2S, CH_4 and other hydrocarbons. They measured the pressure of these gases, which equalled from 10^{-2} to 13 torr at room temperature (RT). Evolution of small amounts (10^{-2} torr) of nitrogen and hydrocarbons in borosilicate glass ampoules was also found by Murray *et al.* [5]. In glass made sodium lamps the residual pressure of hydrogen and water was 0.004–0.011 torr after sealing [6].

The presence of residual gases in the vapour crystal growth system is important since these gases:

1. influence the mechanism of vapour flow (eg. [7]);
2. decrease the rate of crystal growth (eg. [8, 9];
3. influence the morphology of crystals (eg. [10];
4. can change the properties of crystals (eg. [11].

The presence of residual gases during the growth of PbS crystals was observed in 1954 by Pizzarello [12]. Harman and McVittie [10] found the presence of CO and CO_2 in the amounts of 0.5–20 torr at RT in ampoules for the growth of $Pb_{1-x}Sn_xTe$ crystals. Carbon oxides were the products of chemical reactions between the impurities introduced to the system with the starting material. The content of residual gases affected the crystal habit, and their high pressure prevented the growth of large crystals. Russell and Woods [11] observed carbon oxides in quartz ampoules for CdS crystal growth up to 5 torr. CO reacted in the system and also CS_2 and COS were presented in the gaseous phase. The chemical reactions caused changes in stoichiometry and thus in electrical conductivity of CdS crystals. Mazelsky and Fox [13] found a relationship between the growth rate and quality of mercurous halides crystals and residual water vapour in the ampoule.

The presence of residual gases was not sufficiently studied during the crystallization of HgI_2. Omaly *et al.* [14] on the basis of the HgI_2 transport rate in a closed ampoule suggested the existence of $HgCl_2$, $HgBr_2$, Hg and I_2 in the gas phase. Recently Skinner *et al.* [15] reported the presence of NO_2 in ampoules for HgI_2 crystals growth. This gas prevented large HgI_2 crystals being obtained.

The existing growth procedure permits tetragonal HgI_2 monocrystals to be obtained of a mass of up to 1000 g. A decrease in the amount of residual gases in the ampoule shortens the time of growth, which is important especially for experiments in space. A control of the amount of residual gases is essential, since the overall pressure in the ampoule also affects the shape and morphology of the growth of α-HgI_2 crystals [16]. For example a pressure in the range of 2–10 torr favours the growth of platelets.

The presence of residual gases in ampoules for HgI_2 crystallization has been mentioned in our previous works [17, 18]. In the present work we determined the composition and amount of residual gases and also their influence on the rate of HgI_2 vapour transport in differently prepared ampoules. Experimental procedures are described in detail since they affect greatly the results obtained.

2. Experimental procedure

2.1. Starting materials

Mercuric iodide studied in this work was prepared by different procedures. All reagents were POCh Poland products of analytical purity.

0022–2461/90 \$03.00 + .12

Batch A. This material was obtained in aqueous solution from the reaction

$$Hg/NO_3/_2 + 2KI = HgI_2\downarrow + 2KNO_3 \quad (1)$$

Mercuric iodide after thorough washing with water was dried in the air at 330 K and then outgassed (2 h at 10^{-5} torr) and sublimed in a sealed glass ampoule at 490–420 K.

Batch B. The sample was obtained in aqueous solution

$$HgCl_2 + 2KI = HgI_2\downarrow + 2KCl \quad (2)$$

and then carefully washed with water. Drying in vacuo was followed by sublimation of this material in a sealed ampoule (490–420 K).

Batch C. The material was synthesized from mercury and iodine ($n_I : n_{Hg} = 2.2$). Mercury and iodine were placed in a glass ampoule, which was then evacuated, sealed and slowly heated up to 490 K. Excess iodine was sublimed off.

