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KINETICS OF THE CHEMICAL VAPOR DEPOSITION
OF GaAs FROM Ga(CH₃)₃ AND AsH₃

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The kinetics of the chemical vapor deposition of GaAs from trimethyl gallium and arsine in a hydrogen carrier gas is studied in detail to determine the effect of growth conditions on the deposition rate, and to determine the factors affecting the defect morphology of single crystal GaAs layers deposited on (100) GaAs substrates. Thermochemical studies are performed to define species partial pressures in the gas phase. A mass transport model for the reactor is presented to serve as a basis for comparison of experimental data with kinetic models for the growth process.

INTRODUCTION

Gallium arsenide has been studied extensively for application in microwave devices, and more recently in low-cost terrestrial solar cells. The processing of low-defect density single crystal layers and heteroepitaxial layers is a significantly important step in the preparation of these semiconducting devices. The chemical vapor deposition of GaAs from systems containing chlorine as a transport agent has become a common method for preparing GaAs films, yet contaminants are introduced by this method owing to the etching of the reaction vessel and substrate through side reactions involving chlorine.

The vapor phase deposition of gallium arsenide from trimethyl gallium (TMG) and arsine has been shown by Manasevit to be a viable alternative to the conventional growth technique using halide transport agents. This method is free of etching species, requires a furnace with only one temperature zone, and offers the possibility of lower growth temperature. Recently, single-crystal GaAs films were successfully prepared by this method in several laboratories. Most of these studies emphasize the surface morphology and electrical properties of the heteroepitaxial GaAs layers deposited on single crystal, insulating substrates rather than the chemical vapor deposition process.

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To date, few reports have been made on the chemical vapor deposition process by which GaAs films are deposited by the reaction of trimethyl gallium and arsine.

The present work attempts to elucidate the chemical vapor deposition process in detail, and to examine the effects of growth conditions on the growth rate and growth morphology of homoepitaxial GaAs films. Single crystal G(100) GaAs substrates were used in the study in order to avoid the nucleation effects observed in previous studies of the heteroepitaxial growth of GaAs on metallic and graphite substrates.13,14

THEORY

THERMOCHEMISTRY

A thermochemical study of gas phase and gas-solid reactions was performed to predict the dominant reactions involved for the deposition of GaAs from trimethyl gallium and arsine. The dominant reactions are

\[
\begin{align*}
\text{AsH}_3 &= \frac{1}{4} \text{As}_4 + \frac{3}{2} \text{H}_2 \\
\text{Ga(CH}_3)_3 + \frac{1}{4} \text{As}_4 + \frac{3}{2} \text{H}_2 &= \text{GaAs(c)} + \text{CH}_4
\end{align*}
\]

Both of these reactions have large equilibrium constants at elevated temperatures, and therefore, the reactions are driven to the right.

Calculations of thermodynamic equilibrium were performed to determine the equilibrium concentration of TMG on the substrate surface under typical conditions used in chemical vapor deposition experiments. The results showed that the surface concentration of TMG is negligibly small over the entire range of experimental conditions considered, namely $500^\circ\text{C} < T < 900^\circ\text{C}$, $10^{-6} < x_{\text{TMG}} < 10^{-2}$ and $x_{\text{AsH}_3} > x_{\text{TMG}}$.

VELOCITY DISTRIBUTION

The flow distribution for downward flow in the experimental reactor tube containing an inductively heated substrate disk has been visualized by Mantel et al., using a collimated light source.15 This study confirms that the flow distribution is diverging from the center axis of the disk susceptor, so that a boundary layer of nearly uniform thickness develops over a major part of the substrate surface, except near the edge of the substrate, where the boundary layer thickness is decreased. The flow in the experimental reactor issues from a 1 cm diameter tube and diverges from the point of impact on the substrate (or susceptor) surface.

The velocity distribution in the gas phase along the normal from the susceptor (y-dimension) is calculated by solving the momentum and continuity equations in the radial direction.
The form of the velocity profile along the stagnation streamline suggested by applying dimensional analysis to the \( r \)-directed momentum equation is the following:

\[
v_y / \sqrt{\beta v_\infty v R^{-1}} = f(\eta), \quad \eta = \sqrt{\frac{\beta v_\infty}{\sqrt{v R}}}. \tag{4}
\]

The function \( f(\eta) \) has been shown by Kays to be deduced from the heat flow from the disk susceptor.\(^{16}\)

For an isothermal impinging jet issuing from a tube, Scholtz and Trass have shown that the velocity profile along the stagnation contour is

\[
v_y = \gamma y \tag{5}
\]

where \( \gamma \) is a constant of unity magnitude, but dependent on the diameter of the jet orifice and height from the susceptor.\(^{17}\) This result indicates that the velocity profile is independent of the flow rate.

