

The Origin and Time Dependence of the Amount and Composition of Non-Constituent Gases Present in Crystal Growth Systems

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Desorption of inert gases from, and their diffusion through the wall of sealed silica glass ampoules was investigated. Change of the gas pressure and composition with time and temperature was measured. It is shown, that the main component of the gas desorbed from silica is hydrogen, and its build-up in the ampoule may exceed 10 Torr. Extensive outgassing at high temperature under dynamic vacuum significantly reduces that amount. It was found that an important and often dominant source of residual gases is the source material. Considerable quantities of gases, usually carbon oxides, can be produced even by trace amounts of impurities (solid oxides) present in the original source materials. Permeation of helium, hydrogen, and neon through silica glass may lead to significant pressure changes in sealed ampoules under typical materials processing conditions.

1. Introduction

A presence of different, non-constituent gases may be a critical factor in crystal growth systems. In Physical Vapor Transport processes the gas(es) can be used intentionally (to prevent excessively high, unstable growth conditions), or can evolve unintentionally during the course of the process (which may lead to undesired reduction in the growth rate). In melt growth, particularly under low gravity conditions (reduced hydrostatic pressure) the gas present in the system may contribute to formation of voids in the growing crystals and even to a separation of the crystal and the liquid phase¹⁻³. On the other hand, some amount of gas may facilitate 'contactless' crystal growth, particularly under low gravity conditions⁴⁻⁷.

Different non-constituent gases may be present in growth ampoules, and their amount and composition may change during the crystallization process. Some amount of gas appears even in empty ampoules sealed originally under high vacuum: the gas may diffuse in from the outside and/or desorb from the ampoule walls⁸. Residual gases can also be generated by the source materials^{9,10}: even very high purity commercial elements and compounds contain trace amounts of impurities, particularly oxides. The oxides may have low volatilities themselves but their reaction with other species, particularly carbon and hydrogen, may produce volatile compounds like water or carbon oxides. Non-constituent gases, either added initially to the system or evolved during the material processing, may diffuse out of the ampoule during the course of the

experiment. On the other hand, gases present outside (e.g. those used as an ambient or a thermal liner) may diffuse into the ampoule. In either case the growth conditions and the quality of the crystals may be affected. Therefore a reasonable knowledge and understanding of the origin, composition, magnitude, and change with time of gases present in sealed ampoules may be important for a meaningful control and interpretation of crystal growth processes. This problem is of a particular importance for processing of electronic materials in space: (1) safety considerations require the use of sealed systems only, and, (2) high cost of crystal growth processing in microgravity calls for a throughout, accurate description of the processing conditions necessary for a meaningful, efficient, and conclusive interpretation of the space experiment results.

In this paper we present the results of our extensive studies on the origin, magnitude, and composition of gases formed in closed crystal growth systems. The study includes (i) degassing properties of fused silica, (ii) generation of residual gases by source materials, and, (iii) diffusive gas losses from silica glass ampoules.

2. Experimental

The experiments were performed using ampoules made from natural, clear silica tubing of two commonly used brands, GE214 (manufactured by melting quartz sand in electric furnace), and HSQ300 (fabricated from

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natural quartz using hydrogen-oxygen flame). The fabricated ampoules were cleaned with a detergent, then etched with a 10% hydrofluoric acid for a few minutes and thoroughly flushed with deionized water. The cleaned and dried ampoules were outgassed under dynamic vacuum at a predetermined temperature. For some experiments the ampoules were loaded with source material synthesized from high purity (6N) elements and ground before further use. Before sealing the ampoule with the source was baked under dynamic vacuum with or without a prior annealing in hydrogen atmosphere. The sealed ampoules were annealed under predetermined conditions of temperature and time. The amount of gas generated during annealing in the ampoules loaded with source material was measured using the system shown schematically in Fig. 1. The annealed ampoule was placed in the chamber, then the system was evacuated and closed, the ampoule was break opened, and the pressure change in the system was measured. The original pressure in the

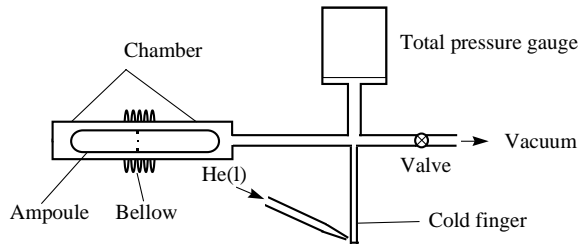


Fig. 1 Measuring system.

