NOTE

An Electron Diffraction Investigation of the Molecular Species in the Vapor Phase of the GaAs-I_2 System

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The growth of single crystals from a vapor phase has become an important technique in the preparation of single crystals of such semiconducting compounds as GaAs. It has recently been discovered[1] that, when a small quantity of iodine is added as a carrier to polycrystals of GaAs, the starting material, the growth takes place at relatively low temperatures of about 700°C, although GaAs itself has only a negligible vapor pressure at such temperatures. It is, therefore, important to identify the reacting species in the vapor phase in order to understand the mechanism of the crystal growth. After we had started the high-temperature diffraction work for this purpose, Silvestri and Lyons[2] published their work on this system by vapor-pressure measurements; they showed that the vapor phase of this system consists mainly of GaI_3 and As_4 and established the $2GaAs(s)+GaI_3(v)\leftrightarrow 3GaI(v)+(1/2)As_4(v)$ reaction in the 560—850°C temperature range.

In the present work, in pursuit of a possible change in the species present in the mixture at different temperatures, a vapor-phase equilibrium of the GaAs-I_2 system at a lower temperature of 440°C has been studied by the sector-microphotometer method of electron diffraction. The above temperature was also selected because the operation of the present high-temperature nozzle was easier below 500°C.

Experimental

Polycrystals of GaAs of a high purity were kindly supplied by the Tokyo Shibaura Electric Co. The sample of iodine was purified by sublimation. About 0.1 g. of the iodine and an excess amount (about 1 g.) of the crystals were placed in the oven of the nozzle at the same time. After the mixture had been degassed for about ten minutes in a vacuum, it was slowly heated to 440°C in about 30 min. The diffraction photographs were taken under conditions almost the same as those described in a preceding paper.[3]

Results and Discussion

One diffraction photograph of the GaAs-I_2 reaction system was analyzed. The molecular intensity curve, $qM(q)$, which was obtained by the drawing of a smooth background line across the experimental total intensity curve was found to be similar to those of the GaI_3 described in a preceding paper.[4] The molecular intensity curve thus obtained is compared with the theoretical curve of the GaI_3 in Fig. 1.

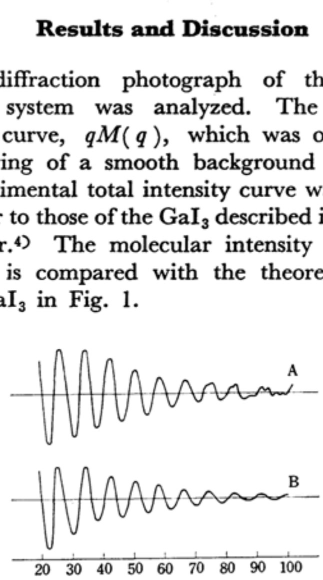

Fig. 1. Molecular intensity curve of GaAs-I_2 at 440°C.
A: Observed $qM(q)$ of GaAs-I_2
B: Calculated $qMq(q)$ for the GaI_3 model

Since the intensity of a small-angle region is sensitive to the specimen, it seemed desirable to examine the $q<20$ region in order to confirm that the system was indeed GaI_3. The photograph taken by the usual procedure was not suitable for this study, since the beam trap of the sector interfered with the observation of the diffraction pattern in this region. Moreover, the nozzle

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1) G. Antell and D. Effer, J. Electrochem. Soc., 106, 509 (1959).
2) V. J. Silvestri and V. J. Lyons, ibid., 109, 963 (1962).
3) Y. Morino, T. Ukaji and T. Ito, This Bulletin, 39, 64 (1965).
4) Y. Morino, T. Ukaji and T. Ito, ibid., 39, 71 (1965).

assembly was not designed for use at a longer camera distance. The features of the diffraction pattern in that range of the scattering angles were, therefore, examined qualitatively by the following procedure. The sector was removed, and the photographs were taken with two different exposure times: about one second, and one and a half seconds. The photographs were then traced with a microphotometer across the diameter of the pattern, and the two intensity curves corresponding to the above exposure times were joined together at the q of about 13, and the curve thus obtained was converted to the molecular intensity curve, $qM(q)$. In Fig. 2 this curve is compared with the theoretical molecular intensity curve calculated with the molecular parameters of the GaI_3 (r_a'(Ga-I)=2.456, r_a'(I-I)=4.250 Å. The mean amplitudes were corrected for the change in temperature as follows: l(Ga-I)=0.076 and l(I-I)=0.185 Å).

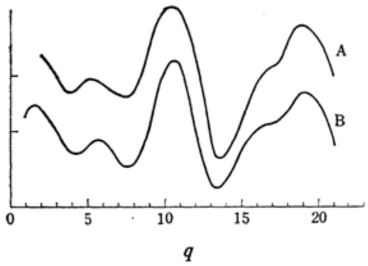

Fig. 2. Small-angle intensity curve of $GaAs$-I_2 at 440°C.
A: Observed $qM(q)$ of $GaAs$-I_2
B: Calculated $qM(q)$ for the GaI_3 model

The features of the experimental intensity curve are in qualitative agreement with the theoretical curve. The radial distribution curve was, therefore, obtained from the experimental molecular intensity curve spliced in the range of the scattering angles q less than 20 by a theoretical curve calculated with the molecular parameters of the GaI_3. The curve is shown in Fig. 3A; it is essentially similar to that of the GaI_3. It should be mentioned, however, that in this curve two fairly large negative areas between the two main peaks are observed, as is an appreciable distortion from the Gaussian form for the I-I peak.

Synthetic radial distribution curve for the GaI_3

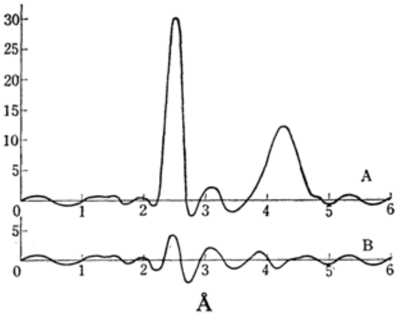

Fig. 3.
A: Radial distribution curve of $GaAs$-I_2 at 440°C
B: Difference between the RD curve of $GaAs$-I_2 and that of the GaI_3 model

model mentioned above was then calculated and subtracted from the experimental curve of Fig. 3A. The curve obtained as the difference between the two curves is shown in Fig. 3B. Three peaks are observed in this curve. Although the peak at about 2.5 Å might correspond to the As—As distance of As_4 (r_a=2.432Å)[3] and the As—I distance of AsI_3 (r_a'=2.554 Å)[4], and the peak at about 3.9 Å, to the I—I distance of AsI_3 (r_a'=3.915 Å), no quantitative discussions can be made, since the heights of these peaks are of the same orders of magnitude as those of ghosts (the negative peaks). The peak at about 3.1 Å has not been assigned to any, possible interatomic distance; it may be a ghost.

In conclusion, the present study has shown that the predominant species in the vapor phase of the $GaAs$-I_2 reaction system at 440°C is GaI_3. It may, therefore, be inferred that a reaction similar to that reported by Silvestri and Lyons takes place at this temperature. The vapor pressure of the GaI_3 is about 700 mmHg (estimated from the amount of the starting iodine), while the arsenic which results from the reaction is expected to remain mainly in the solid phase (the vapor pressure of arsenic is about 10 mmHg at 440°C); it has, therefore, only a little influence on the diffraction photograph.

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