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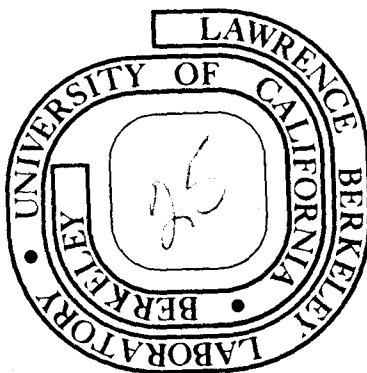
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Tank-Mixing Methods for Producing Time-Varying
Reactive Gas Mixtures

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May 1974

Abstract

Tank-mixing methods are explored toward producing controlled, time-varying reactive gas mixtures for epitaxial reactors. The transient output concentrations of single and multiple mixing tank systems with series and parallel flow are simulated for discrete changes in the input concentration, input flow rate or tank volumes. A simple transient tank mixing system is proposed for composition grading ternary III-V compound alloy epitaxial layers on binary substrates. The system proposed requires changes in both gas composition and mixing tank volume.

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Key Words: chemical vapor deposition, programming reactant concentration, mixing tank methods.

Introduction

The epitaxial growth of semiconducting compound alloy layers with composition gradation through the layers has become important in a number of solid-state device applications⁽¹⁾. Because the lattice parameters of III-V compound alloys vary with alloy composition, composition grading of the ternary alloy during epitaxial, vapor phase growth on binary compound substrates is known to reduce significantly the density of lattice mismatch dislocations and residual lattice stress^(2,3). Indeed, epitaxial layers of the composition $\text{GaAs}_{0.6}\text{P}_{0.4}$ with improved electroluminescence properties have been epitaxially grown on GaAs by grading the GaP mole fraction from 0 to 40% over 25 to 50 μm in order to distribute the dislocations generated by the 1.4% lattice misfit^(2,4). Proper control over the graded composition profile, furthermore, is essential to minimize defect generation differential expansion differences between the alloy layer and the substrate. Defect generation by differential thermal expansion has been shown theoretically to be proportional to the slope of the composition gradation⁽⁵⁾.

Methods of precisely controlling the time-dependent, reactive gas compositions needed in chemical vapor deposition reactors has received relatively little study in spite of the growing need for such methods. Harris et al. (6) utilized a series of step changes in input flow rates to produce graded Zr_xC deposits by chemical vapor deposition. Such discrete changes in reactant gas composition can produce polycrystalline deposits, however, and are to be avoided

in III-V compound epitaxial reactors. Rosler and Benzing utilized a time-sequenced, automatic flow controller modulated by a Data Trak-type time variant controller to program phosphine flow to a $\text{GaAs}_{1-x}\text{P}_x$ reactor⁽⁷⁾. Such automatic programmers are costly and require high precision because flow rate measurement and mechanical control are difficult at low flow rates.

The programming of reactant gas compositions by passive, gas phase mixing is superior to electromechanical programming in a number of ways. Passive gas composition programming based on the output response characteristics of stirred tanks^(8,9), requires simple apparatus, involves no continuous motion and is low in cost. Tietjen and Amick utilized a mixing tank as a ballast vessel to smooth fluctuations in input gas composition to a $\text{GaAs}_{1-x}\text{P}_x$ reactor⁽⁴⁾. Recently Baley and Rogers studied the use of a single mixing tank to produce graded $\text{Ga}_x\text{In}_{1-x}\text{As}$ epitaxial deposits with $\text{HCl} - \text{H}_2$ reactive gas mixtures and metal sources⁽¹⁰⁾.

Because of their relative simplicity and low cost, passive mixing tanks should be applicable to a wide range of epitaxial processes where graded-composition layers are required, provided that a tank-mixing manifold can be devised which produces the required concentration time dependence for a given process. In this paper the applications of tank-mixing methods are explored toward defining the range of output responses that can be expected from a limited number of discrete changes in input conditions to single and multiple tanks. Based on the general study a simplified tank mixing system for composition grading

of $\text{GaAs}_{1-x}\text{P}_x$ layers on GaAs is proposed. It will be shown that discrete changes in more than one operational variable of the mixing manifold is required for eliminating long terminal transients and that changes in both input concentration and either flow rate or tank volume is required to prevent discontinuities in the time-dependent output concentration. Series tank arrangements are shown to offer advantages for adjusting the time-dependent output concentration function from completely mixed tanks.

Step-Input Concentration Responses from Stirred Tanks

When a step-function increase of tracer with concentration C_0 is introduced at time $t = 0$ into the constant flow stream entering a tank-mixing system, the system output-concentration time dependence is described by the step-input response function $\underline{F}(t) = C(t)/C_0$. This function was introduced by Danckwerts for the treatment of nonideal reactor flow distributions ⁽¹¹⁾. The output concentration increases from 0 to C_0 following the step with the time dependence $C_0 \underline{F}(t)$. Thus, for the application of tank-mixing methods to controlling flows of reactive components to chemical reactors, a tank system must be found which provides the desired output concentration function.