ampoule was calculated based on the ampoule-to-measuring-system volume ratio. The composition of the gas was determined by fractional condensation, i.e. the change of the pressure in the system with a change of the temperature of the cold finger cooled with a stream of cold helium (Fig. 1) was recorded and analyzed. For dynamic pressure measurements (ampoules without source material), the experimental ampoule was connected directly to the measuring system (instead of the main chamber) and placed in a furnace. The change of pressure with time at different temperatures was recorded.

3. Results and discussion

3.1 Desorption of gas from silica glass

Fig. 2 shows the change of pressure with time and temperature for ampoules outgassed under dynamic vacuum for 16 hours at room temperature. At each annealing temperature the pressure inside the ampoule tends to reach some maximum value (Fig. 2). The pressure levels off after about 2 days of annealing at a given temperature, the maximum pressure increases with an increase in the annealing temperature (Fig. 2).

At about 1000°C the total pressure in the ampoule reaches a few Torr for GE214 glass, and exceeds 10 Torr for HSQ300 ampoule (Fig. 2). Even higher pressures were observed in ampoules with a larger surface-area (A) to the free-volume (V) ratio. After removal of the accumulated gas from the ampoule and further annealing, the pressure levels off at lower values (Fig. 2). The gas is composed mostly of hydrogen, the other major components are water (GE214 glass) and carbon monoxide (HSQ300). Longer annealing at high temperatures leads to a gradual decrease in hydrogen pressure in the ampoules

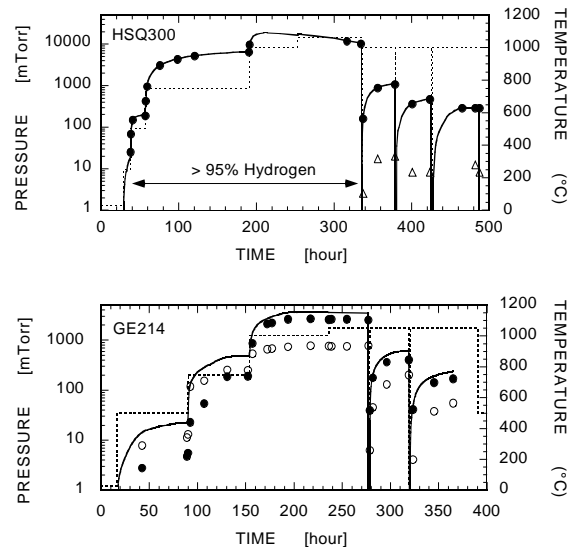


Fig. 2 Change of pressure with time and temperature for ampoules outgassed at RT. $A/V = 1.0 \text{ cm}^2/\text{cm}^3$. Dashed line - temperature, solid line - total pressure, solid circles - hydrogen, open circles - water, open triangles - carbon monoxide.

(Fig. 2). This decrease is apparently due to diffusion of the gas through the wall out of the ampoule (c.f. section 3.3).

Similar features of the pressure-vs-time curves were observed in ampoules outgassed originally at 1000°C (Fig. 3). As in Fig. 2, after about two days of annealing at a given temperature the pressure reaches a maximum, the dominant component of the gas being hydrogen. However, the maximum pressures at each temperature are lower by a factor of 5 - 10 relative to those observed in ampoules outgassed at RT.

Residual gas build-up in graphitized and outgassed (at high temperature) ampoules, Fig. 4, is similar to that observed in corresponding ampoules but without a graphite coating: the total pressure is of the same order and the pressure change with time has the same character as in the ampoules without graphitizing, Fig. 4. However, an apparent increase in the pressure of

