RESIDUAL GAS IN CLOSED SYSTEMS. III. DEVELOPMENT AND REDUCTION OF GASES GENERATED BY THE SOURCE MATERIALS

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ABSTRACT. The amounts and compositions of residual gases formed in sealed ampoules loaded with different sources (elements and II-VI and IV-VI compounds) after consecutive annealings were investigated. A given source was subjected to a series of heat treatments, with intermediate measurements and removal of the gas accumulated in the system. The results of these experiments are discussed in terms of the underlying thermochemical and kinetic phenomena and practical limitations to reducing the amount of residual gases in sealed ampoules.

1. INTRODUCTION

In the preceding papers we discussed desorption of gases from silica glass in sealed ampoules [1] and formation of gases from source materials when applying a single annealing process [2]. The results of the latter work indicated that part of the gas is formed, in a relatively slow process, from impurities dispersed in the bulk of the source. To investigate this process closer, and to determine the method of a more effective reduction of the amount of gas in the system, the process of the gas development was studied by a series of consecutive annealings. The results of those studies are presented in this paper.

2. EXPERIMENTAL PROCEDURES

The experiments were performed by thermal processing of different source materials in sealed silica glass ampoules. The preparation of the materials and of the experimental ampoules is described in ref. [2]. As shown in that paper thermal pretreatment removes the major portion of residual gases. Therefore in this paper, to focus on gases formed by bulk impurities, most of the materials were pretreated under elevated temperature conditions prior to sealing the ampoule. As before, the experiments were performed for a fixed ratio of the amount of the source to the free volume in the ampoule, $n/V_f = 3$ mmole/cm^3. After sealing the ampoule with source was heat treated (annealed for a predetermined length of time or resublimed). After the treatment the amount and composition of the residual gas formed in the ampoule was measured as described in ref. [2]. After each measurement the ampoule was evacuated, filled with inert gas (to prevent oxidation), provided with a new plug, evacuated again and sealed, and the next step of heat treatment and subsequent measurement(s) was performed.

3. RESULTS AND DISCUSSION

The results of our representative experiments are shown in Figs. 1 - 7. The right-downward arrows in the figures symbolize resublimation from a given temperature to an undetermined lower temperature occurring when one end of the ampoule stays outside the furnace. The horizontal arrows in the figures depict the annealing process between subsequent measurements, the accompanying descriptions specify the temperature (in ºC) and time (in hours) of a given heat treatment, and the type of the process (if different from isothermal annealing). Other (than showed at the arrows) heat treatment conditions for a given step are specified in the figures separately. Unless indicated otherwise, the total pressures shown in

the figures include only the oxides (CO, CO_2, and H_2O), i.e. the components that represent volatization of the solid oxide impurities present in the system. The remaining component, hydrogen, is shown separately if needed.

3.1 Elements. For elements, materials of coarse granulation were used. The amounts of gas formed during consecutive annealings, for selected experiments, are shown in Figs. 1a - 1c.
The high residual gas pressure generated after outgassing at room temperature (Fig. 1a) decreases significantly with subsequent annealing(s) until eventually it drops well below the pressure of 1 Torr. The gas was found to be composed of 95 - 100% of carbon dioxide and/or water, except for Sn and Zn where it is dominated by hydrogen (due to thermochemical stability of ZnO and SnO, c.f. discussion in ref. [2]).

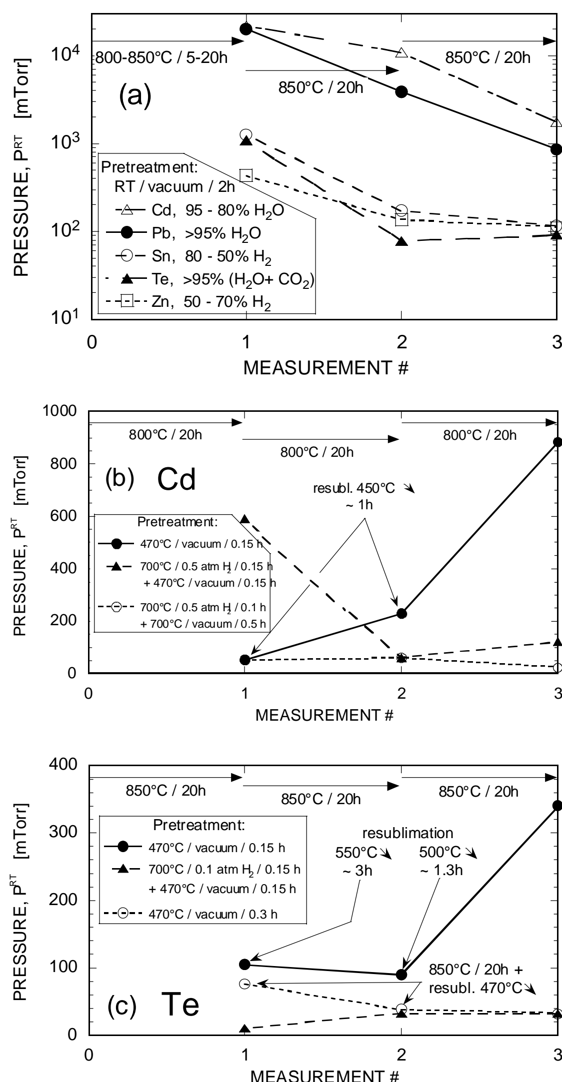


Figure 1. Pressures of residual gas formed in ampoules with elemental source after consecutive thermal processings. (a), sources outgassed at RT; (b) and (c), sources thermally pretreated prior to ampoule seal-off.