The step-input response function for several limiting steady-state conditions of reactor flow are shown in Fig. 1. Backmix, or total backmix, flow occurs when the reactor volume is completely mixed; the output concentration is then the same as that within the reactor. Plug

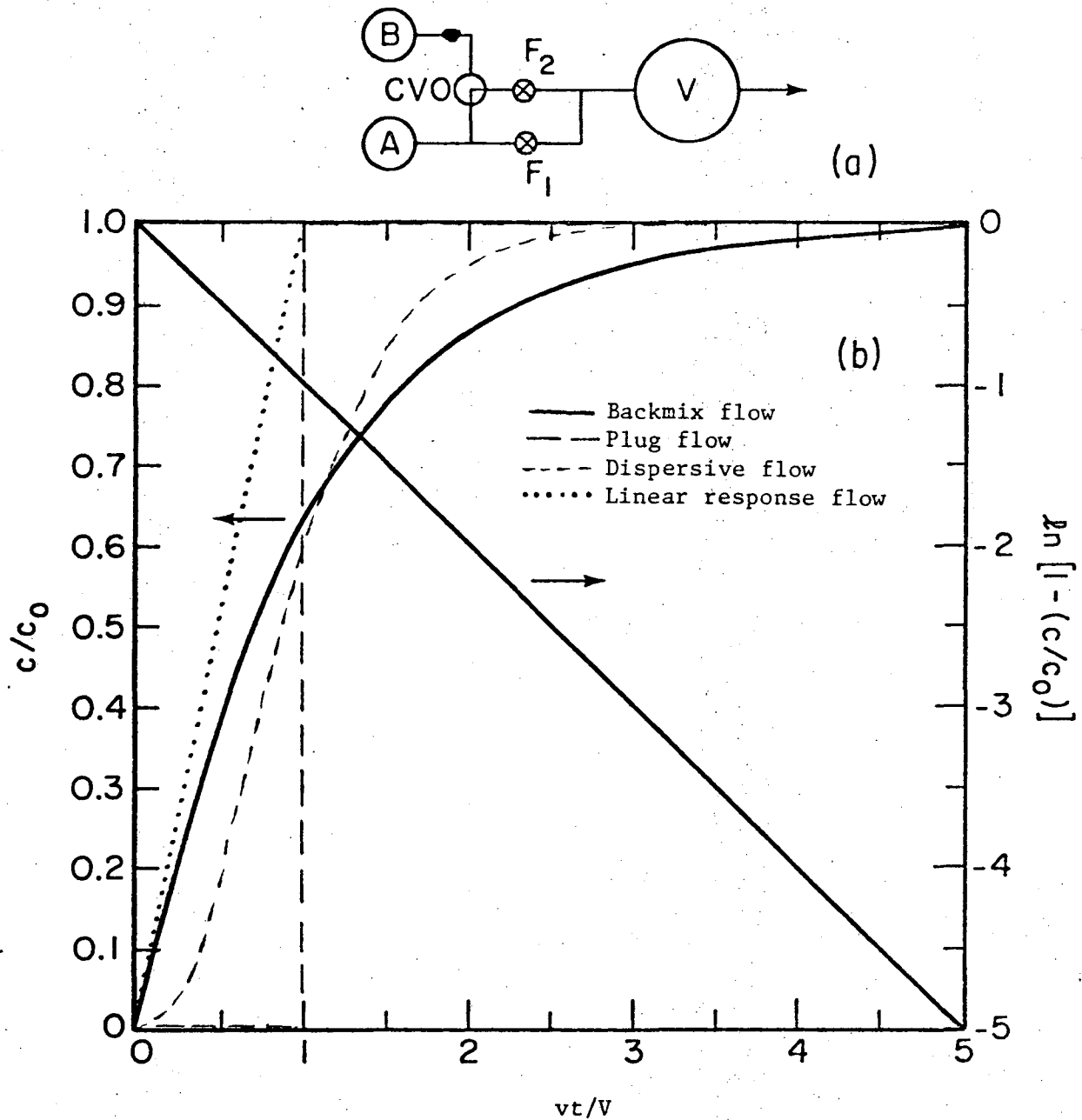
flow denotes one-dimensional flow without lateral mixing, so that a step increase in input concentration is transmitted to the output. Dispersive flow represents an intermediate degree of mixing between these extremes. For linear gradation of concentrations input to chemical vapor deposition reactors, a linear step-inlet response function is required from a mixing tank system.

The output concentration of a tank-mixing system which is initially subjected to a step change in input can be readily calculated provided that the mixing efficiency is known as a function of flow rate. In the following, complete mixing will be assumed for all flow conditions, since efficient mixing is readily achieved experimentally, especially for the mixing of gases. Step-input responses functions for several tank-mixing systems are explored below.

Single Tank Response

The application of a single mixing tank has been applied effectively to composition grading of $\text{Ga}_{1-x}\text{In}_x\text{As}$ epitaxial layers⁽¹⁰⁾. A mixing tank system which accepts a step increase in a reactive component while maintaining a constant input flow rate v is shown schematically in Fig. 1a. Following an initial purge with carrier gas A through control valve CV0 and volumetric flow control values F_1 and F_2 , value CV0 is switched at time $t = 0$, allowing a step increase in the concentration of a reactive gas B to be admitted to the tank.

The concentration C of the reactive component leaving the completely mixed tank of volume V is determined by a differential mass balance,



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Figure 1. Transient output concentrations from a single mixing tank: (a) schematic of mixing tank system; (b) output concentrations versus reduced time for backmix, plug, dispersive and linear response flow.

$$VdC = v(C_0 - C)dt \quad (1)$$

The general solution of this homogeneous differential equation is $Ae^{-(v/V)t}$. Because C varies from 0 at $t = 0$ to C_0 at $t \rightarrow \infty$, the integral solution is

$$\frac{C}{C_0} = 1 - e^{-t/\tau} \quad (2)$$

where τ is the mean residence time of fluid in the system, $\tau = V/v$. This output response is that for backmix flow, shown graphically in Fig. 1b. The slope of this function decreased monotonically, and convergence to 1 is slow. Note that the time rate of increase in C can be adjusted by varying the input concentration, the total input flow rate or the tank volume. The total molar input of a reactive gas to a chemical vapor deposition reactor, vC_0 , is often specified by supersaturation requirements of the deposition reaction, while the tank volume is limited by equipment design to a fixed size. Therefore, for the mixing tank method to remain simple the transient time constant τ can be adjusted most effectively by varying the volumetric flow rate v .