**DEPOSITION RATE**

For a large area jet impinging on the susceptor surface, the mass equation for TMG along the stagnation streamline is

\[
v_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}. \tag{6}
\]

This equation can be integrated twice with the known velocity profile and matched to the concentrations of TMG at the susceptor surface and in the inlet gas. The molar flux of TMG to the surface is then

\[
N_{TMG} = -D \frac{\partial c}{\partial y} \bigg|_0^\infty = \frac{D(c_0 - c_\infty)}{\int_0^\infty \exp \left( \int_0^y v \sqrt{\beta v_\infty v R^{-1}} \, dy \right) \, dy}.
\]
The molar flux of TMG can be deduced by an analogous method to that for heat transfer along the stagnation contour:

\[ N_{\text{TMG}} = 0.76\sqrt{\nu} \nu^{0.6} \nu^{-0.1} \sqrt{\nu} R. \]  

(7)

A similar equation was derived by Scholtz and Trass\textsuperscript{17} for small diameter jets; for a nozzle placed one diameter from the susceptor, their results showed:

\[ N_{\text{TMG}} = 0.36 \nu^{0.64} \nu^{-0.14} \sqrt{\nu} R (c_0 - c_\infty). \]  

(8)

Both results indicate that \( N_{\text{TMG}}(=N_{\text{GaAs}}) \) increases with the square root of the inlet gas flow velocity.

The temperature dependence of the molar deposition rate (Eqs. 7 and 8) is determined by the temperature dependence of \( \nu \) and \( D (-T^{1.6}) \). Therefore, the predicted temperature dependence of \( N_{\text{GaAs}} \) is \( T^{0.8} \).

EXPERIMENTAL

EQUIPMENT

The apparatus used for chemical vapor deposition studies is shown in Fig. 1. This apparatus is similar to that used by Manasevit and Simpson.\textsuperscript{6} The double-walled water-cooled, vertical quartz reactor is 36 mm in ID and 30 cm long. The pyrolytic graphite pedestal which can be inductively heated is 22 mm in diameter with a raised barrier of 1.6 mm wide and 1.6 mm high at the outer rim of the top surface edge.

Bubblers contain liquid organometallic compounds are constructed of pyrex and connected through glass-metal seals to the stainless steel tubing used in the flow metering system. Flow rates of different gases such as the carrier gases, trimethyl gallium and arsine are measured using glass rotometers.

A chromel-alumel thermocouple is inserted through a closed-end quartz tube to the base of the graphite pedestal. The thermocouple readings are calibrated by measuring the melting points of several pure metals placed on the top surface of substrate crystals.

MATERIALS

The trimethyl gallium used has a purity of 99.9999% obtained from Ventron Corp. This compound was maintained at 0°C during deposition by placing an ice bath around the saturator. Pure arsine of electronic grade was obtained from Matheson Gas Product Co. Mechanical and chemically polished \{100\} GaAs wafer obtained from Litronix Co. were used in CVD experiments.
PROCEDURE

Prior to deposition, the substrates were degreased in perchloroethylene, acetone and methanol, then etched in a concentrated HCl solution, rinsed several times in warm methanol and hot, electronic grade isopropyl alcohol and finally blown dry by using filtered nitrogen.

After a substrate was loaded in the reactor, the entire system was thoroughly purged with gas helium for ten minutes. Then the hydrogen carrier gas was introduced into the reactor and the substrate was heated to the deposition temperature. The flow of AsH₃ was initiated when the substrate temperature reached 450°C in order to prevent substrate decomposition. When the operating temperature was reached, the flow rate of hydrogen through the trimethyl gallium saturator was begun.

After the deposition was completed, the trimethyl gallium flow was terminated and the rf power was turned off. The arsine flow was continued until the substrate temperature had dropped to about 450°C.

RESULTS

Growth studies at different gas flow rates were performed in order to investigate the growth kinetics. The flow rate ranges used were as follows: total H₂ carrier gas (1 - 3 L/min); H₂ flow to the trimethyl gallium saturator (3 - 23 cc/min); AsH₃ (5 - 36 cc/min). Studies were also carried out over a wide range of substrate temperatures, from 580° to 930°, in order to study the effect of temperature on growth rate and surface perfection.

Epitaxial layer thickness was determined using an optical microscope after the edges were etched in a 2:1 mixture of HNO₃:H₂O or in a bromine-methanol etching solution. The surface morphology was studied as a function of growth conditions using an AMR 100 scanning electron microscope.

DEPOSITION PROFILE

Deposition rate profiles measured on cleaned and etched wafers revealed that the deposition rate was nearly constant over the middle part of the wafer. The deposition rate appeared to increase with distance toward the edge of the substrate wafer, and some dendritic growth was observed.

A typical deposition profile is shown in Fig. 2 for a substrate temperature of 755°C. At the edge of the wafer the deposition rate was approximately 20% higher as in the center. As a consequence of these findings, all subsequently measured deposition rates were determined from the thickness of the GaAs layer deposited over the middle part of the substrate.
EFFECT OF AsH₃

The deposition rate was found to be independent of the AsH₃ concentration as long as at least a 3-fold excess of AsH₃ over TMC was maintained in the gas mixture. At lower AsH₃ concentrations, liquid gallium droplets were frequently observed on the substrate surface.