2.2. Preparation and sealing of the ampoules

Borosilicate glass (Sovirel France) made ampoules of 1.76 cm diameter and 17 cm length were used in this work. They were equipped with one or two "break-seals" (see Fig. 1a and b, respectively). The following procedure of ampoule cleaning was applied:

1. washing with HNO_3/24 h/, acetone and deionized water;

2. evacuation to 10^{-5} torr with thorough methane–oxygen flame degassing at about 600 K.

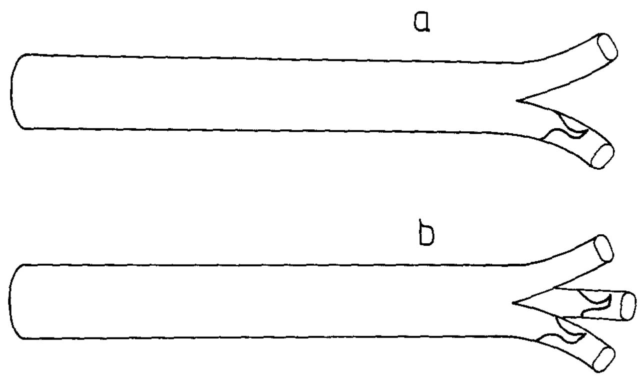

Figure 1 Ampoules used (d_{in} = 1.76 cm, l = 17 cm), (a) one break-seal; (b) two break-seals.

Mercuric iodide was introduced into the ampoule in a dry argon atmosphere. The ampoule was connected to a vacuum line/oil diffusion pump with liquid nitrogen trap/and evacuated up to the pressure of 10^{-5} torr. Then one of the following three procedures was applied:

1. the ampoule was degassed for 1–10 h, usually 2 h (designated by the letters EV in Table I);

2. the bottom part of the ampoule was heated (the furnace temperature was 470 K) and mercuric iodide condensed in the upper part of the ampoule (this is designated by VS in Table I);

3. the bottom part of the ampoule was heated in such a way, so as HgI_2 was deposited in the middle section of the ampoule. After sublimation of a whole charge, the process was repeated and HgI_2 condensed

TABLE I Treatment of the ampoules studied

Ampoule No.	Ampoule type (Fig. 1)	HgI_2 used (see sections 2.1)	Mass of HgI_2 (g)	Ampoule treatment (see sections 2.2 to 2.5)
M1	a	A	5.98	VS; SO; PH (2 h at 550 K);
M2	a	B	6.00	CS; TR (▲, ■, ● in Fig. 3);
M3	a	C	6.14	CS; BS; EV; SO; TR (△, □, ○ in Fig. 3).
M4	b	A	11.07	EV; SO; CS; TR (△ in Fig. 4).
M5	b	A	11.06	VS; SO; CS; TR (□ in Fig. 4).
M6	b	A	11.04	2xVS; SO; CS; TR (● in Fig. 4); PH (24 h at 640 K); BS; 2xVS; SO; CS; TR (◐ in Fig. 4); PH (24 h at 640 K); BS; 2xVS; SO; CS; TR (○ in Fig. 4).
M7	b	A	11.06	VS; SO; PH (0.3 h at 540 K); CS; BS; EV; SO; TR (x and ⊗ in Fig. 5); CS; TR (□ in Fig. 5); PH (24 h at 640 K); CS; TR (● in Fig. 5).
Q1	a	A	6.0	EV: SO: PH (2 h at 550 K):
Q2	a	B	6.0	BS - after breaking the
Q3	a	C	6.1	seal the gas phase was
Q4	a	–	–	analysed by mass spectrometer.

Abbreviations (for details see sections 2.2 to 2.5)
VS, sublimation in dynamic vacuum;
SO, sealing - off;
PH, time (in hours) and temperature (in K) of preheating;
CS, sublimation in closed ampoule;
TR, mass transport rate measurements;
BS, breaking the seal;
EV, evacuation

in the upper part of the ampoule (designated by $2 \times$ VS in Table I).

The ampoules were sealed-off using a methane-oxygen flame (designated by the letters SO in Table I).

2.3. Ampoules annealing

Sealed ampoules were preheated in a vertical or horizontal furnace at a temperature stabilized with an accuracy of $\pm$ 1 K (designated by PH in Table I). The time and temperature of annealing of the ampoules are presented in Table I.