Series Mixing Tank Response

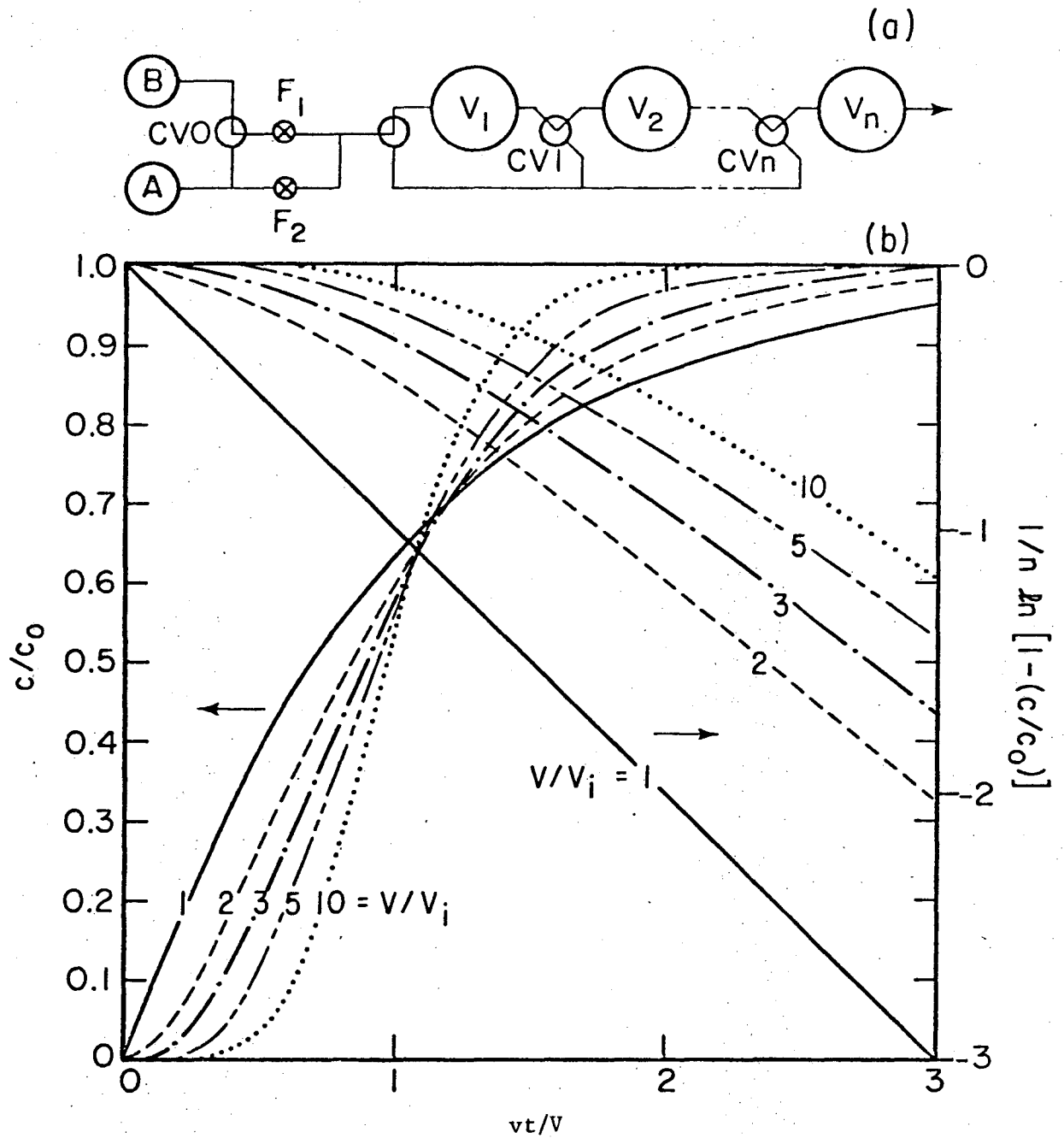
Series mixing-tank systems have been applied effectively to represent nonideal velocity dispersion in chemical reactors. A series of equal sized backmix reaction vessels is the simplest representation. A more elaborate system of backmix reactors of different size, and in a two-dimensional network, was applied by Dean and Lapidus to model nonisothermal, nonideal flow in packed bed reactors ⁽¹²⁾.

The step input response function from a series of mixing tanks differs from that of a single tank in several important respects. With several tanks it is possible to adjust the individual tank volumes to vary the mixing time constants $\tau_i = V_i/v$. Also, the output function from a given tank is modified by passage through successive mixing tanks along the flow path. A series tank-mixing system is shown schematically in Fig. 2a. In this system it is possible to change the total system volume incrementally by introducing the input gas mixture to tank i through values CV_i .

