On the use of AsH₃ in the molecular beam epitaxial growth of GaAs

A. R. Calawa
Massachusetts Institute of Technology, Lexington, Massachusetts 02173

(Received 26 December 1980; accepted for publication 9 February 1981)

High-quality epitaxial layers of GaAs have been grown in a molecular beam epitaxial system using AsH₃ as the arsenic source. Peak electron mobilities of over 130 000 cm²/V sec and 77-K mobilities as high as 110 000 cm²/V sec have been observed in a 5-μm-thick GaAs layer with a carrier concentration of 2.4 x 10¹⁴ cm⁻³. These layers were grown on Cr-doped semi-insulating GaAs substrates. Initial results indicate that AsH₃ may be the preferred species for the growth of high-purity GaAs.

PACS numbers: 81.15.Ef

Molecular beam epitaxy (MBE) of III-V compounds is most commonly done with heated solid sources for the group-V elements. Although arsenic or phosphorous are usually used, although III-V compounds heated to decomposition have also been tried. Some of the disadvantages of these solid sources with regard to convenience and reproducibility have been recently pointed out by Panish, who described some results on the use of gas sources for As and P. These appear also to be effects which are deleterious to the quality of the MBE layers resulting from the polymeric nature of the As and P produced by solid sources. (Elemental sources produce As₂ and P₄, while the compound sources give As₅ and P₂. ³) Although the highest mobility film reported in the literature was grown using As₂, it has been shown recently ⁴ that the dissociation of As₂ on the surface of the growing GaAs film causes the formation of point defects in the MBE layer, which may be eliminated using the dimer, As₅. These preliminary results indicated that the lower polymeric arsenic may be the more desirable species for the MBE growth of high-quality GaAs.

We have been independently studying the MBE growth of GaAs using AsH₃ as a gaseous source of arsenic. With a somewhat different procedure for cracking the AsH₃ than that used by Panish, we have grown GaAs MBE layers of higher quality than heretofore reported in the literature. Although the present evidence is not conclusive, it appears that the high quality of the layers results at least in part from the substantial amount of the monomer AsH₃ produced by the cracking of the AsH₃. (The polymeric state of the arsenic in the system reported in Ref. 2 was not measured, and the author assumed that it was essentially all As₂. This seems justified in view of the furnace temperature and gas pressure.)

Concentrated high-purity 99.9999% AsH₃ is introduced into an otherwise typical MBE growth chamber through a precision leak valve. To provide an effective source of arsenic the AsH₃ must first be dissociated, a process which is carried out in a special cracking furnace, an artist view of which is shown in Fig. 1. Except for the seals near the vacuum flange, the entire furnace is made of tantalum and quartz. The seal between the inner part of the furnace and the flange is vacuum tight to insure that all of the gas passes through the cracking furnace before entering the growth chamber.

The experimentally determined partial pressures of the dissociated gases are plotted as a function of cracking furnace temperature in Fig. 2. These pressures were obtained with a quadrupole mass analyzer, whose ionization chamber was located in the substrate growth position. Inasmuch as possible the data were corrected for the cracking of the gases by the analyzer. This was done by first introducing undissociated AsH₃ into the MBE chamber and obtaining the mass spectrum of the products cracked by the quadrupole mass analyzer as a function of AsH₃ pressure (no As₂ or As₄, was seen). The procedure was followed using elemental arsenic to determine the quadrupole cracking pattern of As₂. This data was then used to correct for the effect of the quadrupole analyzer when the AsH₃ was cracked by the furnace. The recombination of arsenic and hydrogen to form AsH₃ and polymerization of the arsenic to form As₄ in the growth chamber or in the mass analyzer was not taken into account and may result in at least part of the As₄ and AsH₃ seen. The compound AsH is believed to be entirely formed in the mass analyzer and is shown in Fig. 2 to indicate that the dissociation of AsH₃ into arsenic and hydrogen is at least a two-step process, where AsH and H₂ are the primary dissociation products.

![FIG. 1. Artist sketch of the ASH₃ or PH₃ cracking furnace.](image-url)
The total system pressure during growth is approximately 10⁻⁶ Torr, and the dominant background gas is \( \text{H}_2 \), the presence of which has been shown to be beneficial in the growth of high-quality GaAs layers. Although \( \text{AsH}_3 \) can be cracked at temperatures as low as 350 °C, the efficiency is low. In fact, even though the furnace is 18 in. long, the \( \text{AsH}_3 \) does not appear to be completely cracked until the temperature reaches about 850 °C. The lowest stable operating temperature for the furnace was about 620 °C. Below this temperature the \( \text{AsH}_3 \) pressure in the system gradually increased, presumably owing to the limited capacity of the vacuum pump to pump \( \text{AsH}_3 \). From Fig. 2 it can be seen that as the cracking temperature is increased the ratio of \( \text{As}_2 \) to \( \text{As}_3 \) or \( \text{As}_4 \) decreases. This follows from the fact that, as the temperature increases, a larger fraction of the \( \text{AsH}_3 \) is cracked nearer to the inlet of the furnace. Hence the \( \text{As}_2 \) so produced spends more time in a relatively high pressure environment inside the furnace tube and is more likely to polymerize to \( \text{As}_3 \) or \( \text{As}_4 \). The relative importance of this process depends, of course, on the length of the furnace tube. We recognize that the cracking and recombination reactions and the mass spectrometric analysis thereof are highly complex. Nevertheless, we feel that the data of Fig. 2 gives a correct qualitative picture of the process. The effect of the \( \text{As}_2 \) on the electrical properties of the MBE layers will be considered below.