To obtain the vapour source for mass transport rate measurements, mercuric iodide was deposited at the end of the ampoule [19]. The ampoule was placed in a horizontal furnace at 480 K and the end of the ampoule was kept at room temperature. The time of HgI_2 sublimation depended mainly of the pressure of residual gases in the ampoule. This process is designated by the letters CS in Table I.

2.4. Pressure measurements and re-evacuation of the ampoules

The annealed ampoule was connected to an oil manometer attached to a vacuum line and the system was carefully degassed. Next the seal was broken and the pressure of residual gases was measured. The accuracy of measurements was $\pm$ 0.1 torr. Then the ampoule was outgassed up to 10^{-5} torr. The evacuation could be accompanied by sublimation of mercuric iodide (see subsection 2.2). After about 2 h the ampoule was sealed-off.

2.5. Mass transport rate measurements

The vapour transport rate of HgI_2 was measured gravimetrically by compensating the mass decrease in the source observed on a balance. Each transport rate J was determined as an average value from 4–6 measurements under stationary transport conditions. The detailed procedure of mass transport rate measurements and experimental errors of these studies have been described and discussed previously [19]. All the experimental data are presented as the logarithm of J coordinates against the reciprocal temperature T system.

2.6. Mass spectrometric investigations

The ampoules equipped with a "break-seal" (Fig. 1a) were carefully cleaned and filled with different samples of mercuric iodide, respectively. In one of the experiments HgI_2 was not added. Each ampoule was attached to a vacuum line, degassed for 2 h at 10^{-5} torr, sealed-off and then pre-heated (2 h at 550 K). To analyse the residual gases the ampoule was connected to a quadrupole mass spectrometer QSM 500 (Obrep, Poland) and the seal was broken. The ampoule was placed at room temperature.

3. Results and discussion

The treatments of all the ampoules studied in this work are presented in Table I. About 6 g of HgI_2 was placed in each ampoule Q1, Q2 and Q3 (batch A, B and C, respectively). After preheating (2 h at 550 K) the composition of residual gases was determined by means of mass spectrometry. The total pressures in the ampoules studied were also measured. The results obtained (also in the ampoule Q4, to which HgI_2 was not introduced) are presented in Table II.

The final pressure in the glass ampoule used in this work (cleaned, degassed and preheated as described in subsection 2.2 and Table I) was less than 0.1 torr and hydrogen, water vapour and carbon monoxide were first of all the residual gases (see ampoule Q4 in Table II).

The pressure and composition of residual gases in ampoules containing mercuric iodide depended on the kind of HgI_2. As a result of the procedure applied the largest amount of gases evolved in ampoule Q1, in which was placed HgI_2 synthesized in an aqueous solution from $Hg(NO_3)_2$ and KI (batch A). NO was main component of the gas phase. It seems that the starting material (batch A) is contaminated with $Hg(NO_3)_2$ used in the synthesis. Low-temperature sublimation is an insufficient HgI_2 purification method in this case, since $Hg(NO_3)_2$ sublimes *in vacuo* [20]. It is known [21] that $Hg(NO_3)_2$ decomposes at above 420 K according to the reaction

$$Hg(NO_3)_2 \rightarrow HgO + \text{nitrogen oxides } (NO, N_2O, NO_2) \quad (3)$$

NO observed in our mass spectrum could also be a fragmentation product of NO_2 and/or N_2O in the spectrometer.

Water vapour was the main component of the gas phase in the ampoule Q2 containing HgI_2 synthesized in water solution from $HgCl_2$ and KI. Mercuric iodide (batch B) was dried *in vacuo* and then sublimed in the same ampoule. As a result of different procedures applied for the preparation of HgI_2 (batches A and B) the residual water vapour pressure in ampoule Q1 was lower than in ampoule Q2.