Consider a step function increase in the mass flow of gas B with input concentration C_o entering tank 1 at time $t = 0$, preceded by a purge of all tanks. The output concentration from the first tank is again given by Eq. 2 with V replaced by V_1 . The differential mass balance for tank n is related to the output concentration from tank $n - 1$ by

$$VdC^{(n)} = v(C^{(n-1)} - C^{(n)})dt \quad (3)$$

where again $C^{(i)} = 0$ at $t = 0$ and $C^{(i)} = C_o$ at $t \rightarrow \infty$ for all tanks i . Thus, the particular solution contains the terms $B_i e^{-t/\tau_i}$ for all tanks $i < n$, while the general solution contains the term Ae^{-t/τ_n} . The solution for $C^{(n)}$ will then contain the constant C_o and $(n - 1)$ exponential terms. It can be readily shown that the outlet concentration function for the n th tank is



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Figure 2. A series tank mixing system of n tanks with volumes $V_i = V/n$: (a) schematic of the series tank mixing system; (b) transient output concentrations versus reduced time for $n = 1, 2, 3, 5$ and 10 .

$$\underline{F} = \frac{C}{C_o} = 1 - V_1^{n-2} \left\{ V_1 e^{-t/\tau_1} - \sum_{i=2}^n V_i e^{-t/\tau_i} \right\} \left[\prod_{i=2}^n (V_1 - V_i) \right]^{-1}, \quad (4)$$

for tanks of unequal volume.

When all n tanks have the same volume $V_i = V/n$, then the system output concentration function solving Eq. 3 for tank n has the form

$$\underline{F} = \frac{C}{C_o} = 1 - e^{-nt/\tau} \left[\sum_{m=0}^{n-1} \frac{1}{m!} \left(\frac{nt}{\tau} \right)^m \right]. \quad (5)$$

This function is shown graphically in Fig. 2b for different values of n . It can be shown by Taylor series expansion, that C varies as $(nt/\tau)^n$ near $t = 0$. Therefore, the series tank arrangement is useful in eliminating the large discontinuity in the time rate of change of the output concentration at $t = 0$. The maximum slope in the response function of Eq. 5 increases with n , but the rate of convergence near $C \rightarrow C_o$ is nearly constant when normalized to the maximum slope of this function. Therefore, the addition of tanks to the series while holding the residence time τ constant does not increase the rate of convergence of the output concentration function to a steady state value.

Parallel Mixing Tank Response

A parallel arrangement of mixing tanks is also capable of modifying the output concentration function over that from a single tank. Such an arrangement is shown schematically in Fig. 3a. With control values CV_i it is possible to admit a step increase in gas B

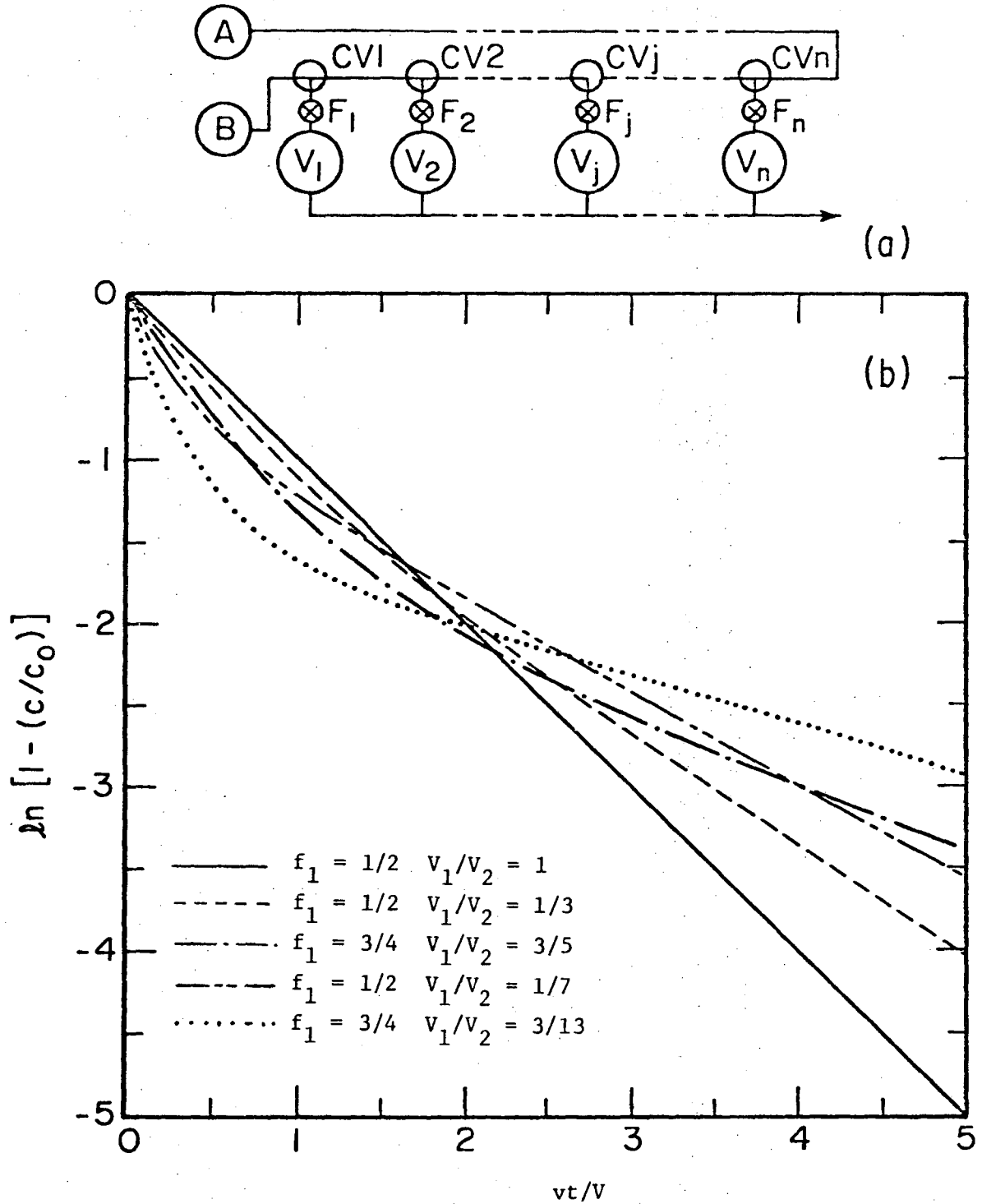
into tanks 1 to j while gas A enters tanks $j + 1$ to n for an n -tank system. As with tank-mixing with tanks in series, the mixing time constant for a given tank, τ_i/f_i , where f_i is the fraction of the total volumetric flow to tank i , can be adjusted through the flow metering values F_i . The overall time constant for the parallel tank arrangement as well as $C(\infty)$ can also be modified by switching the number of tanks connected to the source of reactive gas B, thereby changing in effect the system volume. When $j < n$ the final concentration reached after long mixing times is less than c_o by the factor

