

RESIDUAL GAS IN CLOSED SYSTEMS. II. FORMATION OF GASES FROM THE SOURCE MATERIALS

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ABSTRACT. The amount and composition of residual gases formed in sealed ampoules loaded with different elements or binary II-VI or IV-VI compounds and subjected to various thermal processings, annealing and/or resublimation conducted under different conditions were investigated. The results of these experiments are discussed in terms of the procedural, thermochemical, and kinetic limitations to the process.

1. INTRODUCTION

In the previous paper [1] we presented and discussed our results on formation of residual gases in silica glass ampoules. Substantial amounts of such gases can be generated also by source materials: even very high purity, commercial elements and compounds may contain trace amounts of contaminants, particularly oxides. The oxides may have low volatilities themselves but their reaction with other species, particularly hydrogen and carbon, may produce volatile compounds like water or carbon oxides. The amount of the gas and its composition is dependent on the original purity of the material (oxide contaminants) and the heat treatment of the source prior to sealing [2 - 5]. In many cases, particularly at temperatures below about 900°C and in well outgassed ampoules, this source of residual gas dominates. Even a small amount of oxides can produce a significant quantity of gases. Fig. 1 shows the pressure of a one-oxygen gas molecule (CO, H₂O) that can be generated in a closed system as a function of the oxygen content in the source (after complete volatization

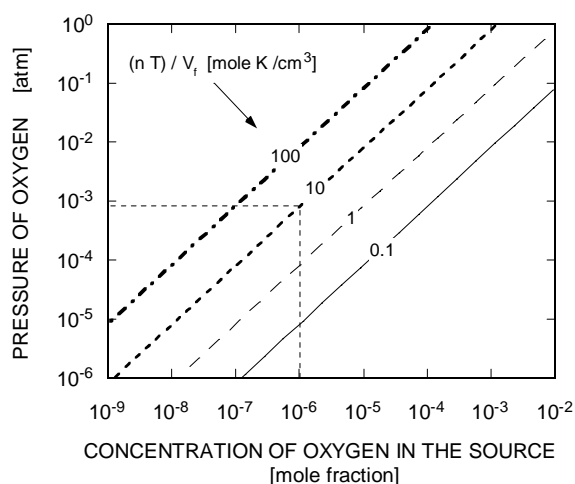


Figure 1. Dependence of the maximum amount (in terms of pressure) of gas that can be formed, as a function of the concentration of oxide impurities in the source. n - the amount of source in moles, T - the temperature, V_f - free volume in the system.

of the oxides) for different material-to-free-volume ratios (nT/V_f , where n is the amount of the source in moles, T is the temperature, and V_f is the free volume). As seen in Fig. 1, for an even moderate value of the nT/V_f parameter of 10 mole/cm³K (corresponding to, e.g., $n = 0.1$ mole, like 24g of CdTe, the free volume $V_f = 10$ cm³, and $T = 1000$ K) and the oxygen content of only 1 ppm, the generated pressure of the residual gas can approach 1 mBar. (It is often being overlooked that the purity of many materials, particularly elements, is given with respect to metal contaminants, marked as mXN or mXNY, e.g. m5N8, thus the amount of oxide impurities can be considerably larger than the nominal purity of the element/compound and the related amount of residual gas formed in the system can be quite high.) Appropriate treatment of the source may allow both for a

reduction of the oxygen content in the materials and a reduced residual gas pressure. We have investigated these phenomena in more details for a number of elements and II-VI and IV-VI compounds. Different source pretreatment and annealing procedures were applied, and subsequent consecutive annealings and measurements were done to determine the origin, magnitude, and composition of the gas in the systems. Our primary goal was to test the effectiveness and limitations of different procedures to reduce the amount and to control the composition of residual gases generated by source materials. In this paper we present the results on gases formed in sealed ampoules after a single annealing. Reduction of the gas amount and its development after subsequent annealings is discussed in a separate paper [6].

2. EXPERIMENTAL PROCEDURES

The experiments were performed by thermal processing of different source materials in sealed silica glass ampoules. The materials were either m6N elements (Se of purity 5N5 was used) or compounds synthesized from such elements. The synthesis was performed under the pressure of 0.1 - 0.5 atm of hydrogen to reduce the amount of oxides in the synthesized products. (It prevented also sticking of the materials to the silica ampoule wall.) PbTe, ZnTe, and CdTe were further purified by resublimation in vacuum. ZnSe as supplied by Eagle-Pitcher Industries, Inc. was used. Cleaned and outgassed under vacuum (at 1000°C for 16+ hours) ampoules of 20 - 30 cm³ in volume were loaded with an appropriate amount of the material such, that the amount of the source per unit free volume in the system was 3 mmole per cm³. The source material was either coarse (CRS, 1 - 3 mm in grain size) or ground and sifted (G&S, < 0.1 mm in size).

