CHEMISTRY LETTERS, pp. 1413-1416, 1987.

Closed-Tube Chemical Transport of V_xSe_2 by Iodine. Observation of Pressure Gradient of Selenium Vapor in a Transport Tube

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The pressure gradient of selenium vapor was observed in the closed-tube chemical transport of $V_xSe_2 + I_2$ system, by using the specially designed transport tube. Vapor pressure of selenium decreases almost linearly with distance x of the tube from the hot to the cold zone. This was explained by the steady-state gas diffusion process by comparison with the transport rate.

Single crystals of a large number of transition-metal chalcogenides can be prepared by adopting the closed-tube chemical transport technique using the halogen gases as transport agents.[1] In general, however, it is not easy to obtain the crystals with desired compositions because these chalcogenides tend to have a wide composition range of nonstoichiometry. Through the chemical transport investigations of $Ti_xS_2 + I_2$ system, Saeki et al. pointed out that there is a close relationship between the chemical composition of starting material and that of grown crystals,[2-4] i.e. under the condition that the amount of Ti_xS_2 is large enough as compared with that of iodine, the sulfur pressure P_{S2} within the tube is fixed at the equilibrium P_{S2} of the starting composition, and therefore the chemical composition of grown crystal is governed by the equilibrium P_{S2} of starting material at the high-temperature side. This consideration also was verified in the chemical transport reactions of $V_xSe_2 + I_2$[5,6] and $V_xS_2 + I_2$ systems.[7] In both experiments, however, it was observed that this mechanism is not valid in the metal-rich composition range; in this range the vanadium contents of the grown crystals are larger than those expected from P_{Se_2} (or P_{S2})-composition isotherms, which implies that P_{Se2} (or P_{S2}) at the low-temperature side is lower than that at the high-temperature side. For $V_xSe_2 + I_2$ system, we explained it is owing to the increase of the transport rate with increasing vanadium content.[5] For further clarification, however, it should be necessary to observe the pressure-gradient of selenium vapor within the tube.

The purpose of the present work is to observe the P_{Se_2} at different positions of the tube for the $V_xSe_2 + I_2$ system. The results obtained will be discussed in terms of the gas diffusion of selenium, by comparison with the results of transport rates.

The experimental conditions of the transport and the method of chemical analysis were the same as described in the previous paper.[5]

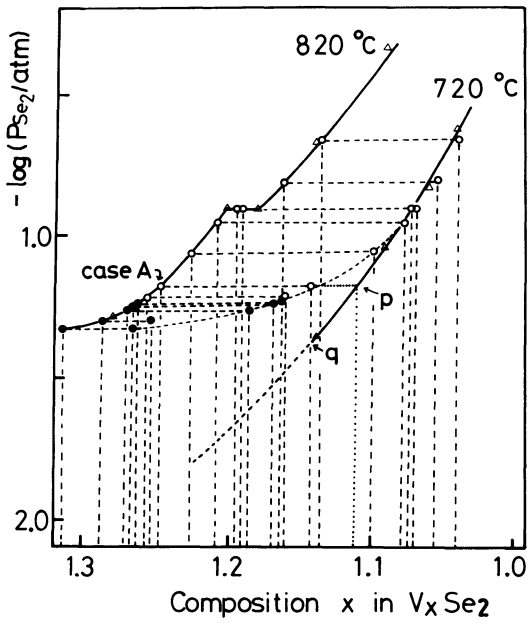

Fig. 1. Relation between the compositions of V_xSe_2 and the equilibrium selenium partial pressure P_{Se_2}. The end point at the left-hand side of the horizontal broken line and that at the right-hand side correspond to the compositions of the residual V_xSe_2 and the grown crystals, respectively. Open circles, closed circles and open triangles show the previous results,[5] the present results and the published data of the equilibrium P_{Se_2},[8] respectively. See text for the notation p and q.