Figure 3 shows the temperature dependence of electron concentration and Hall mobility of a 5.4-μm GaAs layer grown at 1 μm/h with a substrate temperature of 580 °C using \( \text{AsH}_3 \) cracked at 620 °C. The substrate is Cr-doped GaAs. The maximum mobility occurs at 55 K and is about 6 \times 10^{13} \text{ cm}^2/\text{V sec} at 77 K. Since the layer is only 5.4 μm thick, depletion both at the surface and at the semi-insulating GaAs substrate is significant. Taking this into account, we calculate an actual carrier concentration of 2.4 \times 10^{14} \text{ cm}^{-3}. Near room temperature there is an unusually sharp rise in the carrier concentration with increasing temperature. Although there are only a few points, one can estimate from the slope an activation energy of about 0.030 ± 0.010 eV. To our knowledge, there are no known donors with activation energies in this range. At the present time we do not know the origin of this level, but it is present in all of the high-purity layers grown with \( \text{AsH}_3 \). The room-temperature mobility of 7200 \text{ cm}^2/\text{V sec} is somewhat lower than expected from the low-temperature results and may be affected by the presence of this unknown donor level. A second 4.7-μm-thick GaAs layer grown under similar conditions had a 77 K mobility of 104 000 \text{ cm}^2/\text{V sec} with an adjusted donor concentration of 4 \times 10^{14} \text{ cm}^{-3}.

The room-temperature mobility was 8300 \text{ cm}^2/\text{V sec}, which is somewhat higher than in the previous case. Several additional layers were grown, all having 77-K mobilities in excess of 90 000 \text{ cm}^2/\text{V sec}, a result which attests to the reproducibility of the process.

The highest purity layers were grown with the cracking furnace at the minimum temperature of 620 °C. Higher furnace temperatures produced films whose net electron carrier concentration increased monotonically with temperature, ranging from \( 1 \times 10^{14} \text{ cm}^{-3} \) at 620 °C to about \( 2 \times 10^{15} \text{ cm}^{-3} \) at 1350 °C. The impurity responsible for this doping at high furnace temperatures is likely to be silicon from the quartz wall of the furnace. Nevertheless, the extremely low total impurity concentration obtained at the lower temperatures is remarkable. This is especially true in view of the fact that (i) unintentionally doped GaAs layers grown in the same system using elemental arsenic are n-type with an impurity concentration of about 10^{16} \text{ cm}^{-3}, (ii) although high-purity arsine gas was used, no special precautions, other than standard degreasing, were taken to clean the 30-ft stainless-steel tubing supplying the \( \text{AsH}_3 \), (iii) neither the Ga source nor the substrate were baked prior to deposition, and (iv) the only liquid-nitrogen cryoshroud in
the system is that which surrounds the sources. Furthermore, GaAs layers grown by vapor phase epitaxy (VPE) using AsH₃ have never been reported to have as high purity as those grown in an AsCl₃-based system. We feel that the high quality of the layers grown here is at least partially related to the predominance of the As₁ specie over the As₂ and As₄ at a cracking furnace temperature of 620 °C. The effect may be one of reduced defect density, as discussed above, and/or one related to the incorporation of impurities at the surface. The picture is clouded somewhat by the impurity apparently introduced by the furnace at higher temperatures. Additional work utilizing a furnace design which would permit the independent variation of the As₁ concentration will be required to clarify the role of As₁.

Nevertheless, it is clear that the use of cracked AsH₃ as an arsenic source has resulted in the growth of highest quality MBE layers ever reported. The donor concentration in the films is dependent on the cracking-furnace temperature, and the dominant impurity is likely to be silicon from the furnace liner. A study of the temperature dependence of the carrier concentration in the low-concentration layers indicates that an additional and unknown donor is also present, which has an activation energy of 0.030 ± 0.010 eV. These initial results also indicate that As₁ may be the preferred arsenic specie for the MBE growth of GaAs, but further experiments are required to substantiate this hypothesis.

The author thanks M. J. Manfra and J. V. Gormley for their technical assistance and Dr. S. H. Groves and Dr. C. E. Hurwitz for helpful discussions. This work was supported by the Air Force Office of Scientific Research.

High-quality epitaxial layers of GaAs have been grown in a molecular beam epitaxial system using \( \text{AsH}_3 \) as the arsenic source. Peak electron mobilities of over 130,000 cm\(^2\)/V sec and 77-K mobilities as high as 110,000 cm\(^2\)/V sec have been observed in a 5-\( \mu \)m-thick GaAs layer with a carrier concentration of \( 2.4 \times 10^{14} \) cm\(^{-3}\). These layers were grown on Cr-doped semi-insulating GaAs substrates. Initial results indicate that As, may be the preferred specie for the growth of high-purity GaAs.