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The operation of metalorganic bubblers at reduced pressure

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Operating a metalorganic (MO) bubbler at low pressure allows a high flux of MO reagent to be extracted without resorting to high carrier gas flows. This approach is particularly suitable for the MOMBE (metalorganic molecular beam epitaxy) growth of III–V compounds. Using a “see-through” water bubbler, we have compared the theory and practice of reduced-pressure bubbler operation, both with and without a carrier flow. We conclude that the small carrier approach offers a wider flexibility in the choice of reagent flow, and a better stability and day to day repeatability of reagent flow. The reduced pressure operation of triethylgallium (TEGa) and triethylaluminum (TEAl) bubblers is described, in the context of the MOMBE growth of GaAs and AlAs. We show that using the small carrier flow approach, the reagent flow can be accurately controlled and predicted over a wide range.

I. INTRODUCTION

Gas sources represent an attractive alternative to the shorter-lived Knudsen sources that are traditionally used in III–V molecular beam epitaxy (MBE) systems. In a typical MBE type Knudsen source, the criteria for true effusion are rarely satisfied, and even though the cell temperature is held constant, the beam flux and uniformity slowly drift as the charge depletes. In contrast, a gas source can be accurately metered using mass flow controllers and, in principle, can provide a stable and reproducible flux for long periods.

In metalorganic molecular beam epitaxy (MOMBE) metalorganic gas sources are injected into a MBE type growth chamber and the technique is essentially a hybrid of (metalorganic vapor phase epitaxy) (MOVPE) and MBE. Since the early demonstration of the MOMBE growth of GaAs, this technique has been successfully applied to the growth of a wide range of III–V alloys and devices.

A molecular flow environment is maintained in the MOMBE growth chamber so that the mean free path of the gas molecules exceeds the source to substrate spacing (typically 10 cm) and the injected reagent displays beam-like behavior. Therefore, in MOMBE, we can use readily decomposed sources, such as triethylaluminum (TEAl), with none of the attendant gas phase depletion effects that plague higher pressure MOVPE reactors. Other gas hydrodynamic effects such as turbulence or convection are also eliminated by this molecular flow regime.

To maintain a molecular flow, the deposition chamber must be maintained at a pressure below 10⁻³ Torr. With currently available pumping speeds, this means that the maximum gas flow that can be pumped is on the order of 50 sccm. In MOMBE, the maximum carrier flow that will be available at any particular MO bubbler is typically less than 10 sccm. By comparison, carrier flows of tens or even hundreds of sccm are typically used in MOVPE to transport the MO reagents.

Pumping directly on the MO bubbler, with no carrier flow, can provide a high reagent flux. This approach has been used for MOMBE growth. However, if we also pass a small carrier flow (1–10 sccm) through the bubbler then it is shown in this paper that a wider range of reagent flux is available and the stability of the reagent flux is improved.

After a short discussion of the theory of bubblers under reduced pressure operation, we describe the behavior of a “see-through” water bubbler. Water flux can be accurately predicted for pressures as low as 1.5 times the water saturated vapor pressure (SVP). At still lower pressures, an irregular and violent bubbling action makes an accurate prediction of the water flow impossible.

Theory and experiment are then compared for triethylgallium (TEGa) in the MOMBE growth of GaAs.

II. THEORY

A. Bubbler operation with a carrier flow

To calculate the flow of reagent from a bubbler, we consider the typical arrangement shown in Fig. 1. The flow of carrier gas, \( F_c \), sccm, is measured by mass flow controller and then enters the bubbler at some input pressure, \( P_i \). A needle valve, or automated pressure control system maintains the manometer pressure at the desired value.

The carrier gas is assumed to be completely saturated by...
reagent vapor and exits the bubbler at a higher pressure, \( P_o \), where:
\[
P_o = P_i + P_r,
\]
and \( P_r \) is the SVP of the reagent, which is controlled by the reagent temperature.

The flow of reagent, \( F_r \), is given by:
\[
F_r = F_c \frac{P_r}{P_i} \text{ sccm}.
\]
Therefore,
\[
F_r = F_c \frac{P_r}{P_i} (P_o - P_r) \text{ sccm}.
\]

This is the equation used by Schaus et al.\(^7\) to calculate flows of TMGa for the growth of AlGaAs and GaInP. This equation gives a fairly accurate description of the reagent flow for output pressures in the range \( P_o > 3P_r \). However, for lower pressures it needs to be modified.