Development of gas in ampoules with heat pretreated cadmium and tellurium is shown in Figs. 1b and 1c, respectively. Prior to the first sealing the sources were annealed under dynamic vacuum for 0.15 hour under a moderate temperature of 470ºC. In two cases the vacuum annealing was preceded by annealing at 700ºC in 0.5 atm of hydrogen. In one case the vacuum annealing was done at 700ºC for an extended period of time (0.5 hour). After each sealing the source was annealed for 20 hours at high temperature (800ºC for Cd, 850ºC for Te) and/or resublimed from one end of the ampoule to the other, as indicated.

As seen in Figs. 1b and 1c (solid circles), a simple outgassing under vacuum at 470°C followed by two consecutive resublimations generates moderate amounts of gas on the order of 100 - 200 mTorr, the amounts formed/released during the second resublimation do not show any meaningful reduction in the amount of gas (Fig. 1c) and even some increase (Fig. 1b). The final, extended annealing at high temperature leads to a four-fold increase in the amount of gas. That shows, that most of the gas are generated from non-volatile components during the material annealing, and that the process is slow (the resublimation processes were much shorter than the annealing periods and could release only gases formed before the actual sublimation). Unlike in samples sealed without a heat treatment (Fig. 1a), the gas is usually composed of 2 - 3 components in similar amounts. The major gas-forming component is apparently oxygen present in the form of non-volatile oxide impurities. Pretreatment in hydrogen helps to reduce the final amount of gas in the ampoule (solid triangles in Figs. 1b and 1c). When resublimation of tellurium is preceded by an extended annealing at higher

temperatures a significant reduction in the amount of gas, which is preserved also after the final annealing, is observed (open circles in Fig. 1c). Similar results were obtained for tellurium with extended outgassing at lower temperatures (open circles in Fig. 1c). Relative ease in reducing the amount of gas from tellurium is probably due to a relatively high volatility of its oxides [5]. In experiments with hydrogen pretreatment relatively large fraction of the gas (over 50% in the case of tellurium, 20 - 40% in the case of cadmium) is hydrogen (dissolved mainly in the source).

The most effective method of reducing the amount of gas in ampoules with the elements is a pretreatment combining annealing under hydrogen atmosphere with a subsequent, extended high temperature bake-out under dynamic vacuum (open circles in Fig. 1b). After such treatment even a combined annealing and resublimation (Fig. 1c) does not produce a significant amount of gas. However, with a rather volatile material like Cd this procedure leads to a significant loss of the source during the process.

Tin and zinc exhibit somewhat different behavior. Sn source, outgassed under vacuum at 700ºC for 0.15h, and Zn source, outgassed under vacuum at 470ºC for 0.15h, was subjected to subsequent annealings (at 800 - 850ºC / 20h) and measurements. The annealings generated moderate and similar amounts of gas after each step (~200 mTorr for Sn, ~100 mTorr for Zn). A significant portion of the gas consisted of hydrogen. These results confirm a strong thermochemical factor in the gas generation process concluded already in from our previous results [2]. Zinc and tin form the most stable oxides of all the elements investigated in the present study. That may explain the relatively low concentration of gas even after outgassing at RT only (Fig. 1a); the equilibrium pressure of the oxides is rather low, but then also the rate of the oxygen removal is low. Since the annealing temperature is well below 1000ºC, relatively large amounts of hydrogen found in these experiments cannot come from its desorption from silica glass [1, 3, 4]. The hydrogen is probably generated by reaction of the metals with residual moisture (see equ. 3 in ref. [2]) consistent with the chemical equilibria between the species [5].

Selenium outgassed at RT and annealed at 700ºC for 5h produced consistently large amounts of gas (99+% of CO), up to ~30 Torr after consecutive annealings. After outgassing under vacuum at 200ºC / 0.3h the amount of gas dropped to 13 mTorr ($CO+CO_2$). Similarly, after initial thermal pretreatment under vacuum (300ºC / 0.2h) selenium source produced 400 mTorr of gas after the first annealing (700ºC / 5h), but only 13 mTorr after the subsequent ones. Apparently a substantial amount of selenium oxides was formed in the system. High volatility of the oxides at high temperatures facilitates its separation from selenium. However, since the pressure of the oxides at room temperature is very low, its removal from the system requires vacuum outgassing at elevated temperature.