To determine the effect of surface oxidation, two procedures of the compound source materials preparation were applied. In the first one the material was ground and sifted in the air, with the total air exposure time of one hour prior to outgassing. In the second procedure the grinding, sifting, and loading of the material into the ampoule was done in a glove box under the atmosphere of argon, and the entire process (until outgassing) lasted a total of fifteen minutes. The temperature and duration of annealing in these experiments were the same as for the corresponding experiments where the source was resublimed in sealed ampoules (see below).

After evacuating, the material in the ampoule was subjected to a selected pretreatment (i.e. vacuum outgassing at RT, baking in hydrogen atmosphere, and/or baking under vacuum) then sealed and heat treated (annealed for a predetermined period of time or resublimed). In some experiments, to reduce the loss of the source material, the ampoule was connected to the vacuum system through a capillary. The temperature of pretreatment was usually 700°C, lower (300 - 480°C) for vacuum annealing of more volatile elements, higher for less volatile materials (particularly when resublimation was performed). Heat treatment of IV-VI compounds in sealed ampoules was usually done within 100°C of the melting point. For II-VI materials the annealings were done at temperatures suitable for PVT processing. After the heat treatment the amount and composition of the residual gas formed in the ampoule was

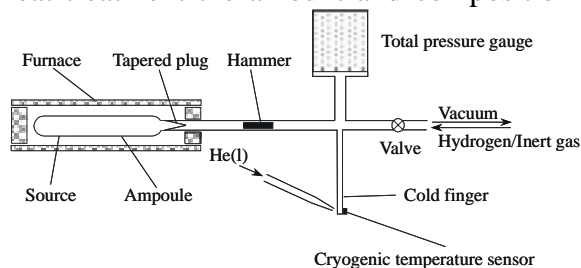


Figure 2. Schematic representation of the experimental system.

measured using the system similar to those used in our earlier studies [1, 2, 7] and shown schematically in Fig. 2. The ampoule is connected to the chamber with a total pressure gauge and the cold finger and, through a valve, to the vacuum. After the system is evacuated and sealed, the tapered tip of the plug is broken with a magnetic hammer and the pressure in the volume is

measured. The original pressure in the ampoule was calculated from the respective volumes of the ampoule and measuring system. The composition of the gas was determined by fractional condensation using the cold finger cooled in a controlled way with a mist of liquid helium. Due to a strong adsorption of water on the surfaces of the measuring system a proper calibration has been done and used to determine the total amount of water formed in the ampoule.

3. RESULTS AND DISCUSSION

The results of our representative experiments are given in Tables 1 - 4. The right-downward arrows (↘) in those tables symbolize resublimation from a given temperature to an undetermined lower temperature occurring when one end of the ampoule remains outside the furnace. The conditions of the material pretreatment are specified with the format "temperature in °C / atmosphere (vacuum or a specific pressure of hydrogen) / duration in hours". The gas formed in the ampoules was found to contain volatile oxides (H₂O, CO₂, and CO) and hydrogen in different amounts and proportions.

3.1 Elements

For elements, materials of coarse granulation were used. The results of our measurements after pretreatment and annealing in sealed ampoules, for several elements, are shown in Table 1. The gas generated in the ampoules is usually dominated either by CO₂ and H₂O, or (when significant fraction of the gas consists of hydrogen) CO and H₂, consistent with our earlier work [8]: more stable oxides (ZnO, SnO, SeO₂) generate preferably CO, less stable form CO₂, while the amounts of hydrogen and water apparently depend on the total amount of H₂ in the system (the hydrogen coming from adsorbed/trapped moisture, silica glass [1, 7], or that dissolved in the source). Substantial amounts of impurity gases form in ampoules evacuated at RT (expts. a, d, f, h, k, and m, Table 1). Except for selenium, a considerable fraction of the gas contains hydrogen or water. At 850°C the amount of hydrogen/water coming from well baked-out silica is very low [1], thus the hydrogen found in the system is coming from the source and/or trapped moisture, as discussed in Section 4. For more stable oxides in the system, ZnO and SnO, the amount of gas is relatively low, and much of the hydrogen remains in the elemental form, consistent with the thermochemistry of the system [8]. It was also found, that backstreaming of organic contaminants from the vacuum system during outgassing at room temperature and their subsequent decomposition into carbon oxides and water during annealing is insignificant.