In ampoule Q3 containing mercuric iodide synthesized from mercury and iodine (batch C) the gas phase was mainly composed of carbon oxides (CO and CO_2), hydrogen and methane. It is known [22], that iodine, even of high purity, is contaminated by organic compounds. The gases observed by us are probably the products of chemical reactions running during the

TABLE II Pressure and composition of residual gases

Ampoule No.	Final pressure (torr)	Composition of the gas phase (mol %)							
		H_2	CH_4	H_2O	N_2	CO	NO	O_2	CO_2
Q1	3.1	15	1	3	–	18	50	–	13
Q2	1.8	7	2	71	–	14	2	–	4
Q3	1.1	26	10	6	–	38	–	–	20
Q4	< 0.1	39	1	35	–	17	3	3	2

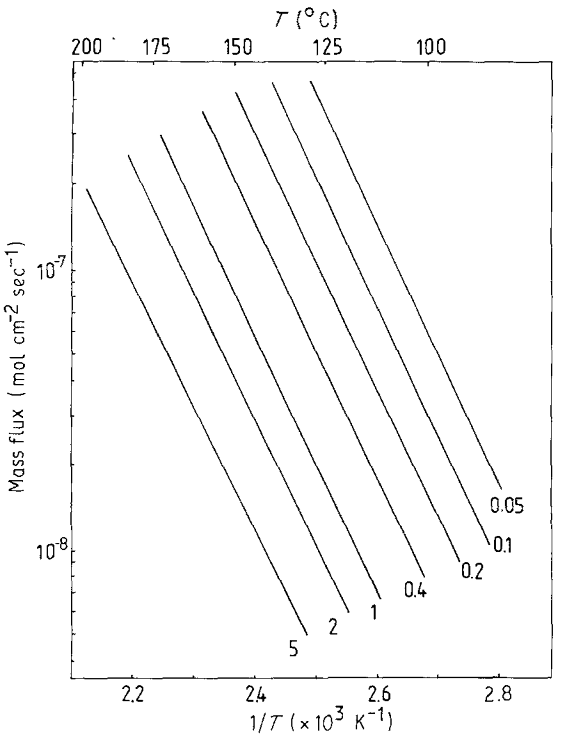

Figure 2 Mass flux of HgI_2 against reciprocal temperature relationships calculated according to 1D vapour transport model for various residual gas pressures at RT. (Lines labelled with residual gas pressure in torr.)

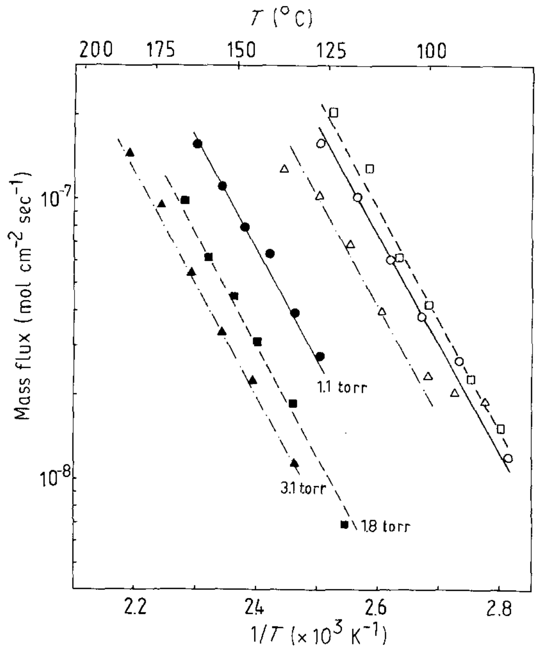

Figure 3 Mass transport rates of HgI_2 measured in the ampoules (▲, △) M1, (■, □) M2 and (●, ○) M3 into which various samples of mercuric iodide were introduced (see Table I).

preheating of the ampoule at high temperature. This mercuric iodide sample (batch C) evolved a smaller amount of residual gases than the studied materials prepared in aqueous solution (batch A and B).