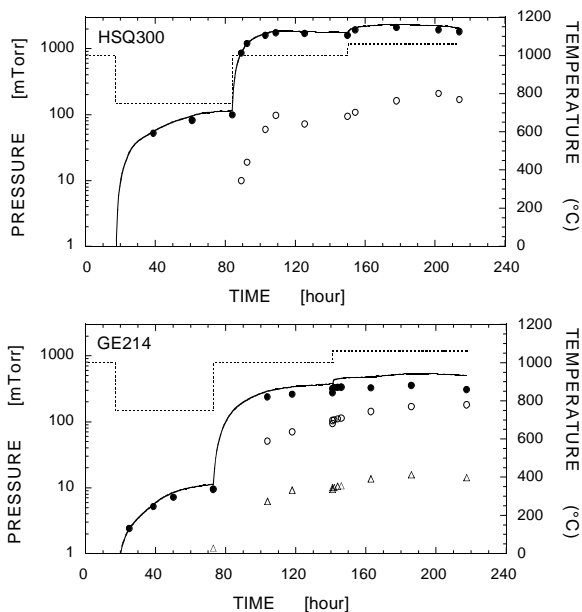


Fig. 3 Change of pressure with time and temperature for ampoules outgassed at 1000°C. $A/V = 1.0 \text{ cm}^2/\text{cm}^3$. Dashed line - temperature, solid line - total pressure, solid circles - hydrogen, open circles - water, open triangles - carbon monoxide.

carbon monoxide in the system (particularly in GE214 ampoules) is observed.

The results of Figs. 2 - 4 indicate, that the pressure of hydrogen in the ampoules is determined by the concentration of H_2 at the ampoule inner wall, and its

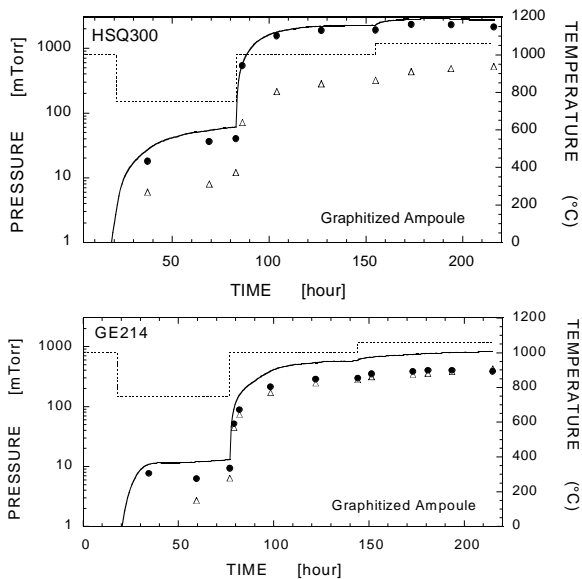
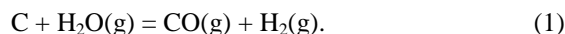


Fig. 4 Change of pressure with time and temperature for ampoules graphitized and outgassed at 1000°C. $A/V = 1.0 \text{ cm}^2/\text{cm}^3$. Dashed line - temperature, solid line - total pressure, solid circles - hydrogen, open triangles - carbon monoxide.

maximum saturation pressure is reached after about two days of annealing at a given temperature. The other major component of the gas is water, apparently desorbed from the surface and bulk of the glass. Diffusivity of water in silica glass is about five orders of magnitude lower than that of hydrogen, but a relatively high solubility of the molecules in the glass may produce a noticeable amount of H_2O vapor inside the ampoule. Diffusivity and solubility of carbon monoxide in silica are much lower than those of hydrogen and water. Thus, the presence of CO in the residual gas is apparently a result of the reaction of water with graphite (even trace amounts) present in the ampoule



Water molecules used up by reaction (1) could be replenished by additional desorption from the glass. However, due to low diffusivity of water in silica, this process is apparently slow and reaction (1) does not have a significant effect on the total pressure in the ampoule observed experimentally (Fig. 4).

Outgassing silica glass ampoules under dynamic vacuum at high temperature removes hydrogen dissolved in the ampoule wall and water molecules adsorbed on the ampoule surface and dissolved near the surface. That allows for a significant reduction of the amount of gas released from silica glass into the sealed ampoule during subsequent annealing.