Apparent removal of most of the impurities (reduction by one or even two orders of magnitude, in some cases to less than 100 mTorr) can be obtained after even short vacuum annealing at an elevated temperature (expts. b, e, g, i, l, and n, Table 1). (Further reduction in residual gas pressure could be achieved, at the expense of the source loss, by extended vacuum annealing at high temperature.) Since the diffusion path in the sources during pretreatment is less than the size of the source itself (for $D = 10^{-5}$ cm²/s and time = 10 min, $\Delta x < 1$ mm), probably most of the impurities (water, oxides) come from the source material surfaces. Surface oxidation might penetrate more than one-atomic layer and contribute more than might be expected from a monolayer of oxide/adsorbate on the actual surface of the material. Annealing in hydrogen may produce increased amounts of gas, particularly water, relative to outgassing in vacuum only (expts. c and j); the water may form in the bulk by fast diffusing hydrogen but may not have enough time to diffuse out and be removed during the vacuum annealing step. Our test experiments showed, that the hydrogen retained in the system after H₂ annealing is contained primarily in the source and not in the silica ampoule wall, consistent with higher diffusivities in the former than in the latter materials.

Table 1 Residual gas pressures and compositions generated in ampoules with elements after a single annealing.

| Exp. | Element | Pretreatment T [°C] / gas [atm] / time [h] | Annealing | | Pressure* [mTorr at RT] | Composition [vol. %] | | | |
|------|---------|--|-----------|----------|----------------------------|----------------------|------------------|-----|----------------|
| | | | T [°C] | time [h] | | CO ₂ | H ₂ O | CO | H ₂ |
| a | Pb | RT / vacuum / 3 | 850 | 5 | > 20,000 | | > 90 | | |
| b | | 700 / vacuum / 0.15 | 850 | 5 | 55 (54) | 12 | 83 | 2 | 2 |
| c | | 700 / 0.1 H ₂ / 0.15 | 850 | 20 | 180 (170) | 7 | 85 | 2 | 5 |
| d | Sn | RT / vacuum / 2 | 800 | 20 | 1,240 (224) | 2 | | 16 | 82 |
| e | | 700 / vacuum / 0.15 | 850 | 20 | 215 (97) | 1 | < 4 | 44 | 55 |
| f | Zn | RT / vacuum / 2 | 800 | 20 | 433 (208) | | | 48 | 52 |
| g | | 470 / vacuum / 0.15 | 800 | 20 | 91 (74) | | | 82 | 18 |
| h | Cd | RT / vacuum / 2 | 800 | 20 | 22,270 (21,900) | 1 | 94 | 3 | 2 |
| i | | 470 / vacuum / 0.15 | 800 | 20 | 1,070 (1,050) | 83 | < 5 | 15 | 2 |
| j | | 700 / 0.5 H ₂ / 0.15 + 470 / vacuum / 0.15 | 800 | 20 | 710 (590) | 33 | 23 | 27 | 17 |
| k | Se | RT / vacuum / 2 | 700 | 5 | 27,000 (27,000) | | | 99+ | |
| l | | 300 / vacuum / 0.15 | 700 | 5 | 396 (396) | 1 | 17 | 82 | |
| m | Te | RT / vacuum / 2 | 900 | 5 | 1,090 (1,090) | 45 | 54 | | |
| n | | 470 / vacuum / 0.15 | 850 | 5 | 22 (18) | 30 | 50 | 4 | 16 |
| p | | 700 / 0.1 H ₂ / 0.15 + 470 / vacuum / 0.15 | 850 | 20 | 38 (11) | 7 | < 20 | 23 | 70 |

*) in parenthesis - pressure without hydrogen

3.2 Compounds

3.2.1 PbTe. The most extensive range of processing parameters was applied to lead telluride samples. Representative results of our measurements after heat treatment of PbTe in sealed ampoules are shown in Table 2. The analysis of these results leads to the following conclusions:

- (1) outgassing at room temperature only leads to the residual pressure on the order of Torr (exp. a). Grinding, sifting and loading of the source under inert gas in a glove box gave similar results;
- (2) outgassing the source under elevated temperature leads to reduction of the residual gas by two orders of magnitude (exp. b);
- (3) without H₂ treatment the residual gas is dominated by CO₂ (expts. b - e), and water (for sources outgassed at RT, exp. a);
- (4) pretreatment with hydrogen has little effect on the amounts of volatile oxides generated in the ampoule (compare expts. d and f);
- (5) under similar thermal processing conditions ground sources generate more residual gas than coarse ones (compare expts. b and c, and g and h). The difference can be quite substantial, particularly if hydrogen annealing is not applied (exp. c);

Table 2. Residual gas pressures and compositions generated in ampoules with PbTe after heat treatment.