In the experiments carried out by us the amount of residual gases evolved in sealed ampoules containing HgI_2 and preheated at 550 K was within the range of (2–12) $\times 10^{-7}$ mol of gases per 1 g of HgI_2. The lowest final pressure of these gases was found in the ampoule into which high-purity mercuric iodide was introduced [23]. This powder was synthesized from elements and purified by multiple distillation by Nicolau [24, 25].

No essential changes of final residual gas pressures were observed between the experiments differing in the condition of HgI_2 introduction to the ampoule, i.e. in air or in dry argon atmospheres.

In the closed ampoules containing small amounts of other gases besides mercuric iodide, the HgI_2 vapour transport between the source and crystallization zones is of an advective–diffusive character [17, 19] and calculations of the total mass flux can be made on the basis of the one-dimensional diffusive model 1D [26]. In Fig. 2 are presented the calculated relationships of the HgI_2 vapour total fluxes against reciprocal temperature [27]. Calculations were made for different pressures of inert gases and for the experimental conditions applied in this work (i.e. transport distance and temperature profile in the furnace, see also [19]). The binary diffusion coefficient D ($cm^2 sec^{-1}$) was calculated from the relationship

$$D = 0.04 \frac{1}{P}\left(\frac{T}{273}\right)^2 \qquad (4)$$

where P (atm) and T (K) are the pressure and temperature in the ampoule, respectively. It can be observed in the Fig. 2 that increases of residual gases pressure causes a decrease in the HgI_2 vapour transport rate at a given temperature, particularly at low residual gas content in the ampoule.

In Fig. 3 are presented the results of HgI_2 vapour transport rate measurements obtained in ampoules M1, M2 and M3 containing different samples of mercuric iodide (batch A, B and C, respectively). The ampoules were treated in the same manner (sublimation before sealing, preheating at 550 K) and then vapour transport rate measurements were carried out. Different results were obtained for particular ampoules, since various amounts of residual gases evolved, i.e. 3.1, 1.8 and 1.1 torr in ampoules M1, M2 and M3, respectively. After evacuation of these gases and resealing of the ampolues about 6–20 times greater transport rates of HgI_2 were obtained at given temperatures in these experiments.

In Fig. 4 is presented the temperature dependence of the HgI_2 vapour transport rate in ampoules differently degassed. Each ampoule M4, M5 and M6 contained about 11 g of HgI_2 (batch A). Ampoule M4 was evacuated for 1.5 h and after sealing-off the vapour source was formed and transport rate measurements were carried out. In ampoule M5 mercuric iodide was sublimed in dynamic vacuum prior to sealing. The mass transport rates measured in ampoule M5 were at given temperatures 2.5 times greater than in ampoule M4. If the sublimation was carried out twice prior to sealing-off (ampoule M6) then the measured mass fluxes of HgI_2 were about 3.5 times greater than in ampoule M4. Ampoule M6 was equipped with two break-seals (Fig. 1b). It could be evacuated and sealed three times and the mass transport rates of HgI_2 measured at a respective temperature became greater and greater (see Fig. 4). When comparing the results obtained in ampoules M4 and M6 at about 400 K a nearly 35-fold increase in the HgI_2 vapour transport

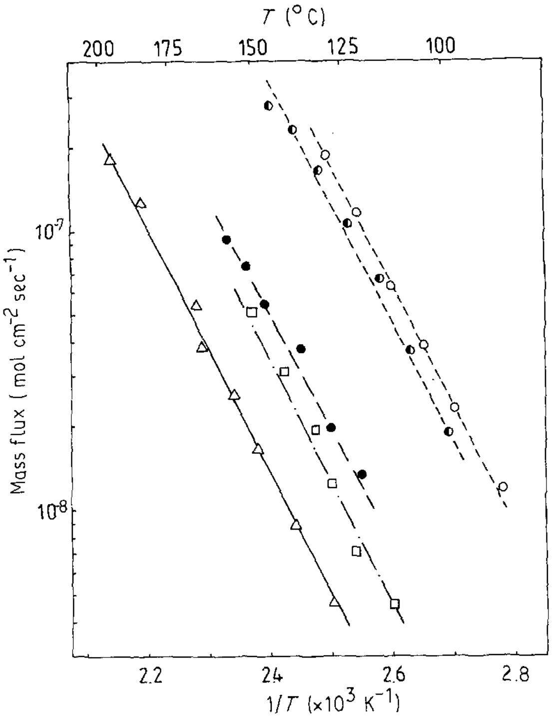

Figure 4 Mass transport rates of HgI_2 measured in the ampoules (△) M4, (□) M5 and (●, ◐, ○) M6 degassed in a different way (see Table I).

rate between the source and crystallization zones was found.