3.2 Effect of the source material

The effect of the source and its pre-treatment on residual gas pressure and composition is illustrated in Table 1 for lead telluride samples. The pressure developed in an empty, reference ampoule is very low, below 10 mTorr at RT (Table 1, exp. 1). Baking the ampoule filled with hydrogen leads to a small dissolution of the gas in the glass and its desorption during subsequent annealing (expts. 2 and 3 in Table 1). The amount of gas in ampoules with lead telluride is higher up to three orders of magnitude relative to that in the empty ones (Table 1). In general, the source produces carbon oxides, apparently generated from trace amounts of oxide and graphite impurities in the system. Relatively small amount of gas formed in the ampoule with a compact, chunk source material (exp. 4) can be explained by slow diffusion of the reactants in the solid and, thus, formation of gases from only a fraction of all impurities present in the material. Larger amounts of residual gases were generated when powdered source material was used (expts. 5 - 10 in Table 1). Formation of gases from oxide impurities in the source material and not from the glass itself is apparent from the dependence of the gas pressure and composition on the amount of the source in the ampoule: the total quantity of oxygen in carbon oxides is directly proportional to the amount of the source in

Table 1 Residual gas pressure and composition in ampoules with PbTe source

Exp. #	Source		Annealing	P(amp.) ***	H ₂	CO	CO ₂	H ₂ O
	amount *	H ₂ treatment **	°C / h	mTorr at RT				
1	-	-	800 / 1	3.8		√	√	
2	-	+	800 / 1	48	90+			
3	-	+	900 / 150	37	70	20		
4	1m, chunks	-	800 / 24	82		10	80	
5	0.2 m	+	800 / 24	135	34	46	6	
6	1 m	+	800 / 24	434	12	62	22	
7	3.5 m	+	800 / 24	1,190	7	67	25	
8	1 m	-	800 / 1 ^(a)	210			90	
9	1 m	-	800 / 24 ^(a, b)	270			75	15
10	1 m	+	800 / 24 ^(a, c)	≈ 12,000			≈ 35	≈ 65

- * m = 0.05 mole of powdered lead telluride
 ** annealing at 700°C for 20 min under 0.5 atm H₂, followed by a bakeout under vacuum for 20 min.
 *** ampoule dimensions: 10mm ID, 20 cm long

- (a) reaction of the source with silica glass
 (b) powdered source exposed to air for 160 h prior to loading
 (c) highly oxidized source

the ampoule (expts. 5 - 7 in Table 1). Materials annealed in hydrogen produce similar amount of gas relative to corresponding experiments without hydrogen treatment but, as a result of a removal of at least some of the oxide impurities from the original source, show a lower content of carbon dioxide in the gas. Presence of gaseous hydrogen in the ampoules indicates an absence of lead oxides in the material and can serve as a test of the effectiveness of the purification process. Oxidation of the source exposed to the air for a few days does not have any apparent effect on the residual gas pressure and composition (exp. 9). In the case of heavily oxidized starting source material, the current pre-treatment procedure is insufficient as indicated by the presence of carbon dioxide and water, an absence of hydrogen and carbon monoxide, and a very high pressure in the system (exp. 10 in Table 1). The presence of lead oxide(s) in materials not heat-treated in hydrogen atmosphere is also reflected in an opaque appearance of some parts of the ampoule (due to reaction of the oxides with silica leading to a formation of lead silicates). Similar results as those reported above for PbTe were obtained also for other source materials (CdTe⁹, ZnSe¹⁰).

3.3 Diffusion through the wall

As shown in section 3.1, after a longer annealing at higher temperatures the pressure of hydrogen inside the ampoule decreases with time. Fig. 5 shows a change of the pressure of helium, hydrogen, and neon with time

in silica glass ampoules annealed at 1000°C. The rate of the pressure change is dependent on dimensions of the ampoule and can be approximated by the equation⁹

$$\frac{P(t) - P^\circ}{P(\text{init}) - P^\circ} = \exp\left(-\frac{K A R T}{V d} t\right), \quad (2)$$

where P(init) and P(t) are the initial (at t = 0) and current (at time t) pressure of a given gas, respectively, P° is the (constant) pressure outside the ampoule, K is the permeation constant, A the surface area of the glass (the average of the inner and outer surfaces), R the gas constant, T the absolute temperature, V the free volume inside the ampoule, and d the wall thickness. Accumulation or loss of gas dissolved in the glass is

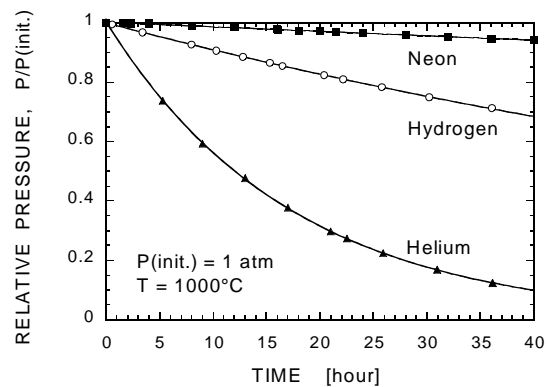


Fig. 5 Diffusive loss of gases from silica glass ampoules.