| Exp | Pretreatment T [°C]/gas [atm]/time [h] | Heat treatment | | Pressure* [mTorr at RT] | Composition [vol. %] | | | |
|-----|---|----------------------|----------|----------------------------|----------------------|------------------|----|----------------|
| | | Temperature [°C] | time [h] | | CO ₂ | H ₂ O | CO | H ₂ |
| a | G&S, RT / vacuum / 2 | resubl. 880 ↘ | 0.6 | 18,000 | 18 | 82 | | |
| b | G&S, 700 / vacuum / 0.15 | resubl. 880 ↘ | 0.6 | 165 (165) | 93 | | 7 | |
| c | CRS, 700 / vacuum / 0.15 | resubl. 850 ↘ | 1 | 4 (4) | >90 | | | |
| d | G&S, 700 / vacuum / 0.15 | 850 | 5 | 110 (107) | 64 | 26 | 7 | 3 |
| e | G&S, 850 / vacuum / 0.15 | 850 | 16 | 110 (102) | 81 | 8 | 4 | 7 |
| f | G&S, 700 / (0.5 H ₂ / 0.15 + vacuum / 0.1) | 850 | 5 | 285 (117) | 3 | | 38 | 59 |
| g | G&S, 700 / (0.5 H ₂ / 0.15 + vacuum / 0.1) | 850 | 5 | 475 (351) | 3 | 32 | 39 | 26 |
| h | CRS, 700 / (0.5 H ₂ / 0.15 + vacuum / 0.1) | 850 | 2.5 | 125 (34) | 1 | 18 | 8 | 73 |
| i | CRS, 700 / (0.5 H ₂ / 0.15 + vacuum / 0.1) | 950 | 26 | 340 (136) | 1 | | 39 | 60 |
| j | G&S, 700 / (0.5 H ₂ / 0.15 + vacuum / 1) | 850 | 5 | 235 (70) | 4 | | 26 | 70 |
| k | CRS, 700 / (0.5 H ₂ / 0.15 + vacuum / 0.1) | resubl. 900 → 850 | 25 | 215 (120) | 8 | 38 | 10 | 44 |

*) in parenthesis - pressure without hydrogen

(6) larger amounts of gas are generated during higher temperature/longer annealing conditions (compare expts. h and i);

(7) extended outgassing under vacuum has only a limited effect on the amount of gas generated during the subsequent annealing (compare expts. f and j);

(8) similar amounts of gas in ampoules d and e, where the former has been vacuum outgassed at lower temperature (700°C vs. 850°C) but annealed for a shorter time (5h vs. 16h) than the latter implies, that higher outgassing temperature improves somewhat the effectiveness of the gas reduction process;

(9) extended annealing and resublimation to a high temperature generate similar amounts of gas (compare expts. i and k).

(10) in case of hydrogen pretreatment, up to 75% of the gas may be composed of H₂. The amount of volatile oxides formed is typically around 0.1 Torr (at RT).

The single most important factor in reducing the amount of residual gas is vacuum outgassing of the source at elevated, not at room temperature. Preparing and loading the source in a glove box does not make a lot of difference: the amount of gas generated during annealing is still on the order of Torr. Large amounts of residual gas found in ampoules outgassed at RT might be due to surface adsorption and/or oxidation. However, a simple calculation shows that a monolayer of an adsorbate or oxide layer on the surface of the source grains could produce, upon desorption, not more than about one Torr of gas. At least one order of magnitude higher pressure generated in ampoule a indicates, that most of the impurities removed during vacuum annealing comes from the bulk.

As long as the source is outgassed at an elevated temperature, the amounts of residual gases are in the range of 0.1 - 0.5 Torr at RT. Other factors do not affect the amounts of gas generated in the system much. The coarseness of the source material has only some effect. A large reduction in the amount of gas was observed only when coarse source was resublimed to ambient temperature (exp. c); otherwise its magnitude was comparable to powder materials. Part of the effect seems to be due to smaller, relative to powdered materials surface for adsorption and can explain the difference in pressures between expts. b and c, where the source was resublimed in a short time. In case of annealing the difference may be due to a reduced area of the solid-gas interface for diffusion of impurities out of the source. The smaller surface area reduces then the rate of the gas generation but not the real amount of impurities present in the bulk of the source.