$$\sum_{i=1}^j f_i . \text{ Obviously, only those tanks whose inputs are altered contribute}$$

to the time dependence of the output response function.

The parallel mixing tanks offer limited advantage over a single tank for modifying the time-dependence of the output concentration. In fact, when all n tanks have the same volume $V_i = V/n$, as well as the same flow rate $vf_i = v/n$, then the output function C is identical to that given in Eq. 2 for a single mixing tank. The advantage of the parallel tanks lies in independent control of the mixing time constants for different tanks. Because the tank volumes V_i can be chosen independently from the flow rates to each tank, the step-input response function for n tanks in general form is

$$\underline{F} = \frac{C}{C_o} = 1 - \sum_{i=1}^n f_i e^{-f_i t / \tau_i} : \quad (6)$$



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Figure 3. A parallel tank mixing system of n tanks:
 (a) schematic of the series tank mixing system;
 (b) transient output concentrations versus reduced time for a system of two tanks.

The initial transient output functions from two parallel tanks under different conditions are shown in Fig. 3b, where the overall time constant is held constant while the flow rate fractions and tank volume fractions are varied. With parallel mixing tanks, the time rate of change in $\underline{F}$ is always increased relative to that for a single mixing tank for short times. However, the rate of convergence of C to C_0 is always decreased when parallel tanks are substituted for a single tank with the same volume.

Intermediate Transients

The transient output concentrations from series or parallel mixing tanks can be further modified by additional step-increases in input reactant concentrations at fixed times. Intermediate transient modification can be achieved by resetting C_0 , v or V . Wherever the molar flow rate from the tank mixing system is to be continuous, however, as in chemical vapor deposition reactors, it is necessary to carry out the intermediate transients so as to maintain the total molar flow rate a continuous function of time. In the following, the consequences of discrete changes in C_0 with fixed v and V are presented.

For a single mixing tank, the initial concentration is given by Eq. 2. If at time t_1 the input concentration is changed from C_0 to C_{01} with the input flow rate left unchanged, then the tank output at times $t > t_1$ becomes

$$C = C_1 + (C_{o1} - C_1) \left(1 - e^{-(t-t_1)/\tau} \right) \quad (7)$$

where $C_1 = C(t_1)$ from Eq. 2. This concentration function is discontinuous in slope at times $t = 0$ and $t = t_1$, and converges slowly to C_o .

For a series system of n mixing tanks with equal volumes $V_i = V/n$, the output concentration from tank n following a change in input concentration to the first tank from C_o to C_{o1} at t_1 becomes

$$C = C_{o1} - C_o \left[\sum_{i=1}^n a_i \frac{(nt/\tau)^{n-i}}{(n-i)!} \right] e^{-nt/\tau} \quad (8)$$

where

$$a_i = 1 + \left(\frac{C_{o1}}{C_o} - 1 \right) \left(\sum_{m=1}^i \frac{1}{m!} \left(\frac{-nt_1}{\tau} \right)^{m-1} \right) e^{nt_1/\tau}.$$

The series tank system allows the elimination of discontinuities in the output concentration function at time t_1 , and maintains the total molar flow rate, vC , a continuous function of time.

Finally, for a parallel system of n tanks, a change in input concentration from C_o to C_{oi} for the i th tank at time t_1 will produce an intermediate output concentration transient given by

$$C = C_o \sum_{i=1}^n \left\{ \frac{C_{oi}}{C_o} - \left[1 + \left(\frac{C_{oi}}{C_o} - 1 \right) e^{f_i t_1 / \tau_i} \right] e^{-f_i t / \tau_i} \right\} \quad (9)$$

The time dependence of this intermediate transient remains unchanged if the flow rate through each tank is held constant. The isolation of one or several tanks from the system at t_1 will decrease the transient time constant by increasing the flow rate through the remaining tanks; at the same time, however, the total molar flow rate from the system changes discontinuously. Such discontinuities are generally avoided in chemical vapor deposition reactors.