EFFECT OF TMC

At any deposition temperature and total H₂ carrier gas flow rate, the growth rate was found to be linearly proportional to the TMC concentration. This dependence is shown in Fig. 3, for a substrate temperature of 755°C. Similar results have also been observed for GaAs growth on single crystal insulating substrates.

EFFECT OF TOTAL FLOW RATE

In general, the deposition rate was found to increase with increasing total gas flow rate at a constant substrate temperature and concentrations of TMC and AsH₃. The experimental dependence of the growth rate on total gas flow rate for a deposition temperature of 755°C and for mole fractions of TMC and AsH₃ of 0.045% and 1.2%, respectively, is shown in Fig. 4.

EFFECT OF SUBSTRATE TEMPERATURE

The dependence of the GaAs growth rate on the substrate temperature is shown in Fig. 5 for flow rates of 1 l/min (filled circles) and 2 l/min (open circles), $p_{\text{TMC}}^0 = 6.5 \times 10^{-4}$ atm and $p_{\text{AsH₃}}^0 = 6 \times 10^{-3}$ atm. The growth rates for both flow rates decrease linearly with inverse temperature between 640° and 720°C, indicating surface reaction kinetic rate control in that temperature range. The temperature dependence is approximately $T^{-0.8}$ in the range from 700°C to 900°C. A further increase in temperature causes the deposited GaAs to decompose, thereby limiting the growth rate.

SURFACE MORPHOLOGY

The surface morphology was studied as a function of the substrate temperature and molar concentrations. The results for the temperature range from 582°C to 950°C are shown in Fig. 6 for a TMG flow of $5 \times 10^{-5}$ moles/min and $p_{\text{AsH₃}}^0 = 3 p_{\text{TMC}}^0$.

Surfaces of the epitaxial layer obtained were specular but showed hillocks and pits when viewed in the scanning electron microscope.

DISCUSSION

The experimental results are in good agreement with the theoretical expressions for diffusion controlled growth rates: the GaAs
growth rate varies approximately with the 0.5 power of the gas flow velocity, and it varies with the 0.7-0.8 power of the absolute temperature.

The linear dependence of the growth rate on the trimethyl gallium concentration and the above results indicate that a diffusion controlled model adequately explains the experimental results for 700°C<T<900°C.

The hillocks and pits found on the surface indicate that some contamination of the surface occurs, presumably by oxidation of the trimethyl gallium.

The hillock feature are similar to those found on GaAs deposited from Ga(\(\text{Cl}_2\)) and AsH\(_3\) or from Ga(\(\text{Cl}_2\)), HCl and AsH\(_3\).\(^{18}\) The hillocks observed had a rectangular shape, with the long dimension lying along <110> directions.

The density of pits is found to be independent of the TMG flow rate. Pits are bounded generally by sharp edges. The size of the pits varies up to 5 \(\mu\)m. It is hypothesized that the pits are formed by Ga\(_2\)O\(_3\) particles which become trapped in the deposited GaAs layer; owing to differences in the coefficients of thermal expansion, the GaAs covering over the particle is broken away during cooling from the growth temperature.

CONCLUSION

A diffusion controlled model is sufficient to describe the chemical vapor deposition of GaAs from trimethyl gallium and arsine in a hydrogen carrier gas over the temperature range from 725°C to 875°C. At lower temperatures the growth is surface reaction rate controlled. At higher temperatures, decomposition of the GaAs reduces the growth rate.

A model for the deposition rate is developed based on the jet impingement character of the experimental reactor. The model is consistent with the observed dependences of the GaAs deposition rate on the inlet flow velocity and the substrate temperature.

Defects in the epitaxially grown layers are of two types: hillocks and pits. The hillocks are similar to those observed when GaAs is deposited using chloride transport. Pits are presumed to be produced as a consequence of oxidation of the trimethyl gallium.

ACKNOWLEDGMENT

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NOMENCLATURE

c: molar concentration of TMG, moles/cm³

c₀: molar concentration of TMG at the substrate, moles/cm³

c∞: molar concentration of TMG in the inlet gas, moles/cm³

D: diffusivity of TMG, cm²/s

N: molar flux, moles cm⁻²s⁻¹

p: partial pressure of a gas component, atm

p₀: inlet partial pressure, atm

R: radius of the disk susceptor, cm

Re: Reynolds number (=βν_r R/v)

x: mole fraction of a gas phase species

y: normal coordinate lying along the susceptor axis

v: gas velocity, cm/s

v_r: radial velocity of the reactor gas, cm/s

v_y: normal velocity of the reactor gas, cm/s

v_∞: inlet gas velocity

β: shape factor (-1)

γ: a constant

ν: kinematic viscosity, cm²/s

REFERENCES

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Fig. 1 Apparatus for chemical vapor deposition studies.

Fig. 2 GaAs growth rate as a function of radius from the center of the wafer.
Fig. 3 Dependence of GaAs growth rate on the TMG flow rate.

Fig. 4 Dependence of GaAs growth rate on total gas flow rate.
Fig. 5 Dependence of GaAs growth rate on substrate temperature.
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