3.2 PbTe. Development of gas in the ampoule with lead telluride during consecutive heat treatments, for several experiments without initial H_2 annealing, is shown in Fig. 2a. After the first step (resublimation) both ground and coarse samples that have been pretreated by vacuum resublimation (open squares and full triangles in Fig. 2a) show very low amounts of gas. The sample outgassed under vacuum without resublimation (open circles) generates a few times more gas. Apparently the initial resublimation removed volatile impurities from the bulk of the materials, as well as from their surface (thus the ground and coarse sources produce similar amounts of gas). The sample that has only been annealed and not resublimed under vacuum still had volatile impurities trapped in the bulk, and those impurities were released during the first heat treatment of the series (resublimation). While the second resublimation generates similar amounts of gas for all these experiments, the result of the subsequent extended annealing (step 3) indicates that the samples that underwent only resublimation contain apparently more impurities left and produce more gas than the sample

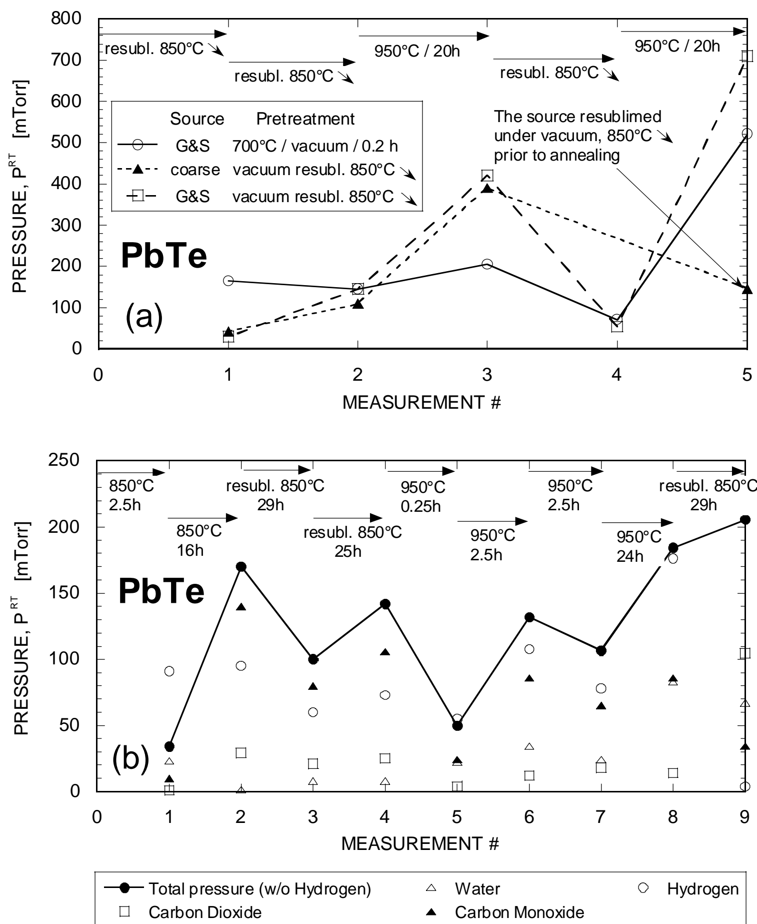


Figure 2. Pressures of residual gas formed in ampoules with PbTe source after consecutive thermal processings. (a), pretreatment without hydrogen: 700°C / vacuum / 0.15h; (b), pretreatment with hydrogen: 700°C (0.5 atm H_2 / 0.15h + vacuum / 0.1h).

which has only been annealed during pretreatment. After step four (resublimation) the pressures drop significantly again, to raise after subsequent extended annealing at high temperature (step 5). Only the sample that underwent resublimation under vacuum shows a quite low level of the gas in the system. The above results indicate, that during resublimation in sealed ampoules a part of the formed/released gas may be re-trapped in the condensing material. The generation of gas in the bulk is apparently slow. After subsequent heat treatments (measurements #2 and higher) the gas contains, in nearly all cases, more than 95% of CO_2 and H_2O. That is an indication of rather high amounts of oxides still present in the source.

Slow development of gas is also clearly seen in Fig. 2b. This series of measurements was performed with the source preannealed in hydrogen (700ºC / (0.5 atm H_2 / 0.15h + vacuum / 0.1 h)). As seen from the figure, the pressure of gas (excluding hydrogen) after each subsequent treatment is about 200 mTorr or less, depending on the processing conditions. Lower amounts of the oxides are generated after shorter annealings than after longer ones (Fig. 2b). The amount of hydrogen is similar in all measurements, usually in quantities somewhat less than that of the remaining gases combined, except for the last experiments where a significant drop in hydrogen pressure is observed. The content of carbon dioxide in the gas is apparently suppressed by a presence of hydrogen: except for the final annealing, the amount of CO_2 is much less than that of carbon monoxide. In general, the composition of the residual gas is quite consistent in the entire series. Despite extensive and multiple processing the source of the residual gas apparently did not change much, and the amounts of gas after each treatment are similar (except for very short, step #5, or moderately short at low temperature, step #1, annealings). Apparently only relatively small fraction of the impurities trapped in the bulk of the source got volatized during the annealings.