3.2.2 Tellurides of Sn, Cd, and Zn. The pressures and compositions found after annealings of the tellurides are shown in Table 3. The following conclusions can be derived from these results:

Table 3. Residual gas pressures and compositions generated in ampoules with tellurides after heat treatment.

| XTe | Exp | Pretreatment T [°C] / gas [atm] / time [h] | Heat treatment | | Pressure* [mTorr at RT] | Composition [vol. %] | | | |
|------|-----|---|---------------------|-------------|----------------------------|----------------------|------------------|----|----------------|
| | | | Temperature [°C] | time [h] | | CO ₂ | H ₂ O | CO | H ₂ |
| SnTe | a | G&S, RT / vacuum / 2h | 800 | 17 | 13,400 | 4 | 88 | 1 | 7 |
| | b | G&S, 600 / vacuum / 0.15 | resubl. 800 ↘ | 17 | 890 (880) | 61 | 5 | 33 | 1 |
| | c | CRS, 600 / vacuum / 0.15 | resubl. 800 ↘ | 2 | 48 (40) | 40 | | 43 | 17 |
| | d | G&S, 700 / (0.5 H ₂ / 0.15 + vacuum / 0.1) | 850 | 0.3 | 215 (37) | 1 | 5 | 11 | 83 |
| ZnTe | e | G&S, RT / vacuum / 2h | 1030 | 0.3 | 9,300 | 3 | 93 | 1 | 3 |
| | f | G&S, 700 - 800 / vacuum / 0.3 | resubl. 1030 ↘ | 0.3 | 200 (200) | 72 | | 28 | |
| | g | CRS, 700 / vacuum / 0.15 | resubl. 980 ↘ | 0.6 | 110 (110) | 25 | 6 | 68 | 1 |
| CdTe | h | G&S, RT / vacuum / 2h | 850 | 1 | 9,500 | 18 | 30 | 22 | 30 |
| | i | G&S, 700 / vacuum / 0.15 | resubl. 850 ↘ | 1 | 600 (590) | 19 | 4 | 76 | 1 |
| | j | CRS, 700 / vacuum / 0.15 | resubl. 850 ↘ | 0.3 | 9 (9) | 71 | | 29 | |
| | k | G&S, 900 / (0.5 H ₂ / 0.15 + vacuum / 0.1) | 900 | 1 | 215 (24) | | 4 | 7 | 89 |

*) in parenthesis - pressure without hydrogen

- (1), the amount of gas generated in ampoules outgassed at RT is about 10 Torr (expts. a, e, and h). Large, if not dominant component of the gas is water. Similar results were obtained for sources prepared and loaded in a glove box;
- (2), outgassing the source under vacuum at an elevated temperature reduces the amount of residual gas by at least one order of magnitude (expts. b, f, i);
- (3), coarse sources, particularly those of SnTe and CdTe, produce less gas than powdered materials heat treated under the same conditions;

(4), hydrogen pretreatment reduces the amount of oxides in the system by over one order of magnitude (but with a simultaneous increase in hydrogen content).

Similarly as for PbTe, the most important factor reducing the amount of residual gas generated in the ampoule is the elevated temperature of the source during outgassing. Further reduction in the amounts of gas was observed when coarse sources were resublimed to low temperature (expts. c, g, and j, Table 3). Reduced amounts of oxides were found when the source was pretreated with hydrogen (expts. d and k).

It should be noted that in systems annealed at higher temperatures (about 1000°C and more) and for an extended period of time the contribution of gases desorbed from silica glass of the ampoule may be comparable to that generated by the source itself (i.e. without H₂ pretreatment) [1, 2, 7]. In this study this applies to ZnTe and ZnSe samples. At lower temperatures and/or shorter annealing times (provided that a sufficient ampoule outgassing under vacuum has been done) the relative contribution from silica may be significant only if the amounts of gas generated from the source are very low (<< 1 Torr). The gases released by silica are dominated by hydrogen [1, 2, 7].

3.2.3 Selenides. The results of our experiments with selenides, PbSe and ZnSe, are shown in Table 4. As in previous experiments, the amounts of gas produced from sources outgassed at

Table 4. Residual gas pressures and compositions generated in ampoules with selenides after heat treatment.

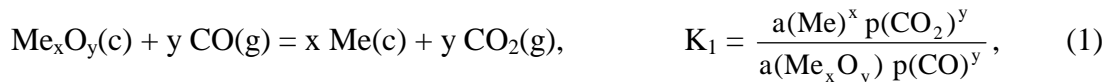
| XSe | Exp | Pretreatment T [°C] / gas [atm] / time [h] | Heat treatment | | Pressure* [mTorr at RT] | Composition [vol. %] | | | |
|------|-----|--|---------------------|-------------|-------------------------------|----------------------|------------------|----|----------------|
| | | | Temperature [°C] | time [h] | | CO ₂ | H ₂ O | CO | H ₂ |
| PbSe | a | G&S, RT / vacuum / 2 | 920 | 1.7 | 6,700 | 95 | | 5 | |
| | b | G&S, 700 / vacuum / 0.15 | resubl. 920 ↘ | 1.7 | 270 (255) | 22 | | 73 | 5 |
| | c | CRS, 700 / vacuum / 0.15 | resubl. 920 ↘ | 1.5 | 17 (17) | 22 | | 75 | 3 |
| | d | G&S, 700 / (0.5 H ₂ / 0.15+ vacuum / 0.1) | 750 | 1 | 180 (60) | 7 | 12 | 14 | 67 |
| ZnSe | e | G&S, RT / vacuum / 2 | 1,030 | 4 | 10,600 | 17 | | 83 | |
| | f | G&S, 700 / vacuum / 0.15 | resubl. 1,030 ↘ | 4 | 1,960 (1840) | 15 | | 79 | 6 |
| | g | CRS, 1,140 / vacuum / 0.15 | 1,100 | 72 | 320 (320) | 52 | <15 | 47 | |
| | h | G&S, 900 / (0.5 H ₂ / 0.3 + vacuum / 0.1) | 1,100 | 60 | 490 (190) | 13 | <6 | 25 | 61 |