Preheating of ampoules containing HgI_2 caused an increase of the total pressure and decrease of the HgI_2 transport rate. These changes did not occur when the ampoule was annealed for 24 h at 640 K. In Fig. 5 are presented the results obtained in ampoule M7. After HgI_2 sublimation *in vacuo* and sealing-off, the ampoule was preheated, the seal was broken, gases evolved were outgassed and the ampoule was resealed. Immediately mass transport rate measurements were carried out at 365, 380, 392 and 403 K (marked as X in Fig. 5). The temperature was then lowered to 369 K and mass fluxes of HgI_2 were measured at eight different temperatures within the 369–410 K range (⊗ in Fig. 5). It is evident that evolution of gases occurred during the first annealing of the ampoule at temperatures higher than 392 K and because of this at repeated HgI_2 transport rate measurements the mass fluxes obtained were about 2.5 times lower (a similar effect is observed in ampoule M1 at 364–373 K, see △ in Fig. 3). Annealing of ampoule M7 caused a further decrease in the transport rate, two-fold after annealing at 480 K (□ in Fig. 5) and further two-fold after annealing for 24 h at 640 K (● in Fig. 5). After completion of these measurements the seal was broken and the pressure of residual gases was measured, 0.7 torr at RT.

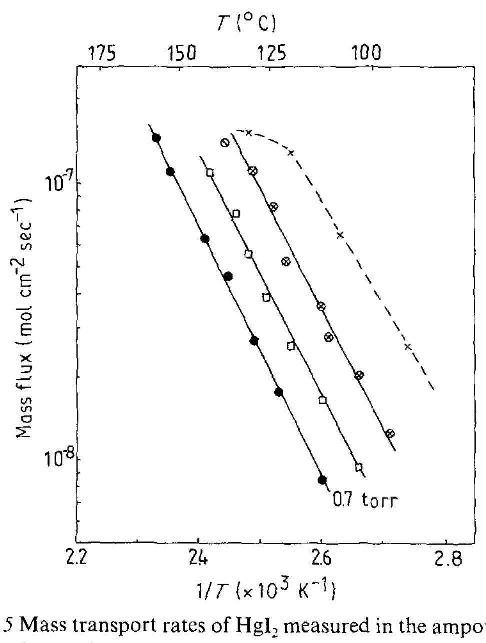

Figure 5 Mass transport rates of HgI_2 measured in the ampoule M7 preheated at various conditions (see Table I).

4. Conclusions

1. In HgI_2 crystal growth systems residual gases are present. They are mainly NO, H_2O, H_2, CO, CO_2 and CH_4. The composition of gases differs considerably depending on the mode of synthesis and purification of mercuric iodide.

2. The evolution of (2–12) × 10^{-7} mol of gases per 1 g of HgI_2, depending on the HgI_2 used, was found when applying the same sealing-off and preheating procedures.

3. Residual gases, mainly H_2, H_2O and CO evolve in small amounts (< 0.1 torr at RT) in washed, degassed, sealed-off and then annealed borosilicate glass ampoules.

4. Evolution of gases causes a decrease in the rate of HgI_2 vapour transport between the source and crystallization zone, i.e. decrease in the rate of α-HgI_2 crystal growth.

5. The application of an appropriate procedure causes a decrease in the content of residual gases in ampoules and increase in the HgI_2 mass flux value. The use in this work of ampoules with two break-seals and the carrying out of successive ampoule preheatings and HgI_2 sublimations in dynamic vacuum caused about 35-fold increase in the HgI_2 transport rate.