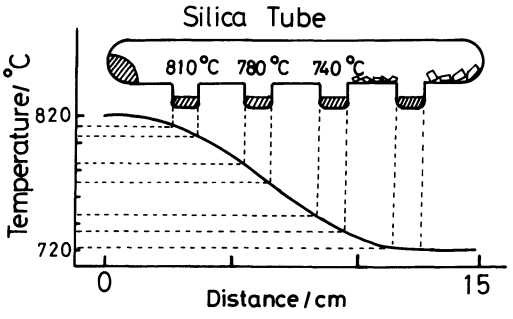

Fig. 2. Schematic diagram of the transport tube specially designed for the observation of P_{Se_2} at different positions of the tube. The temperature gradient in the actual transport is shown below.

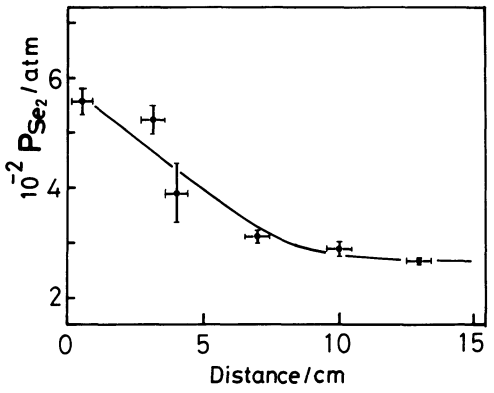

Fig. 3. Observed P_{Se_2} as a function of distance x in the chemical transport of V_xSe_2 (compositions of starting material, residual material and grown crystals are x=1.238, 1.264, and 1.187, respectively).

Figure 1 shows the relationships between the chemical compositions of V_xSe_2 (both residual materials and grown crystals) and the equilibrium vapor pressure P_{Se_2}, where the isotherms (full lines) are taken from the published data.[8] The open and the closed circles represent the previous results[5] and the present results, respectively. For $x < 1.21$ (x is the composition of residual material V_xSe_2), the compositions of grown crystals are fairly consistent with the intersections of the horizontal tie lines on the P_{Se_2}-composition isotherm of 720 °C, which

implies that the vapor pressure of selenium is uniform throughout the tube. But for $x > 1.22$, the compositions of grown crystals tend to deviate from the isotherm of 720 °C towards the metal-rich compositions. This means that the P_{Se_2} is no longer uniform in this composition range. Let us consider it in more detail for the case of A (see Fig. 1), where the composition x of residual material is 1.250. If the P_{Se_2} (=0.066 atm) is assumed to be uniform within the tube, the grown crystals should have the composition at the intersection of horizontal tie-line on the isotherm of 720 °C (point p): x=1.114. But it is not the case; the observed composition of grown crystals is x=1.142. The value of actual P_{Se_2} at the cold zone, therefore, is assumed to be 0.041 atm which is obtained from the point q on the isotherm of 720 °C corresponding to x=1.142. In this case the pressure difference of selenium vapor (ΔP_{Se_2}) in the tube is 0.025 atm.

By using the similar procedure, we can estimate the P_{Se_2} at different positions in the tube. For this purpose, we used the specially designed transport tube as illustrated in Fig. 2. The small silica baskets were attached to the transport tube at regular intervals; each basket contains a small amount of V_xSe_2 (about 100 mg) with the same composition as the starting material. This transport tube was set up under the same condition as the actual chemical transport. After the reaction the compositions of samples in the baskets were determined by the chemical analysis. As the solid selenides in the baskets are in equilibrium with the selenium vapor pressure over them, the values of P_{Se_2} at different positions of the tube can be obtained by fitting the compositions of the samples to the corresponding P_{Se_2}-composition isotherms; isotherms for different temperatures have been reported in Ref. 8.

Figure 3 gives the P_{Se_2} (atm) as a function of distance x of the tube; the composition of starting material is $V_{1.238}Se_2$ (residual material is $V_{1.264}Se_2$) and the temperature gradient 820-720 °C. The value of P_{Se_2} decreases almost linearly with distance for $x < 8$ cm. Non-linear part of P_{Se_2} curve at $x > 9$ cm corresponds to the region where the temperature is scarcely changed with x. Thus, we will focus on the linear part of P_{Se_2} curve.