*) in parenthesis - pressure without hydrogen

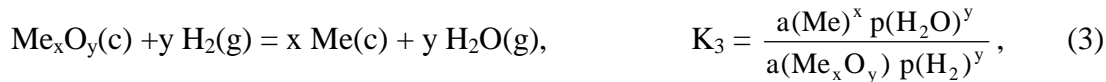
room temperature (expts. a and e), whether prepared in the air or in a glovebox, are about one order of magnitude or more higher than when the outgassing is done at an elevated temperature (expts. b and f). Different that for tellurides, the gas does not contain hydrogen. In experiments without H₂ preannealing the gas consists essentially of carbon oxides. Coarse sources produce a pressure much lower than that formed from the ground material only when resublimed to ambient temperature (exp. c). Pretreatment with hydrogen reduces the amounts of volatile oxides, adding however a significant portion of H₂ to the gas (expts. d and h in Table 4).

4. SUMMARY AND CONCLUSIONS

As shown in Section 3 above, residual gases generated from the source materials consist of carbon oxides, water, and/or hydrogen. Different sources of these gases are possible. The as-supplied elements may contain gases, most likely hydrogen, dissolved in the material during the manufacturing process. Such hydrogen could produce both elemental H₂ and water found in larger quantities in the experiments with room temperature outgassed sources. This source of hydrogen is quite probable in the case of our elemental sources. Large quantities of gas found in RT-outgassed compound sources could not be unambiguously attributed to the materials preparation conditions. PbTe, ZnTe, and CdTe were resublimed under vacuum after synthesis and could not contain larger quantities of H₂/H₂O dissolved in the resublimed material. On the other hand, as-synthesized PbSe, formed under 0.1 atm of hydrogen, did not produce any noticeable amount of hydrogen or water (exp. a in Table 4). That suggests that, at least for our compound sources, the residual gas is not released from but generated in the source material from rather non-volatile impurities. This conclusion is further supported by the fact, that after fast resublimation the ampoules contain rather low amounts of gas. The (metal) oxides, which typically have low volatility, could react with hydrogen and (unavoidable) trace amounts of carbon forming water and carbon oxides. Since both carbon and the metal oxides are solid, the formation of carbon oxides has to proceed through intermediate species in the cycle:



where (g) and (c) denote gaseous and condensed phase, respectively, K's are the equilibrium constants, p's are the partial pressures, and a's are diffusivities of the respective species. Hydrogen can react directly with the oxide:



while water can react with carbon and recycle hydrogen:



The interrelation between carbon oxides, water, and hydrogen is determined by the reaction



The equilibrium constant of reaction (5) is between 0.77 at 1000K and 1.9 at 1300K. Under such conditions, unless large amounts of hydrogen or free carbon are present (leading, at higher temperatures, to CO pressure being much higher than that of CO₂), all of the above gaseous species can contribute to a similar degree to the residual gas in the system. With a limited accessibility of carbon (limited to trace impurities dispersed in the bulk of the source) larger amounts of oxides lead to relatively large fraction of the oxygen in the gaseous phase being in the form of carbon dioxide, as observed experimentally. It should be noted, that metal impurities forming more stable oxide (than those of the matrix components) act as a getter, reducing the equilibrium pressure of the gaseous oxides over the source. They reduce the effectiveness of the oxide volatilization process also but, particularly at low concentrations of oxygen, may reduce the actual residual gas pressure in the system.