3.3 PbSe. Development of residual gas from PbSe pretreated with hydrogen (700ºC / (0.5 atm H_2 / 0.15h + vacuum / 0.1h)) is shown in Fig. 3. Development of the volatile species is rather slow, what is particularly visible when comparing the first two annealings: an increase of the annealing time from 1h to 5h corresponds to an over 10-fold increase in the gas pressure. The

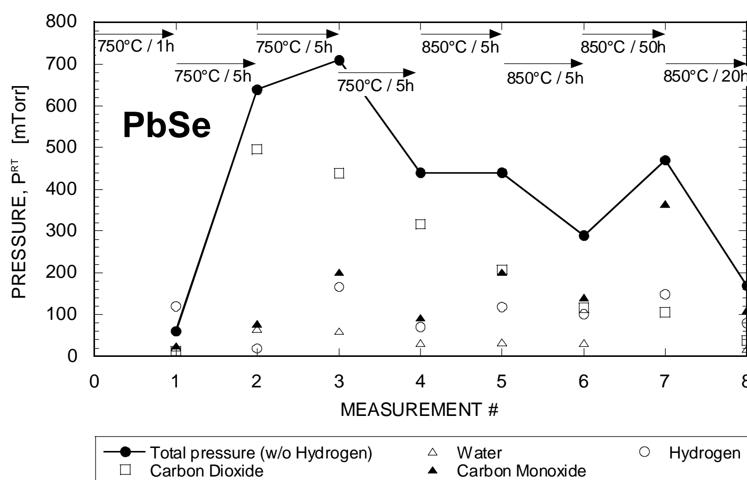
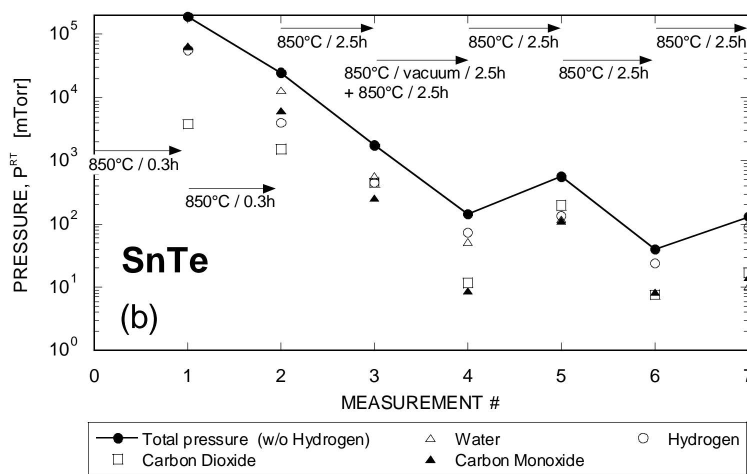


Figure 3. Pressures of residual gas formed in ampoules with PbSe source after consecutive thermal processings. Source ground and sifted. Pretreatment: 700°C (0.5 atm H_2 / 0.15h + vacuum / 0.1h).



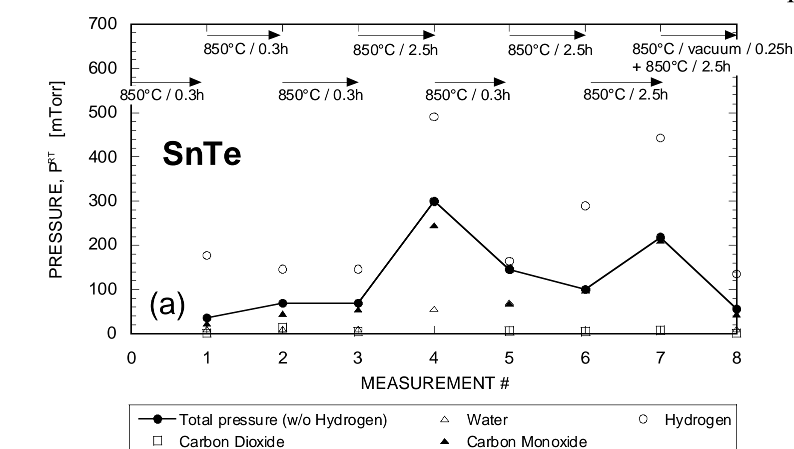


Figure 4. Pressures of residual gas formed in ampoules with SnTe source after consecutive thermal processings. Source ground and sifted. Pretreatment: 700°C (0.5 atm H_2 / 0.15h + vacuum / 0.1h). (a), typical source; (b), highly contaminated source.

dependence of pressure on temperature and time during consecutive annealings is consistent with what may be expected for a process of diffusion out of the bulk of the solid particles: increased pressure with an increase in the annealing time (steps 1 and 2, and 6 and 7 in Fig. 3), reduction in pressure after subsequent annealings under the same conditions (steps 3 and 4, and 5 and 6). The gas contains moderate, and approximately the same (about 100 mTorr) amounts of hydrogen, and a mix of other gases. Similar as in ampoules with PbTe, hydrogen suppresses the amount of CO_2 that dominates when the pressure of hydrogen is low (measurements 2 - 4 in Fig. 3). In general, the pressure of carbon dioxide decreases with subsequent annealings that is an indication of a gradual decrease in the amount of oxygen (oxides) in the source material.