In a real system, the pressure is typically measured downstream from the bubbler and the pressure sensor is separated from the bubbler by a short length of tubing of conductance, \( C_r \). The downstream pressure, \( P_d \), is related to the output pressure of the bubbler by:
\[
P_o = P_d + \left( \frac{(F_c + F_r)}{C_r} \right),
\]
where \( F_c \), \( F_r \), and \( C_r \) are in units of sccm.

So \( F_r \) is now given by:
\[
F_r = F_c P_i \left( \frac{P_o - P_r + (F_c + F_r)}{P_i C_r} \right) \text{ sccm}.
\]

The importance of this extra term will be system dependent. In the ideal system, where the tube is of infinite conductance, it disappears and Eq. (5) reverts to Eq. (3). However, in a typical gas manifold, this correction must be applied to accurately predict the reagent flow at low bubbler pressures.

**B. Bubbler operation at reduced pressure with no carrier flow**

Again we consider the bubbler arrangement shown in Fig. 1. Assuming that the bubbler remains saturated with reagent vapor, then the reagent flow is limited by the pumping speed at the bubbler, which will generally be conductance limited.
\[
F_r = C_r (P_o - P_d) \text{ sccm}.
\]

As shown in the next section, there are two variants of this approach. In the first, \( P_o \) is varied while \( C_r \) and \( P_r \) are held constant, in the second only \( C_r \) is varied.

**III. EXPERIMENTAL**

Bubbler operation was studied at pressures down to the reagent vapor pressure. In a preliminary series of experiments, we used a “see-through” glass bubbler containing water, to observe the bubbling process at very low pressures. We then used commercial stainless steel bubbleers of TEGa and TEAl, at reduced pressure, for the MOMBE growth of GaAs and AlAs.

**A. Water bubbler with a small carrier flow**

For a preliminary evaluation of reduced pressure operation, we used a graduated quartz bubbler containing water and connected as shown in Fig. 1. Water was convenient for this study, having a vapor pressure and specific gravity typical of that for MO reagents with none of the attendant safety or cost problems. The glass “see-through” bubbler also allowed the bubbling process to be observed in detail.

The helium carrier gas flow, \( (F_c) \) was varied between 10 and 100 sccm, and the water flow out of the bubbler was measured by observing the change of water level as a function of time. The downstream pressure, \( P_d \) was set by the

**Fig. 2. Water flow \((F_r)\) as a function of downstream pressure \((P_d)\)** (a) \( F_r = 11 \) sccm, (b) \( F_r = 19 \) sccm, (c) \( F_r = 33 \) sccm, (d) \( F_r = 76 \) sccm.
manual needle valve at pressures between 15 and 320 Torr. At pressures higher than this, the time required for an accurate measurement of water flow became prohibitive.

Figures 2(a)–2(d) show the variation of water flow, \( F_w \), with downstream pressure, \( P_d \), for helium carrier flows, \( F_c \), of 11, 19, 33, and 76 sccm, respectively. In addition to the measured data, we have plotted the theoretical variation according to Eqs. (3) and (5) using the conductance, \( C_s \), as a fitting parameter. Values outside of the range 5 sccm < \( F_c < 50 \) sccm tended to be less accurate due to a violent bubbling action (described below) for \( F_c > 50 \) sccm or higher measurement errors for \( F_c < 5 \) sccm, where the change of water level was small. A conductance value, \( C_s \), of 10 sccm was used for the calculation of the curves shown in Fig. 2.

It can be seen that the extrapolation term in Eq (5) is important only for low values of \( P_d \), where the water flow is highest. At pressures of three or more times the water SVP, the Eqs. (3) and (5) predict essentially the same water flow.

For water flows within the range 5 sccm < \( F_c < 50 \) sccm there is a good agreement between the experimental data and Eq. (5). However, at higher water flows, the data is more scattered.

Observing the bubbling action, it was found that for water flows up to approximately 20 sccm, a steady stream of small bubbles was obtained. However, as the water flow was further increased, either by increasing \( F_c \) or lowering the \( P_d \), the bubbles became larger and the bubbling action became less regular and more violent. Under these conditions, the bubble often expanded to fill the entire inner diameter of the bubbler and a “foam” developed on top of the liquid. The upper meniscus of the “foam” would then travel to the top of the bubbler and upon bursting would leave water in the horizontal exit port. (Therefore, it appears therefore that bubblers with vertical exit ports are more appropriate for operation under high flow conditions.) These effects tended to increase the apparent water flow, by redistributing water away from the main body of the liquid, and were undoubtedly responsible for the high readings for \( F_c > 50 \) sccm and the increased scatter in the data for this range.