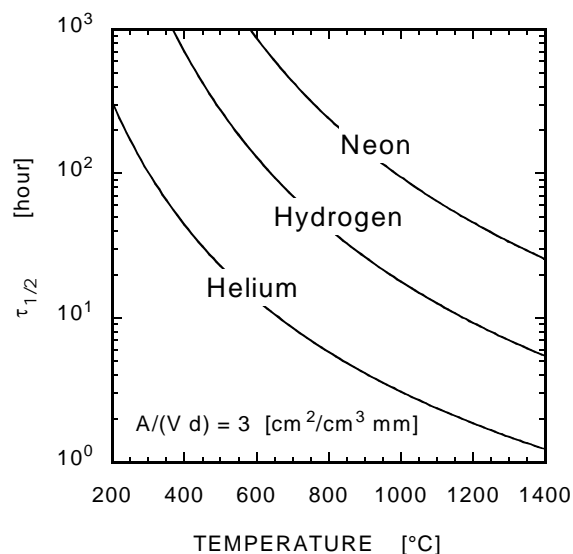


Fig. 6 The rate of the pressure change (half-time) as a function of temperature.

ignored (it may become an important factor in case of hydrogen at low, <10 Torr pressure¹¹). Permeation constant K is exponentially dependent on temperature, thus the temperature has a major impact on diffusive pressure changes in the ampoules. Fig. 6 shows the dependence of the half time (i.e. the time after which the original difference between the pressure inside and outside the ampoule decreases by 1/2), $\tau_{1/2}$, as a function of temperature for an ampoule with the $A/(V d)$ ratio of 3 (which is a typical value for many crystal growth systems). As follows from Fig. 6, a considerable rate of helium in- or out- flow may take place even below 500°C. Permeation of hydrogen is slower, but may become a significant factor even below 800°C. Permeability of neon is about five times lower than that of hydrogen, so the respective $\tau_{1/2}$ values are correspondingly larger and permeation of neon may become significant only around 1000°C (Fig. 6). Permeability of other common gases like argon, nitrogen, oxygen, and carbon oxides are two or more orders of magnitude lower than that of neon, and their diffusion through and dissolution in fused silica under typical experimental conditions can be ignored.

4. Conclusions

Desorption of different gases from the surface and bulk of fused silica glass ampoule walls leads to a build-up of residual gas pressure which may exceed 10 Torr at high temperatures. Outgassing the ampoules under vacuum at high temperatures may considerably reduce the amount of gas formed during subsequent annealing. The gas evolved from silica glass consists mostly of hydrogen. The pressure of hydrogen tends to level off, its maximum value increases with an increase in the

annealing temperature. In graphitized ampoules, a comparable to hydrogen amount of carbon monoxide may be generated, particularly when silica containing some amount of water is used.

Considerable amounts of residual gas may be generated by the source material present in materials processing (crystal growth) systems. The gas is apparently formed from trace amounts of oxide and graphite impurities present in the material. The pressure of the gas increases with an increase in the amount of the source material, its magnitude is typically between a fraction and several Torr. In case of highly contaminated (oxidized) materials, the amount of residual gas formed may be one or more orders of magnitude higher than that in purer systems. Purification of slightly contaminated source materials by annealing under hydrogen atmosphere apparently reduces the amount of solid oxide impurities, but has no obvious effect on the total pressure of carbon oxides in the ampoule under our experimental conditions.

Lighter molecules, helium, hydrogen, and neon, can diffuse through the wall of the container and change the gas pressure and composition in closed systems. Considerable changes of the pressure inside typical experimental fused silica ampoules can occur, even at moderate temperatures, for helium and hydrogen. At higher temperatures a substantial pressure change can take place for neon as well.

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