3.4 SnTe. Development of residual gas from SnTe source is shown in Fig. 4a for material pretreated with hydrogen (700ºC / (0.5 atm H_2 / 0.15h + vacuum / 0.1h)). The amounts of residual gas generated during consecutive annealings depend on the annealing time: lower amounts of gas evolve after shorter annealings and, generally, some reduction in the amount of the generated volatile oxides with subsequent heat treatments is

observed. A vacuum bakeout before the last annealing (step #8) leads to a substantial reduction of the pressure.

In the experiments discussed in Sections 3.1 - 3.3 (except for the RT-evacuated elements, Fig. 1a) only moderate changes of pressure with subsequent annealings were observed. Fig. 4b shows evolution of pressure in the ampoule with (accidentally) highly contaminated source but after the same pretreatment as in Fig. 4a. As can be seen, even a short initial annealing generated large amounts of residual gas (over two orders of magnitude higher than in our typical experiments). Initially the pressure drops fast, by about one order of magnitude with each subsequent annealing step, until it stabilizes at about 100 Torr. It seems, that the massive contaminants formed a separate phase (on the surface of the source), therefore their volatization was quite effective (high activity and short diffusion path for the volatization products). After removal of most of those impurities the remaining portion of the oxides remains dissolved in the matrix, therefore its activity is reduced and its volatization is hindered.

3.5 CdTe. The results for cadmium telluride shown in Fig. 5 have been obtained after pretreatment without hydrogen (700ºC / vacuum / 0.15h). As can be concluded from the results, apparently a major source of impurities is present in the bulk of the grains: the coarse material produces increased amounts of gas with consecutive heat treatments. The ground material has a higher content of impurities, perhaps due to insufficient removal of surface contaminants during pretreatment. As a result, its initial resublimation generates nearly one Torr of gaseous oxides. Even after effective removal of the gases in the second step (resublimation under vacuum), the final annealing produces high amounts of gas again, apparently due to relatively high amount of oxides left in the matrix after the preceding processes. Similar as for other materials without hydrogen pretreatment, the gas is dominated by carbon dioxide with smaller amounts of carbon monoxide. In related ampoules with a ground source but pretreated with hydrogen, the amounts of residual gas that formed after consecutive heat treatments were found to be smaller: after two steps the amount of volatile oxides was about 100 mTorr or less, that of hydrogen up to two times higher, and CO_2 was virtually absent from the system. Apparently hydrogen facilitates volatization of oxides in CdTe, consistent with the results obtained for elemental cadmium (c.f. Section 3.1).

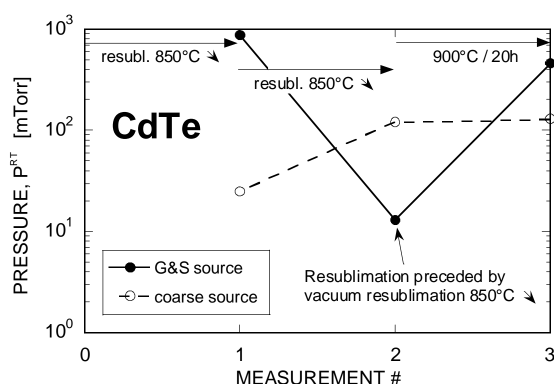


Figure 5. Pressures of residual gas formed in ampoules with CdTe source after consecutive thermal processings. Pretreatment: 700°C / vacuum / 0.15h.

3.6 ZnTe. Development of gas in ampoules with ZnTe is shown in Fig. 6. The amounts of gas formed after pretreatment and resublimation of the ground powders (full symbols), even the one exposed for many hours to air (solid triangles), are not much higher than those found for the coarse source (open circles in Fig. 6). That shows that the pretreatment procedure applied was equally effective in removal of surface contaminants from each material. Resublimation preceded by that done under dynamic vacuum (step 2) leads to a strong reduction in the amount of gas except for the source exposed to air for a long time (Fig. 6). However, similar as observed already for other materials (Figs. 1b, 1c, 2a, 5), this reduction is only temporary: extended annealing at high temperature increases the pressure by a factor of

several for the ground source, to a lesser extend for the coarse one. After extended annealing at 1000ºC (step 3) the gas contains relatively large amounts of hydrogen, either in elemental form or as water (coarse and ground source, respectively). Hydrogen apparently comes from the silica wall (due to high temperature and long annealing time) and most of it forms water in the system containing larger amounts of oxygen. It is consistent with our earlier studies [1, 3, 4] which showed that after annealing at higher temperatures (≥1000ºC) and for an extended period of time the amount of gases desorbed from silica glass of the ampoule (mostly hydrogen) may be comparable to that generated by the source reported in this work. In this study that applies primarily to ZnTe and ZnSe samples.