Our results indicate, that generation of at least part of the gas is slow, on the order of hours. That suggests, that oxide impurities dispersed in the bulk of the source may contribute

significantly to the gas in the system. The oxides in the bulk get removed rather slowly for two reasons: thermochemical and kinetical. At very low concentration levels practically all oxide impurities are dissolved in the matrix. As a consequence, the activities of the oxides (and related equilibrium pressures of volatile oxides) are correspondingly lower than when they are present as a separate phase. Fig. 3 shows the dependence of the degree of removal/volatization of the oxides on their stability for different concentrations of the oxide and the material-to-free_volume ratios (n/V_f). The stability is represented by the Gibbs energy of formation of carbon monoxide in the reaction



The calculations were made assuming that the entire source is in equilibrium with the gaseous phase. Fig. 3 shows the results of the calculations for two different n/V_f ratios (0.1 and 0.001 mole/cm³) and two final (equilibrium) concentrations (molar fractions of 10^{-2} and 10^{-8}), for the temperature of 1300K. The initial concentration of a given oxide is X_{in} , and X_{eq} is its concentration after the system equilibrates thermochemically. It was assumed that the activity of the oxide is equal to its mole fraction in the solid. As can be seen from Fig. 3, the degree of volatilization depends primarily on the stability of the oxide, and strongly on the n/V_f ratio in the system. The actual concentration of the oxide in the matrix, particularly at small n/V_f values, is of lesser relevance (Fig. 3). For less stable oxides, like PbO, the thermochemical effectiveness of volatilization is high even at large n/V_f ratios. For moderately stable oxides (SnO) the effectiveness of the process is strongly dependent on the n/V_f ratio. For very stable oxides (ZnO) only small n/V_f ratios

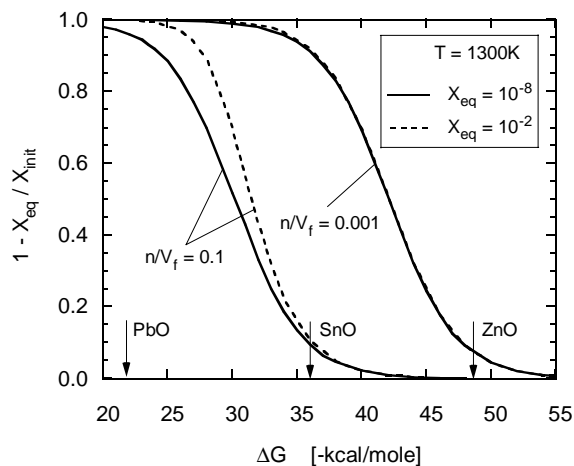


Figure 3. Degree of volatilization of oxides by carbon as a function of the Gibbs energy of formation of carbon monoxide from carbon and MeO oxide.

allow for a noticeable volatilization (removal) of oxygen from the source. However, the equilibrium pressures of the volatile species over such oxides are rather low anyway [8] so their reduction may not be of a major concern. It should be noted, that equilibrium in the reduction reactions (eqs. 1 and 3) may depend on the stoichiometry of the matrix: for compositions with the metal content below that of the metal-rich homogeneity range (at the actual annealing temperature) the activity of the metal product will be less than unity and, thus, the equilibrium pressures of the volatile products (CO_2 and H_2O in eqs. (1) and (3), respectively) will be higher [8]. Similarly, if the activity of the oxide is higher than its mole fraction, the volatilization is more effective than shown in Fig. 3 (in the extreme case, when the concentration of the oxide exceeds its solubility limit, it forms a separate phase).

The second limitation to the process of evolution of residual gases comes from the diffusion step necessary to transport the reacting species (CO and H_2 , eqs. 1 and 3, respectively) to the oxides dispersed in the bulk, and to take the reaction products (CO_2 , H_2O) out of the condensed phase. Taking the thickness of the liquid (for experiments with the annealing temperature higher than the melting point) of about 2 mm, and diffusivity equal to 10^{-5} cm²/s, the diffusion time is on the order of 1 hour. For diffusion in solid sources, even when powdered materials are used, the diffusion time may be even longer. These estimates are consistent with the time scale of the processes observed in our investigation. As diffusion of the volatilization products progresses their partial pressures in the ampoule increase slowing

the entire process. Conducting the process under dynamic vacuum is of no help, since it removes also the species (H_2 and CO), which facilitate oxide volatilization.

Coarse sources may contain lower amounts of oxide impurities due to relatively small surface area exposed to oxidation/adsorption prior to the material processing. In a system with the n/V_f ratio of 3 mmole/cm^3 , a mono-atomic layer of impurities on a compact source ($\sim 10 \text{ cm}^2$ in the surface area) could generate only about 10 mTorr of residual gas. When the source is made of grains of about 3 mm in size, its surface (and the amount of surface impurities) is higher by a factor of about 4. For powdered source with grains of 0.1 mm in size and one oxygen atom per 20 sq. Å of the grain surface, the total amount of the impurities corresponds to about 2 Torr of CO or H_2O (at RT). However, the oxides of Te, Se, Pb, Sn, and Cd are relatively volatile and can easily be removed from the source surface during outgassing at 700°C [8]. ZnO is much less volatile and most of it may remain with the source ($ZnTe$, $ZnSe$).