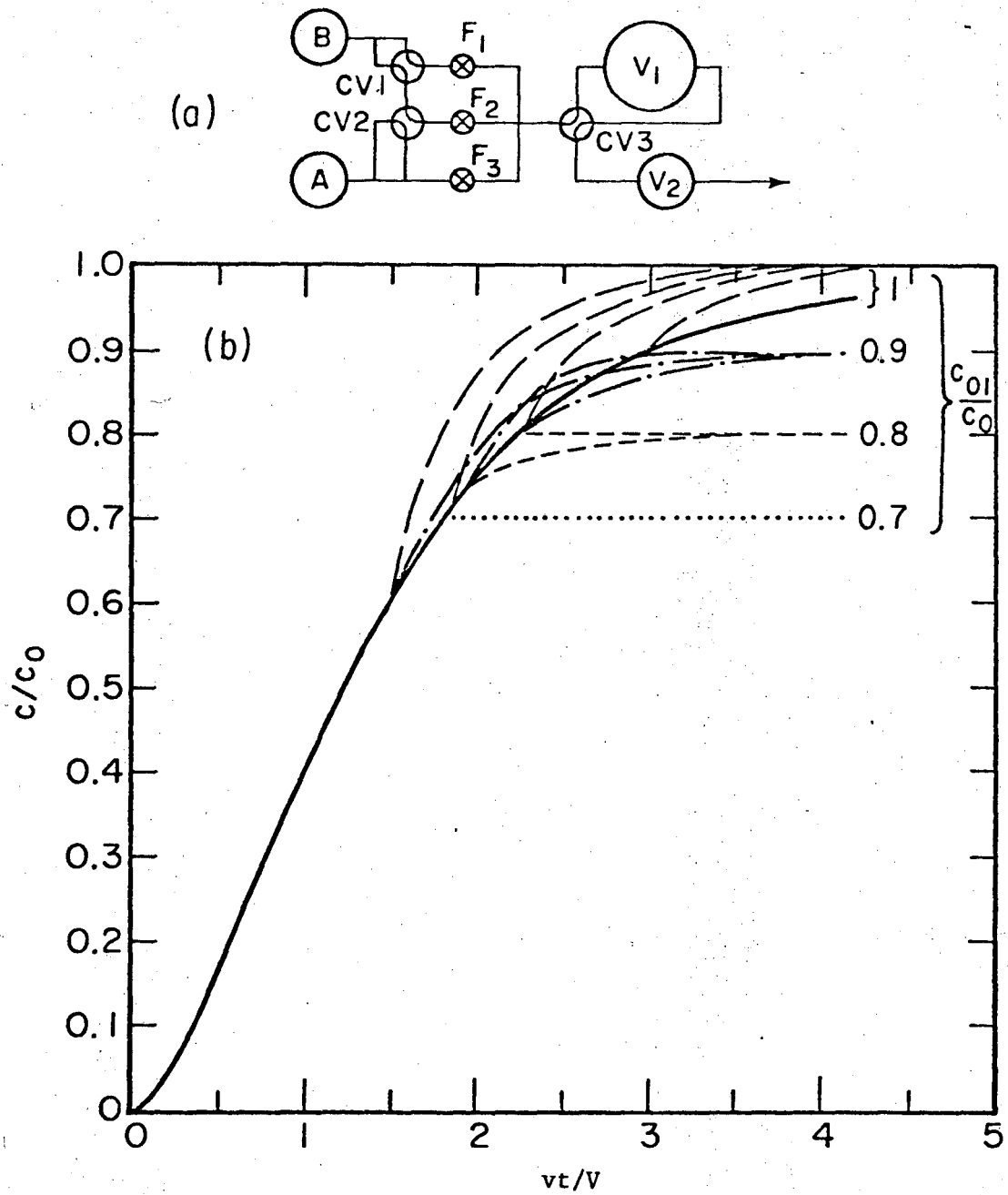
Terminal Transients

In many chemical vapor deposition processes where alloy composition gradients are required in the deposited layer, a definite composition of the final material deposited must be established. Furthermore, in epitaxial layers of electro-optical alloy compounds such as $\text{GaAs}_{1-x}\text{P}_x$, a layer of constant composition is required over the composition-graded layer for device fabrication. The establishment of a controlled composition following the initial or intermediate transient in reactant concentration requires a rapid terminal transient in the tank mixing system with a time constant considerably shorter than that for deposition of the graded alloy layer.

For both series and parallel mixing tank systems the time constant required for the major concentration transient is sufficiently large that the rate of approach to the tank input concentration is slow. A single tank will require a time period of 4.61 mixing time constants for the output concentration to attain 99% of its asymptotic value. The mixing constant V/v can be reduced, however, by either decreasing

the tank volume or increasing the volumetric flow rate after the tank concentration has reached a value less than 80% of the input concentration. At the same time, it is necessary to maintain the molar flow rate of the reactant species a continuous function of time, i.e., with constant vC_o for a series tank system, or constant $\sum f_i C_o$ for a parallel tank system. The two requirements cannot be met unless either the input concentration or system flow rate is changed at the same time that the system volume is reduced.

A simple, series mixing tank system for achieving a rapid terminal concentration transient is shown in Fig. 4a. Initially the two tanks are filled with the non-reactive gas A. During the initial transient gas B is admitted through valves CV1 and CV2 as shown in the figure, so that the input concentration of gas B is $C_o = (v_1 + v_2)/v$. After the output concentration has reached C_1 which is less than C_o , valves CV2 and CV3 are repositioned to replace gas B with gas A in the central line and to bypass the first mixing tank. The new input concentration is then $C_{o1} = v_1/v$. Finally, if C_{o1} and C_1 are equal, the steady state condition will have been reached. This process is exemplified by the dotted line at $C_{o1} = 0.7C_o$ in Fig. 4b for which $V_1 = 2V_2$.