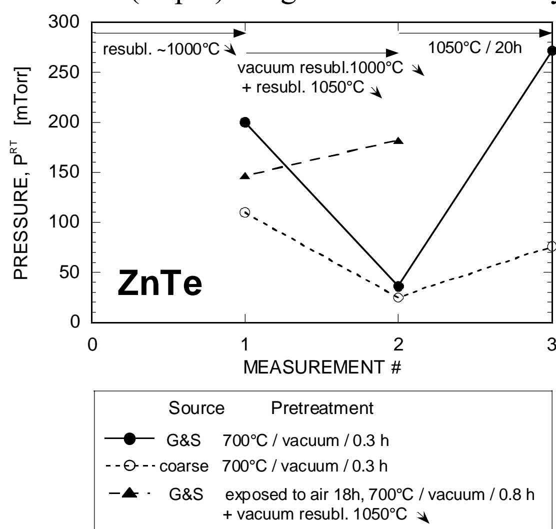


Figure 6. Pressures of residual gas formed in ampoules with ZnTe source after consecutive heat processings.

Extended exposure of the powdered material to air (solid triangles in Fig. 6) apparently affects the amount of impurities, and the amounts of gas generated from the material during the subsequent thermal processings are higher than for the other samples. However, the absolute amount of gas is rather moderate, apparently due to high thermochemical stability of zinc oxide.

3.7 ZnSe. The development of gas from ZnSe source was studied using a ground source pretreated in hydrogen (700ºC / (0.5 atm H_2 / 0.15h + vacuum / 0.15h)). The experiment consisted of a series of consecutive annealings aimed at an effective reduction of the amount of residual gas pressure in the system, what was done using the ampoule shown schematically in Fig. 7 (see the inset). To increase the amount of impurities removed from the source, the total volume of the system (relative to the other experiments presented in this paper) has been increased by connecting an extra, large chamber to the regular experimental ampoule (n/V_{a+ch} = 0.7 mmole/cm^3, Fig. 7). After four annealings the smaller (V_a) chamber was sealed-off and a regular crystal growth process commenced. The n/V_f ratio in the growth ampoule was 14 mmol/cm^3 (as compared to 3 mmol/cm^3 in other experiments reported in this paper). The total pressures and compositions in the system after the annealings are shown in Fig. 7. In addition to the actual pressure in the whole volume (V_a + V_{ch}), Fig. 7 shows the hypothetical pressure that would have existed had the gas

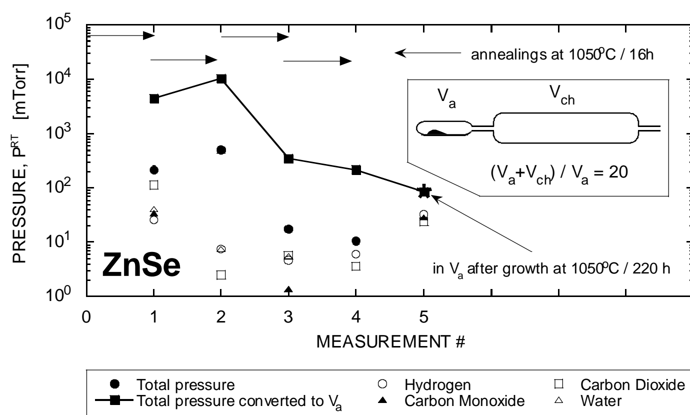


Figure 7. Pressures of residual gas formed in ampoules with ZnSe source after consecutive thermal processings. Source ground and sifted. Pretreatment: 700°C (0.5 atm H_2 / 0.15h + vacuum / 0.15h).

been confined to the volume V_a of the small ampoule only, assuming that the same total amount of gas had evolved from the source. (In reality, some thermochemical equilibria between the gas and the source surface exist therefore, under the real conditions, the amount of gas released to the small volume would have been somewhat less.) As seen in Fig. 7, the small n/V_f ratio in the system allowed for a significant (about 20-fold) reduction of the residual gas pressure after only four annealing cycles. The final pressure in the (growth) ampoule was only about 100 mTorr, what allowed to achieve high growth (mass transport) rate at a relatively low temperature of 1050°C. At lower pressures a significant fraction of the gas is hydrogen which, at those temperatures, comes primarily from the silica glass.

4. SUMMARY AND CONCLUSIONS

Based on the results of our experiments, both thermochemical (the chemical equilibria between the solid and the gaseous phase) and diffusional limitations play a role: dependence of the pressure on the annealing time indicates diffusional limitations, slow reduction in pressure with consecutive annealings implies the thermochemical equilibria factor. As shown in our previous paper [2], most of the impurities (oxides) present on the surface of the source can usually be easily removed by a heat treatment. The removal may be less effective in case of more stable oxides (here: ZnO and SnO). A considerable reduction in pressure after the first four annealings (about one order of magnitude at each consecutive annealing step) was observed for highly contaminated material (Fig. 4b): apparently a significant fraction of the oxide impurities was on the surface of the material and could be volatized relatively fast due to higher diffusion in the gas phase than in the solid. Also, much higher activity of the oxides in the surface layer of the material relative to those dissolved in the bulk increases the equilibrium pressure of the products (eqs. (1) and (3) in ref. [2]) and effectiveness of the oxygen removal. Once that source of residual gas is depleted, further reduction of the amount of gas formed in the ampoule requires both volatization and removal of the volatization products trapped in the bulk of the source, the process that is controlled by much slower diffusion in the solid. At this point thermochemical limitations to the oxide vaporization process become more pronounced, since the oxides dissolved in the matrix have activities which may be much smaller than unity and equilibrium pressures of the volatization products (eqs. 1 and 3 in ref. [2]) become correspondingly lower.