In the case of real MO reagents, while this unstable bubbling regime undoubtedly exists, we apparently did not encounter it under the wide range of experimental conditions used in this work. We infer this from the excellent agreement between experiment and theory, and the small scatter of data points that we describe below.

Several factors undoubtedly contribute to this. First, it should be noted that MO reagent flows of 5 sccm or less were used here, while water flows of > 50 sccm were necessary to observe the unstable bubbling regime. Second, the tendency to “foaming” will be reagent dependent and will be greater for liquids with a higher surface tension, e.g., soap solution. Also, the foaming action will be driven by agitation of the liquid that occurs during the passage and “bursting” of bubbles. This agitation will tend to be more violent for liquids with a higher specific gravity and a higher viscosity. (A good example of this is the violent bubbling action observed for molten lava.)

In the absence of data for viscosity and surface tension for MO reagents, the boundaries of this unstable bubbling region can at present only be determined experimentally. However, as shown below for TEGa and TEAl, we found no evidence of instability under our experimental conditions.

B. Forced evaporation from the water bubbler

1. Case 1: \( C_s \) constant, \( P_d \) varied

The same experimental setup was used to study reduced pressure operation with no carrier gas flow passing through the bubbler. For a given water temperature the only variable in this case is the downstream pressure, \( P_d \). This pressure was controlled by adjusting the flow of helium gas through the bypass line. All three valves (\( V_1, V_2 \) and \( V_3 \)) were left open and observation confirmed that bubbling did not occur during these measurements. Therefore, all loss of water was therefore by evaporation.

If valve \( V_1 \) was left closed, then an intermittent but violent bubbling action occurred as gas trapped in the submerged bubbler input port escaped. Again, this violent bubbling action transferred liquid into the exit port and made an accurate determination of the water flow impossible.

Figure 3 shows the measured and theoretical variation of water flow \( F_w \), with \( P_d \). The previously determined conductance, \( C_s \), value of 10 sccm, was used for the calculation from Eq. (6). At low values of \( P_d \), we again find a high water flow, however as \( P_d \) approaches the water SVP value, the water flow rapidly decreases. In this case, the water flow changes by three orders of magnitude for a pressure variation of only 10 Torr. Clearly, the stability and reproducibility of reagent flow will be inferior in this mode of operation, as very small pressure changes will cause large shifts in reagent flow.

By comparison, if we use a small flow of carrier gas, as shown in Fig. 2, we need to change the pressure by more than two orders of magnitude to achieve the same change of water flow.

2. Case 2: \( C_s \) varied, \( P_d \) constant

Examination of Eq. (6) shows that the reagent flow can also be varied by maintaining a constant downstream pressure and varying the conductance, \( C_s \). While this approach was not studied in this work, it has been successfully used by several MOMBE groups, so it is appropriate to consider it here.
In this variant, the downstream pressure is that of the MOMBE chamber and the variable conductance is either a manual leak valve, or the control valve of a mass flow controller (MFC) that is placed downstream from the bubbler. In the first case, a calibrated, precision needle valve controls flow stability and repeatability but will be susceptible to drift and clogging. The drift problem is solved by using an automatic valve as part of a control loop, as in the work of Tsang who used a MFC downstream from the bubbler. However, in this case, the MFC is exposed to the reagent and the heating action of the MFC may cause some decomposition, particularly in the case of weakly bound reagents such as TEAL. These undesirable effects, which are well known from MOCVD experience, may contaminate the reagent flow or eventually clog the MFC.

Comparing the small carrier approach [Sec. A and Eq. (5)] with the two variants of carrier free operation (Sec. B, cases 1 and 2) we conclude that the small carrier approach is superior. The three-parameter control of the small carrier approach [see Eq. (5) and below] offers a wider range of reagent flows and avoids the drift and clogging problems that occur in other systems.

C. MOMBE growth of GaAs and AlGaAs

We have designed a MOMBE gas manifold for reduced pressure bubbler operation, with small carrier flows of 1-10 sccm per bubbler. This manifold delivers TEGa, TEAl, and TEIn reagents in hydrogen carrier gas, to a VG Semicon V80H diffusion pumped MBE system. GaAs growth rates in the range 0.2–3 μm hr⁻¹ have been achieved.

The MO reagents were contained in vertical stainless steel bubblers (type #65270, CVD Inc.) connected as in Fig. 1. This sub system feeds a custom vent/run switching system (not shown), which connects to the gas injector located at the K-cell flange of the MBE-type deposition chamber.