As the total pressure in the tube is about 1 atm, we can assume that the rate-determining step in this case is the diffusion.[1] As is well known in the steady-state diffusion, the linear dependence of concentration c (or vapor pressure P) on distance x is deduced from Fick's law $J=-D\,\partial c/\partial x$, by assuming both J (diffusive flux) and D (diffusion constant) to be constant. The linear change of P_{Se_2} with x as shown in Fig. 3 clearly indicates that the material is transported by steady-state diffusion process.

Figure 4 shows the transport rate as a function of x of residual V_xSe_2. The closed circles (solid line) indicate the experimental results; the transport rate increases with x. This is explained as follows. In the case of diffusion-limited transport, the transport rate depends on several factors such as pressure difference of transport gas between the hot and the cold zone (ΔP), diffusion coefficient (D), length of the diffusion path (s) and so on.[1] In the present system, ΔP_{Se_2} increases greatly with x as shown in Fig. 1. We can assume, thus, the change of the other factors (D and s etc.) is negligibly small as compared with that of

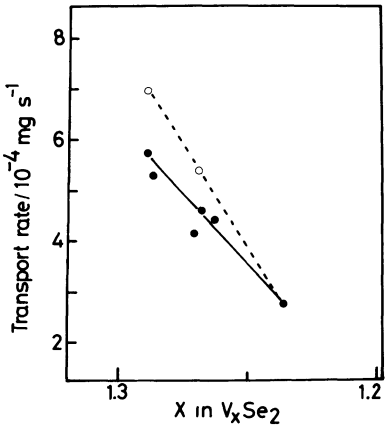

Fig. 4. Transport rate as a function of x (x is the composition in residual V_xSe_2). Closed circles represent the observations. Open circles represent the results estimated from the pressure difference ΔP_{Se_2} within the tube. See text for detail.

ΔP_{Se_2}. On this assumption, we obtain a linear relationship between the transport rate and ΔP_{Se_2}. The values of ΔP_{Se_2} can be estimated from the data in Fig. 1, while we are obliged to use the values of P_{Se_2} hypothetically extrapolated from the observed isotherm of 720 °C. The open circles (broken line) in Fig. 4 show the x dependence of transport rate estimated from ΔP_{Se_2}. Since D or s is unknown in this system, we can estimate only the relative values of transport rate. Thus, in Fig. 4 are shown the calculated results obtained by fitting the values of $V_{1.236}Se_2$ to the observation. The calculation is qualitatively consistent with the experiments.

As a result, we observed the pressure gradient of selenium vapor in the transport tube for the $V_xSe_2 + I_2$ system ($x > 1.22$), which is explained in terms of the steady-state diffusion of selenium gas. The materials with a less amount of vanadium also may be transported by the diffusion, but it was not observed presumably because a large amount of selenium gas does not cause the non-uniformity of P_{Se_2} within the tube.

The authors would like to express their sincere thanks to the late Professor M. Nakahira for many fruitful suggestions and discussions.

References

1) H. Schäfer, "Chemical Transport Reaction," Academic Press, New York & London (1964).
2) M. Saeki, J. Cryst. Growth, 36, 77 (1976).
3) M. Saeki, Mat. Res. Bull., 12, 773 (1977).
4) M. Saeki, M. Ishii, I. Kawada, and M. Nakahira, J. Cryst. Growth, 45, 25 (1978).
5) T. Ohtani, H. Nakamura, M. Nakahira, and M. Ishii, J. Less-Common Met., 77, 185 (1981).
6) M. Nakahira, T. Ohtani, and H. Nakamura, React. Solids, 1982, 321.
7) M. Wakihara, K. Kinoshita, H. Hinode, and M. Taniguchi, J. Cryst. Growth, 56, 157 (1982).
8) K. Hayashi and M. Nakahira, J. Solid State Chem., 24, 153 (1978).

(Received April 6, 1987)