Our experiments show, that reduction in residual gas pressure by their release by resublimation has its limitations. As shown in earlier sections, the pressure in the system right after resublimation may be very low, but in many cases this effect is temporary since much of the oxides remains in the material and subsequent annealing(s) can generate additional and even larger amounts of gas. Resublimation of the source under dynamic vacuum may reduce the amount of only those impurities whose volatilities are higher than that of the matrix [5]. For such impurities the partial pressure ratio of the subliming species is

$$Pi/ Pm = Xs, \quad (1)$$

where Pi and Pm are the partial pressure of the impurity and the matrix, respectively, and Xs is the mole fraction of the impurity in the source. Assuming the (effective) activity coefficient of the impurity deposited within the material as unity, the amount of impurities co-deposited with the matrix materials is

$$Xd = (Pi/ P_i^0) = (Pm/ P_i^0)\ Xs, \quad (2)$$

where Xd is the mole fraction of the impurity in the depositing material and P_i^0 its saturated pressure. After nth resublimation the concentration of the impurity will be Xd = Xs

$(Pm/P_i^0)n$. In case of impurities less volatile than the matrix, after the initial transient a separate phase of the impurity forms, steady-state conditions set in, and the partial pressure ratio is established at

$$Xd = P_i^0 / Pm . \quad (3)$$

Accordingly, some purification takes place only if the initial concentration of the impurity in the matrix exceeds the ratio determined by equ. (3), which also gives the minimum achievable concentration of the impurity in the material.

Besides removal of impurities the sublimation, either under dynamic vacuum or in sealed ampoule releases the products of oxide volatization (CO2, H2O) still trapped in the solid. The removal may be very effective because the saturation pressures of those products are very high. However, as indicated by our experiments, resublimation to low temperature in closed ampoule may trap the released gas back in the deposited material. The alternate procedure, resublimation under dynamic vacuum removes also the intermediate volatile species (H2 and CO) necessary for volatization of the oxides, thus under such conditions the volatization process is hindered.

As discussed above, resublimation may only reduce the amount of impurities, not eliminate them. In addition, by a different mechanism, non-volatile oxides may be transported too. As shown in the Appendix, even impurities of very low volatility and with negligible co-sublimation rate may be transported via a dynamic mechanism by other subliming species: the momentum of the flowing molecules may float/push solid particles of ?m size and have them moved to the deposition region. Since oxide impurities are usually well dispersed in the matrix, they form very fine particles, which can drift along the resubliming species. (We observed that phenomenon directly in our laboratory practice.) This phenomenon may have an additional, adverse effect on the purification process: the surface oxides which could be volatized relatively easily may, after resublimation not preceded by the oxide reduction/removal, get "buried" inside the resublimed material and become more difficult to remove. To prevent transfer of those or other solid particles during resublimation the source should be separated from the deposition zone by a frit filter.

Our series of consecutive heat treatments (with intermediate removal of the gas from the ampoule) show, that the dependence of the residual gas pressure on the n/Vf ratio observed in our studies (ZnSe - c.f. Section 3.7, PbTe [3], CdTe [6]) is not just a result of volatization of a given amount of impurities to different volumes of the gas phase (what would have been the case had nearly all the residual impurities were released to the gas phase during a single annealing) but of thermochemical equilibria between the gaseous species and a rather limited reduction of the concentration of the contaminants in the solid.

Annealing in hydrogen has usually limited effect on removal of oxide impurities from materials. For most elements [5] hydrogen can remove oxygen from the oxide. While the process is rather fast for oxides present on the surface of the source, and hydrogen will diffuse relatively fast into the bulk of the material, the removal of the volatization product (water) is much slower. Therefore, the effect of annealing in hydrogen on reduction of the amount of residual gas is usually limited, and acts rather as a suppressant of CO_2 species. Relatively large effect was observed only for cadmium.

In general, removal of gas-generating impurities is limited by a presence of metal oxides; non-metal, tellurium and selenium (and certainly sulfur) oxides are relatively volatile and can be removed rather easily. Therefore it may be expected that typical features of generation of residual gases (and removal of oxides) from II-VI and IV-VI source materials not investigated in the present work (like CdS and SnSe) will be similar to related same-metal compounds presented in this paper.