The MOMBE layers were grown at substrate temperatures within the range 550 to 650 °C and with an arsenic flux (from a conventional K-cell) between 6×10⁻⁵ and 1.5×10⁻⁴ mbar. The substrates were undoped semi-insulating GaAs prepared as for conventional MBE growth.

Reference to Eqs. (3) and (5) shows that the reagent flux is controlled by three parameters, the carrier gas (in this case hydrogen) flow through the reagent liquid, \( F_{\text{c}} \), the reagent vapor pressure, \( P_r \), and the output pressure of the bubbler (\( P_{\text{b}} \)). As described above, we actually measure pressure at a point downstream from the bubbler, where the pressure, \( (P_{\text{b}}) \) is lower.

Figure 4 shows the multilayer structure grown to test the variation of growth rate with carrier flow. The downstream pressure was maintained at 16.4 Torr and the TEGa bubbler was held at 23 °C \( (P_r = 5.3 \text{ Torr}) \). Each GaAs layer was grown at a different carrier flow and the different layers were separated by AlAs layers 500 Å thick. The TEAl bubbler was held at 31 °C with a downstream pressure, \( P_{\text{c}} \), of 1.8 Torr. After growth, the wafers were cleaved, stained, then examined by scanning electron microscopy. The thickness of each GaAs layer was measured and converted to a growth rate. It was assumed that the growth rate was directly proportional to the reagent flux and a proportionality constant \( \text{(GaAs growth rate / TEGa flux)} \) of 1.2 μm h⁻¹ sccm⁻¹ was determined by fitting to the experimental data. (This constant will depend on the deposition chamber and gas injector geometry, and will be system dependent.)

In Fig. 5, we have plotted the variation of GaAs growth rate with \( F_{\text{c}} \), the hydrogen carrier flow. The curves shown in this figure were calculated using Eqs. (3) and (5) with a conductance, \( C_v \), value of 5.0 sccm.

We note that at the higher carrier flows, the growth rate is a nonlinear function of the carrier flow, which is well described by Eq. (5). To be sure that the variation of growth rate shown in Fig. 5 was due only to changes in the TEGa flux, we performed the following companion experiment: A constant TEGa flux was injected into the MOMBE growth chamber while the total hydrogen flow was varied between 1–10 sccm. The growth rate did not vary for layers grown under these conditions.

The variation of GaAs growth rate with downstream pressure was also measured, using a multilayer sample similar to that of Fig. 4. Here, the GaAs layers were grown with different \( P_r \) values and they were again separated by AlAs marker layers grown as before. The TEGa bubbler temperature was held at 23 °C and the carrier flow was kept constant at 1.2 sccm.

Fig. 4. The multilayer GaAs/AlAs test structure.

Fig. 5. The variation of GaAs growth rate with carrier flow.
Figure 6 shows the variation of growth rate with downstream pressure. The curves shown in this figure were calculated using the same growth rate constant as before. However, in this case, the best fit was obtained for a conductance, $C_s$, value of 1.0 sccm. Again, there is an excellent agreement between the experimental data and the growth rate predicted from Eq. (5).

In the above experiments, the small carrier at reduced pressure approach was also used for the TEAl bubbler, in order to grow the AlAs marker layers. In a separate experiment with the TEAl bubbler at 42 °C ($P_r = 0.4$ Torr) and a carrier flow of 3 sccm, an AlAs growth rate of 0.3 μm h$^{-1}$ was measured. This again demonstrates the power of the low pressure approach in obtaining high flux rates (and therefore usable growth rates) from low vapor pressure reagents such as TEAl.

IV. SUMMARY

Operating at reduced pressure is a powerful way of obtaining high reagent flow rates when the permissible flow of carrier gas is low, as in the case of MOMBE, or when the vapor pressure of the MO reagent is low.

It has been shown that with water as the reagent, flows of up to 50 sccm can be accurately predicted. For higher flows, obtained when the pressure approaches the water SVP, an unstable bubbling action occurs. Under these conditions foam is created on top of the liquid and liquid can be transported out of the bubbler.

While simple evaporation can also provide a high reagent flux, this approach is either susceptible to small pressure fluctuations (case 1) or may suffer from needle valve or MFC clogging (case 2). By comparison, the small carrier flow approach offers more flexibility in the choice of reagent flux and avoids clogging problems.

The small carrier at reduced pressure approach is shown, to be suitable for MOMBE growth using TEGa and TEAl. With these reagents, it appears that a stable bubbling action takes place for reagent flows at least up to 3 sccm. This means that the reagent flow and semiconductor growth rate can be accurately controlled and predicted [using Eq. (5)] for practical growth rates up to several microns per hour.

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