Acknowledgements

The authors wish to thank Mr H. Magieko from the Research and Development Centre of Vacuum Electronics in Warsaw for the help in mass spectrometric measurements. We acknowledge Dr Y. F. Nicolau from Centre of Nuclear Studies in Grenoble for sending us samples for analysis.

References

1. J. YARWOOD, "High Vacuum Technique" (Chapman and Hall, London, 1967).
2. H. SCHAFFER, in "Preparative Methods in Solid State Chemistry", edited by P. Hagenmüller (Academic Press, New York, 1972).
3. E. KALDIS, in "Crystal Growth. Theory and Techniques" edited by C. H. L. Goodman, Vol. 1 (Plenum Press, London, 1974).
4. G. SCHMIDT and R. GRUEHN, *J. Cryst. Growth* **57** (1982) 585.
5. J. J. MURRAY, R. F. POTTIE and R. L. SANDER, *J. Mater. Sci.* **8** (1973) 37.
6. W. KROONTJE, B. J. De MAAGT, M. H. J. VAN RIJSWICK and L. SPRENGERS, *J. Vac. Sci. Technol.* **A4** (1986) 2293.

7. J. R. ABERNATHEY, D. W. GREENWELL and F. ROSENBERGER, *J. Cryst. Growth* **47** (1979) 145.
8. W. PALOSZ, *ibid.* **61** (1983) 412.
9. F. C. WANG, R. H. BUBE, R. S. FEIGELSON and R. K. RATE, *ibid.* **55** (1981) 268.
10. T. C. HARMAN and J. P. McVITTIE, *J. Electron. Mater.* **3** (1974) 843.
11. G. J. RUSSELL and J. WOODS, *J. Cryst. Growth* **46** (1979) 323.
12. F. PIZZARELLO, *J. Appl. Phys.* **25** (1954) 804.
13. R. MAZELSKY and D. K. FOX, *Prog. Cryst. Growth Charact.* **15** (1987) 75.
14. J. OMALY, M. ROBERT, P. BRISSON and R. CADORET, *Nucl. Instr. Meth.* **213** (1983) 19.
15. N. L. SKINNER, C. ORTALE, M. M. SCHIEBER and L. VAN DEN BERG *J. Cryst. Growth* **89** (1988) 86.
16. J. LASKOWSKI, J. PRZYLUSKI and K. CONDER, *Cryst. Res. Technol.* **23** (1988) 1231.
17. K. CONDER and J. LASKOWSKI, *Nucl. Instr. Meth. Phys. Rev.* **A** (1989) in press.
18. J. LASKOWSKI, H. KUC, K. CONDER and J. PRZYLUSKI, *Mater. Res. Bull.* **22** (1987) 715.
19. K. CONDER, J. PRZYLUSKI and J. LASKOWSKI, *J. Cryst. Growth* **74** (1986) 416.
20. GMELIN HANDBUCH DER ANORGANISCHEN CHEMIE, Vol. 34, Tl. B, Lfg. 1 (Verlag Chemie, Weinheim (1965) p. 120.
21. L. W. COLLINS, E. K. GIBSON and W. W. WENDLANDT, *Thermochimica Acta* **11** (1975) 177.
22. M. PIECHOTKA and E. KALDIS, *Monatsh. Chemie* **118** (1987) 137.
23. J. LASKOWSKI, M. OLEDZKA, unpublished results (1988).
24. Y. F. NICOLAU, *J. Chem. Techn. Biotechnol.* **33A** (1983) 350.
25. Y. F. NICOLAU and A. M. ANDRÈANI, *J. Cryst. Growth* **87** (1988) 117.
26. M. M. FAKTOR and I. GARRETT, "Growth of Crystals from the Vapour" (Chapman and Hall, London, 1974).
27. M. OLEDZKA, MSc thesis, Warsaw University of Technology (Warsaw 1988).

Received 18 November 1988
and accepted 14 April 1989