As shown in this work, the characteristic features of generation of residual gas from different materials are quite similar: the time scale of evolution of the gas is on the order of hours, relative change of the amount of gas formed during subsequent annealings is rather small (except for extensive surface contaminants), the residual gas pressure after several heat treatment cycles is usually about 100 - 200 mTorr (at RT). A significant degree of removal of oxide impurities and related reduction in the amount of residual gas pressure requires a rather complex, multi-step process. Volatization of impurities (primarily oxides) from materials and reduction of the amount of residual gas formed in sealed systems depends on a number of factors. In general, a single-step procedure is not sufficient to obtain a significant and permanent reduction of the residual gas pressure to the level of 0.1 - 0.3 Torr (at RT). The optimum procedure depends primarily on the properties of the material, like its melting point temperature, volatility, and stability/volatility of its oxides. Applying only simple material pretreatment, the residual gas pressure on the order of 1 - 10 Torr (at RT, for $n/V_f = 3$ mmole/cm^3) may be expected. The removal of the oxide impurities is more effective and the pressures are lower for systems with smaller n/V_f ratios, and vice versa.
Particularly large quantities of residual gas may be expected to form in processes where the material synthesis is followed directly by crystal growth in the same ampoule, as is being done in some techniques. In general, the results discussed in this paper show the complexity of the process of generation of residual gases in crystal growth system. Reduction of the amount of gas depends on different factors, like the material coarseness and volatilities of the matrix and impurity, and need to be tailored to the specific system and requirements.

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Appendix

The effect of a moving gas on a spherical particle of radius R is shown schematically in Fig. A1. Vector V_g represents the average net velocity of the gas, and *d*m is the mass of gas colliding with the particle. Assuming one-dimensional flow of the gas, the momentum changes in directions perpendicular to the average velocity vector cancel out, and the net effect acting on the entire particle is due to the component of the momentum change in V_a (i.e. x) direction, Δp. This momentum change is

$$d(\Delta p) = dm\,(V_g + V_g \cos(2\alpha)) = 2\,dm\,V_g\,\frac{R^2 - r^2}{R^2}\,. \qquad \text{(A1)}$$

Figure 1A. Schematic representation of a collision of gas with a spherical particle.

The mass of gas of density ρ_g, colliding with the particle between r and r+*d*r during the time interval Δτ is

$$dm = 2\,\pi\,r\,dr\,\rho_g\,V_g\,\Delta\tau, \qquad \text{(A2)}$$

what gives

$$d(\Delta p) = 4\,\pi\,\rho_g\,\Delta\tau\,V_g^2\,\frac{R^2 - r^2}{R^2}\,r\,dr. \qquad \text{(A3)}$$

Integration over the entire collision area, $0 < r < R$, yields

$$\Delta p = \pi R^2 \rho_g \Delta\tau V_g^2 . \qquad (A4)$$

This momentum change exerts the force on the particle equal to

$$F = \Delta p / \Delta\tau = \pi R^2 \rho_g V_g^2 . \qquad (A5)$$

Floating becomes possible when this force equals the weight of the particle

$$\pi R^2 \rho_g V_g^2 = 4/3 \pi R^3 \rho_s g, \qquad (A6)$$

where ρ_s is the particle density and g is the gravity. Substituting $\rho_g = (P M_w)/(R_g T)$, where P is the gas pressure, M_w its molecular weight, R_g the gas constant, and T the temperature, the maximum radius, R_f, of a particle that could be floated is

$$R_f = \frac{3 P M_w V_g^2}{4 R_g T g \rho_s} = \frac{3 \rho_s R_g T}{4 g P M_w} V_s^2 , \qquad (A7)$$

where V_s is the deposition velocity ($V_s \rho_s = V_g \rho_g$).

Under dynamic vacuum, without kinetic limitations and under molecular flow conditions, the free vaporization rate (in terms of molar flux) is determined by the Hertz-Knudsen equation

$$J = P / \sqrt{2 \pi R_g M_w T} = V_s \rho_s / M_w . \qquad (A8)$$

Combining eqs. (A7) and (A8) to eliminate V_s we get

$$R_f = (3 / 8 \pi) (P / g \rho_s). \qquad (A9)$$

For ρ_s = 4 g/cm^3 and P = 0.01 mBar, R_f is about 3 µm. Under these conditions and T = 1000K and M_w = 100 g/mole the resublimation rate is about 0.4 mm/h (equ. A8).

Under higher pressures viscous flow dominates, and the resublimation rate can be expressed by [5]

$$J = \frac{a^2}{16 R_g T \eta L} P^2 , \qquad (A10)$$

where a is the radius of the ampoule, L is the source-deposit distance, and η the viscosity of the gas. At P = 0.1 mBar, $\eta = 8\ 10^{-4}$ g / (cm s), and T = 1000K, resublimation under vacuum over a distance of 10 cm in an ampoule of 2a = 15 mm in diameter occurs at a rate of approximately 3 10^{-3} mole/cm^2 h (c.f. equ. 3 in ref. [5]). For a deposit with the density of 0.04 mole/cm^3 (M_w = 100 g/mole, ρ_s = 4 g/cm^3) this rate corresponds to a linear deposition rate of $V_s \approx 0.5$ mm/h. Under such conditions the R_f value is only about 0.05 µm. However, an increase of the resublimation rate to a more commonly applied rate of a few mm per hour (easily achievable even at P below 10^{-3} atm, equ. A10) increases the critical particle size to about R_f = 1 µm (from eqs. A7 and A10 $R_f \sim V_s^{1.5}$). Even larger particles than indicated by eqs. A7 and A9 can be moved by pushing/rolling along the walls of the container instead of floating.

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