As seen in the Tables, the sources outgassed at room temperature contain large amounts of water. To verify if such amounts can be retained on the source surface after outgassing we performed a test experiment. An ampoule was filled with a quartz wool in the amount such that its total surface area corresponded to that of our finely ground source. Hydrophilic nature of silica assures that a large part of its surface could contain adsorbed water. The ampoule with the wool was outgassed at 1000°C for 16 hours, and then exposed to ambient conditions with humidity of about 50 - 70% for over one day. Under such conditions the surface of silica gets densely covered with water [9]. Then the ampoule was outgassed under vacuum at room temperature for 2 hours, sealed off, and annealed at 800°C for one hour, and the amount of water in the ampoule was measured. The amount found was on the order of 20 mTorr. That result indicates, that the effect of surface adsorption on the amount of gas formed in the ampoule is negligibly small. Generally, comparable amounts of gas formed from coarse and finely ground sources outgassed at elevated temperatures show, that surface oxidation is of minor importance also. That means, that outgassing under vacuum at high temperature removes impurities from the bulk of the source. One might expect that finely ground source will facilitate desorption of impurities during annealing and, thus, much higher pressures of gas will be generated relative to coarse materials. However, at high temperatures the powders sinter and the advantage of a large area of the materials for removal of impurities is largely lost. Moreover, slow volatilization of source impurities limits the effectiveness of purification during the outgassing process.

Hydrogen can remove oxygen from most elements [8]. The reaction with H_2 is rather fast for oxides present on the surface of the source and may facilitate their volatilization. When it comes to reaction with oxides dispersed in the matrix, hydrogen diffuses relatively fast into the material, but removal of the volatilization product (water) from the bulk is much slower. Therefore annealing in H_2 has often only limited effect on removal of oxide impurities from materials.

During bakeout in hydrogen some of the gas can dissolve in the source and silica. Taking the diffusivity of hydrogen as $2 - 3 \cdot 10^{-5} \text{ cm}^2/\text{s}$ (literature data for diffusion in silica at 700°C), during a 15 minute annealing the hydrogen penetrates solids to a depth of about 0.05 mm. That indicates, that a more significant solution of hydrogen may be expected only in the case of finely ground materials. Assuming a complete saturation of the source with hydrogen, the annealing carried out under the pressure of 0.5 atm, the ratio of the volume of the source to that of the ampoule $V_s/V_a = 0.1$, and the physical solubility with the Bunsen coefficient (i.e. the ratio of the concentration of hydrogen in the material and in the gas) of 0.02, the total amount dissolved in the source corresponds to about 0.2 Torr (at RT). When annealing in hydrogen is followed by that under dynamic vacuum, part of the dissolved hydrogen is

removed from the solids. Consistent with the above, in experiments where annealing in H₂ was applied some portion of the residual gas contained hydrogen. In the case of physical solubility practically all such hydrogen should be released to the vapor phase during the annealing step. However, after hydrogen pretreatment, meaningful and even higher than expected amounts of H₂ may be found. That phenomenon can be explained by chemical solubility of hydrogen in silica and in the source material. With chemical solubility mechanism, larger amounts of hydrogen (than in the case of physical solubility) can dissolve in the materials, and its release back to the vapor phase is rather slow [10]. The relative importance of chemical solubility of H₂ in silica is particularly pronounced at low pressures [10]. At higher annealing temperatures (above about 1000°C) a presence of H₂ was observed even without hydrogen pretreatment. This gas has, apparently, been desorbed from the silica ampoule walls, consistent with our other studies on outgassing of silica glass [1, 7].

As shown in this work, the characteristic features of generation of residual gas from different materials are quite similar for all materials investigated. The time scale of evolution of the gas is on the order of hours. The process of volatilization of impurities (oxides) from the materials and reduction of the amount of residual gas in sealed systems depends largely on the source preparation and pretreatment procedures. Applying only simple outgassing at RT prior to sealing, residual gas pressure on the order of 1 - 20 Torr (at RT and $n/V_f = 3$ mmole/cm³) may be expected. Most of the impurities can be removed by vacuum bakeout at an elevated temperature. Such procedure leads to reduction of residual gases in the system to a small fraction of one Torr (at RT and at n/V_f of a few mmole/cm³). (Appropriately different pressure ranges may be expected for systems with other n/V_f ratios [4]). Smaller amounts of gas were observed with coarse sources. However, as shown in our subsequent paper [6], this effect is largely temporary. Further than by a single annealing reduction in the amount of gas (and oxide impurities) is apparently more difficult to achieve since its presence is due to non-volatile impurities dispersed in the bulk of the materials. We studied that issue with a series of subsequent annealings of the source materials. The results of that study are presented in a separate paper [6].

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