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Figure 4. Terminal transients, showing the effect of simultaneous changes in tank input concentration and tank system volume for convergence to a steady-state concentration C_{01} : (a) schematic of flow system; (b) output concentration as a function of time.

The abrupt discontinuity in $C(t)$ for the forgoing example can be avoided by repositioning values $CV2$ and $CV3$ in Fig. 4b at a time when $C_1 \leq C_{o1}$. The terminal transients resulting from this procedure are shown in Fig. 4b for values of $C_{o1}/C_o = 0.8, 0.9$ and 1.0 . Because the system volume has been decreased by a factor of 3 during the terminal transient, the rate of approach to steady state is more rapid by the same factor.

Composition Grading in Binary Alloys

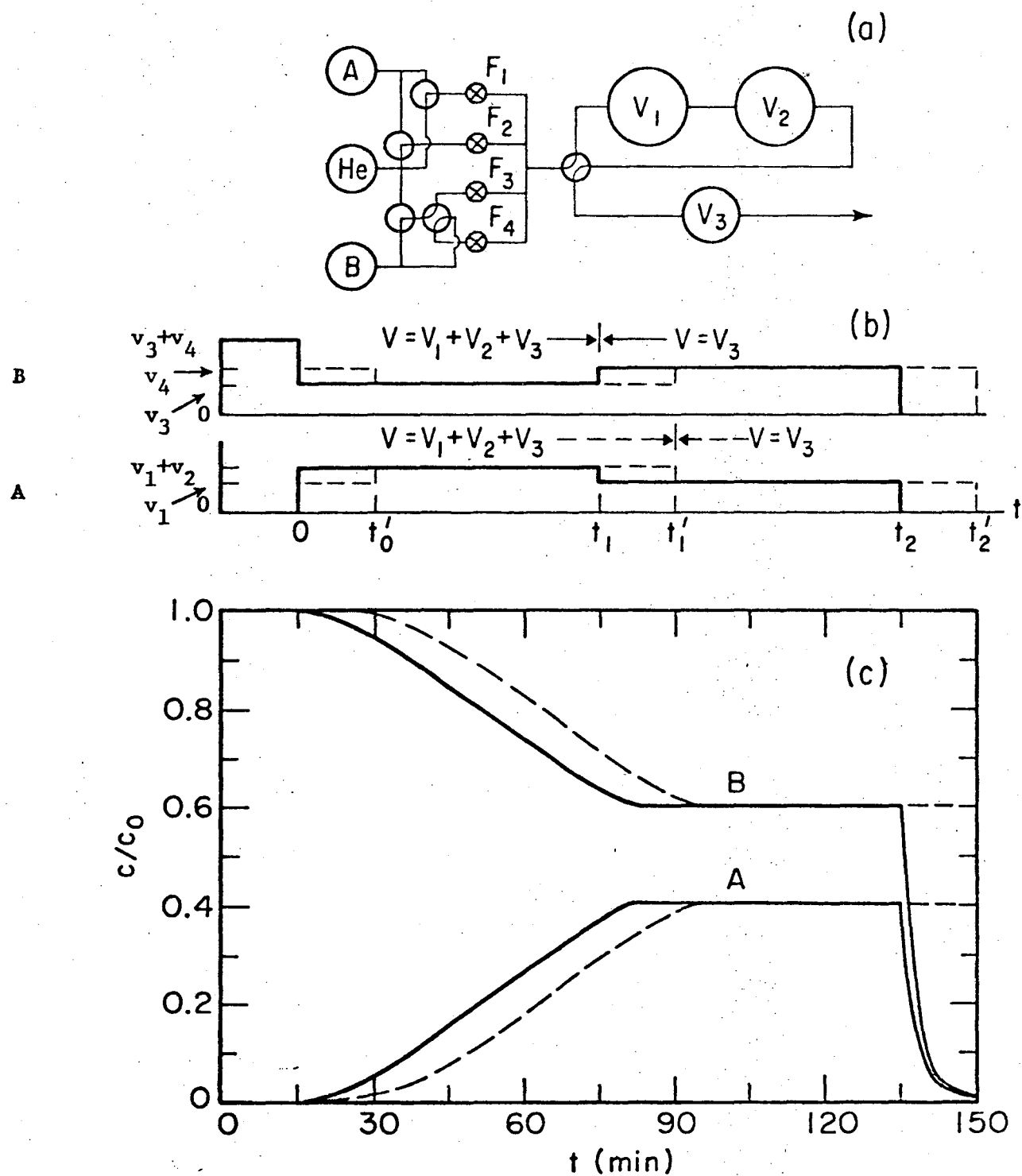
The tank mixing processes explored in the foregoing sections provide a simple basis for controlling reactive gas mixtures for alloy composition grading in chemical vapor deposition processes. For binary alloys with the chemical formula $A_x B_{1-x}$, or for binary compound solid solutions, $(AC)_x (BC)_{1-x}$, the gaseous reactants are volatile forms of components A and B , such as hydrides, halides or organometallic compounds. Generally, both reactive gas concentrations must be programmed as a function of time to achieve a deposited layer with graded composition, with the range in gas composition of each dictated by thermodynamic constraints. When the alloy is to be deposited onto one of its components, such as W_3C onto graphite, or $GaAs_{0.6}P_{0.4}$ onto $GaAs$, the gradation is from the reactive gas composition in equilibrium with the pure component to that in equilibrium with the alloy.

A simplified mixing tank manifold for programming binary reactive gas mixtures is shown in Fig. 5. In this manifold the inert gas He is substituted for reactive components A or B whenever concentrations of the latter are reduced, in order to maintain the total flow rate a constant. Series tanks are recommended to minimize the discontinuity in initial transients, while a by pass of all but the final mixing tank provides a short time constant for the terminal transient to a steady state.

When the volumetric flow rates of reactants A and B are programmed as shown in Fig. 5b, the normalized output concentrations are those shown in Fig. 5c. The solid curves show the consequence of flow rate changes at times 0 and t_1 , with tanks 1 and 2 by passed at time t_1 . The dashed curves show the effect of introducing the final flow rates required for steady state at time 0, followed by the above flow programming at time t'_0 , with the total tank volume reduced at time t'_1 . As the dashed curves show, the initial time rate of change in reactant concentration is thereby reduced.

The total tank volume required for composition grading of a binary alloy is a function of the gradation time period and the total flow rate changes required. For the system shown in Fig. 5, the tank volume required is

$$V = \sum_{i=1}^3 V_i \approx \left(1 + \frac{v_2}{v_1}\right) v t_1 = \left(\frac{v_4}{v_3}\right) v t_1. \quad (10)$$



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Figure 5. Time-varying composition programming of a binary reactive gas mixture: (a) schematic of flow system; (b) flow rate programming for components A and B; and (c) output concentrations as a function of time.

The approximate total tank volume required for the flow programming shown by the dashed lines in Fig. 5 is also given by this expression if $(t'_1 - t'_0)$ is substituted for t_1 .

The tank volume V_3 required for the final transient must be small compared to the total volume of all tanks to make the transition to steady state rapid. Discontinuities in the time rate of change in concentrations at t_1 can be minimized by equating the time derivatives of the intermediate and final transient concentrations at t_1 . Thus, for two mixing tanks in series,

$$\frac{V_3}{V} \approx \frac{C_{o1} - C_1}{4C_o} e^{2t_1/\tau} \quad (11)$$

In principal, the ratio V_3/V can be made arbitrarily small provided that the terminal transient is initiated at a time when $(C_{o1} - C_1)/C_o$ has a correspondingly small value.

Application to the $\text{GaAs}_{1-x}\text{P}_x$ System

For epitaxial, chemical vapor deposition of $\text{GaAs}_{0.6}\text{P}_{0.4}$ onto GaAs substrates the concentration of AsH₃, entering the reactor is commonly held constant, while the concentration of PH₃ is programmed to increase slowly from a null value during an initial period of growth to minimize dislocation generation in the epitaxial alloy layer. The PH₃ concentration is then increased linearly to 20% of the constant AsH₃ concentration over a time period of approximately one hour. The PH₃ concentration is then held constant for an additional hour during which the compound alloy $\text{GaAs}_{0.6}\text{P}_{0.4}$ is deposited.

The simplified mixing tank system of Fig. 4 can be applied to program the molar flow rate of PH_3 to the reactor by programming the PH_3 flows of v_1 , $v_1 + v_2$ and v_1 as shown by the dashed line in Fig. 5b. Here, gases A and B are H_2 and PH_3 respectively. The mixing tank output concentration of PH_3 is then shown by the dashed curve in Fig. 5c. For a total volumetric flow rate of 10 l/min of H_2 containing 1% of AsH_3 to the reactor, a total PH_3 flow rate of 0.04 l/min will be required from the mixing tank system at steady state. For a grading period t_1 the total mixing tank volume required is

$$V = v \left(1 + \frac{v_2}{v_1} \right) t_1 . \quad (12)$$

Thus, for $v_1 = 1.5 v_2$, $v_3 = 0$ and $t_1 = 60$ min, a total tank volume of 4 l is required. The gradation time t_1 can be reduced by increasing the added H_2 flow rate v_3 to a finite value.

Discussion

The experimental study of Bailey and Rogers⁽¹⁰⁾ has shown that the output concentration from a single mixing tank corresponds closely to theoretical expectations, and that simple tank mixing methods are applicable to reactant concentration programming in chemical vapor deposition reactors. For industrial applications it is essential that the mixing tanks be well mixed so that the output response from incremental input programming can be described by the complete mixing

assumption. Wherever tank flow rates are low and incomplete mixing likely, then the terminal transient time constant should be increased to minimize discontinuities in the time dependent output concentration from the tank-mixing system.

It was shown earlier that time dependent concentration programming can be produced by discrete changes in C_{input} , v or V for both series and parallel mixing-tank systems. In order to avoid discontinuities in molar flow rates, however, it is necessary to change two of these parameters simultaneously. This requirement is essential for achieving rapid convergence to a steady state following composition programming. An alternate procedure to the one outlined in this study is the simultaneous change in C_{input} and v . A third alternative in which v and V are changed imposes restrictions on the system time constants.

The tank-mixing methods described in this study can be applied to liquid flow systems as well as gaseous flow systems. The use of series and parallel mixing tank systems provides enhanced flexibility in the application of such methods to time-dependent, reactant composition programming.

Acknowledgments

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List of Symbols

C	molar concentration, moles/cm ³
$C^{(n)}$	molar concentration of tank n , moles/cm ³
CV_i	flow control value i
f_i	flow rate fraction passing through tank i
F_i	flow metering value i
t	time following an initial step-function input of reactant, s
t_1	transient mixing time, s
v	volumetric flow rate, cm ³ /s
v_i	volumetric flow rate through value i , cm ³ /s
V	tank system volume, cm ³
V_i	volume of tank i , cm ³
τ	mean residence time, $(=V/v)$, s
τ_i	mean residence time for a tank of volume V_i , s

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