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**Type of Report:** Interim Technical

**Time Covered:** From Oct. 86 to Aug. 87

**Date of Report:** 87-8-12

**Page Count:** 12

**Subject Terms:** gallium arsenide, aluminum arsenide, photodeposition, Lewis acid-base adducts, thin films

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Contract N00014-81-C-0642

R&T Code No. 629-779
Technical Report No. 1

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by

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Prepared for Publication
in the
Materials Research Society Symposium B Proceedings
Volume 75

Hughes Research Laboratories
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August 1, 1987

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EXCIMER LASER-ASSISTED DEPOSITION OF GaAs, AlAs, AND [Al,Ga]As FROM LEWIS ACID-BASE ADDUCTS

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ABSTRACT
Laser-assisted deposition of GaAs, AlAs and [Al,Ga]As thin films on Ge(100) substrates from trimethylgallium-trimethylarsenic and trimethylaluminum-trimethylarsenic Lewis acid-base adduct source materials is reported. A parametric study has been performed in which reactive gas pressure, substrate temperature, laser fluence, laser wavelength (248 nm or 193 nm), and orientation of the laser beam with respect to the substrate have been varied. In the case of irradiation parallel to the substrate, stoichiometric films of GaAs and [Al,Ga]As have been obtained. The data suggest that for irradiation perpendicular to the substrate a competition exists between desorption and photodeposition, which adversely affects film stoichiometry under the conditions studied.

INTRODUCTION
Laser-assisted reactions are being actively investigated as a means for depositing compound semiconductor films at reduced temperatures and with a degree of spatial control not available with conventional thermal methods. Particular attention has been directed toward the laser-assisted deposition of III-V materials. For example, InP has been deposited via ArF (193 nm) excimer laser dissociation of organometallic starting materials [1], and GaAs has been deposited using a cw Ar laser beam for spatially localized heating [2-4]. In this paper, we discuss recent work on the excimer laser-assisted deposition of GaAs, AlAs, and [Al,Ga]As from organometallic Lewis acid-base adducts, specifically, trimethylgallium-trimethylarsenic (GaAs adduct) and trimethylaluminum-trimethylarsenic (AlAs adduct). Adducts offer several potential advantages over conventional gas source materials. These include, for example, the ability to deposit stoichiometric films using a single reactant gas, and the use of wavelengths longer than 193 nm to promote the deposition reaction.

Previously, we have demonstrated that stoichiometric films of GaAs could be produced by irradiation of the GaAs adduct at its equilibrium vapor pressure (approximately 7 Torr at 25°C) in a static gas cell at 248 nm [5]. In the present work we have utilized a low pressure metalorganic chemical vapor deposition (MOCVD) system, and have performed a systematic variation of reaction parameters in order to establish conditions under which stoichiometric films could be obtained; the ultimate goal being the low temperature growth of epitaxial layers with controlled composition. Experimental parameters which were varied include: reactant gas pressure, substrate temperature, laser fluence, laser wavelength (193 or 248 nm) and orientation of the incident laser pulse with respect to the substrate (parallel or perpendicular). In addition, we have extended the earlier studies to include an investigation of the AlAs adduct.

EXPERIMENTAL
The low pressure MOCVD system is shown schematically in Fig. 1. The reaction vessel consisted of a modified stainless steel six-way vacuum cross which was pumped by a Balzers 1101 s turbomolecular pump (TMP). The base pressure of the system was approximately 10⁻⁴ Torr. During deposition experiments, the TMP was isolated from the system by a vacuum gate valve, and the chamber was pumped by a liquid nitrogen-trapped mechanical pump. Helium carrier gas was
passed through an oxygen and water filter before entering the reactive gas bubblers and was then introduced into the reaction chamber using mass flow controllers. Typical flow rates for the reactive gases and for the helium window purge were 200 and 700 sccm respectively. The total pressure in the chamber, usually maintained at 15 Torr, was controlled by a capacitance manometer and regulating valve feedback assembly. The sample was mounted with In to a resistively heated stage to ensure good thermal contact. The stage temperature could be varied from 20°C to 700°C. The temperature was monitored using a thermocouple which was embedded in the heater stage, while a proportional controller maintained a constant temperature during deposition. The sample holder allowed substrates to be mounted either horizontally or vertically in the chamber so that laser irradiation either normal or parallel to the substrate could be performed.

A Lumonics TE861-4 excimer laser was used as the UV source in these experiments. The laser was operated at either 248 nm (KrF) or 193 nm (ArF) at a repetition rate of 10 Hz. The laser fluence was varied from 20 mJ/cm² to 300 mJ/cm² in a typical set of experiments. Laser fluences reported have not been corrected for absorption by the gas. At 193 nm, assuming a 6 cm optical path length, we estimated a 2% attenuation at the substrate for typical pressures used for AlAs deposition, and a 20% attenuation for typical pressures used for GaAs deposition. There was negligible attenuation of laser fluence at the substrate due to absorption of the adducts at 248 nm.

The GaAs adduct was obtained as electronic grade (99.9999%) from Alfa Products and was used without further purification. The AlAs adduct was synthesized in our laboratory by combining trimethylaluminum (TMAI) with a 5-10% excess of trimethylarsenic (TMAs) and subliming the resultant solid adduct onto a cold finger at -30°C. The vapor pressure of the AlAs adduct at 25°C was ~0.5 Torr. Partial pressures of the adducts used in our experiments varied from 10⁻³ Torr to 0.4 Torr. A typical growth period was on the order of 30 minutes. Composition of the deposits was determined by Auger Electron Spectroscopy (AES).

It is important to note that these adducts are in dissociation equilibrium with their Lewis acid-base components.

\[
(CH_3)_3Ga:As(CH_3)_3 = (CH_3)_3Ga \quad \text{and} \quad (CH_3)_3As \quad \Delta H = 10 \text{ kcal/mole} \quad [6]
\]

\[
(CH_3)_3Al:As(CH_3)_3 = (CH_3)_3Al \quad \text{and} \quad (CH_3)_3As \quad \Delta H = 25 \text{ kcal/mole} \quad [7]
\]

The degree of dissociation is affected by both pressure and temperature, to an extent determined by the free energy associated with the reaction. The UV absorption spectra of the two adducts, at their equilibrium vapor pressures at 25°C, are presented in Fig. 2. Using these spectra, we calculated an

Fig. 1. Low pressure MOCVD system.
Fig. 2. UV absorption spectra of the adducts. The cell pathlength is 13 mm. (a) GaAs adduct at 7 Torr. (b) AlAs adduct at 0.5 Torr.

extinction coefficient on the order of $10^2 \text{(Torr-cm)}^{-1}$ at 248 nm for each adduct. We have also determined the extinction coefficient for TMAs at 248 nm to be on the order of $10^1 \text{(Torr-cm)}^{-1}$. Measured extinction coefficients for the GaAs adduct, AlAs adduct and TMAs at 193 nm were 1, 0.3, and 4 (Torr-cm)$^{-1}$, respectively.

The Ge(100) substrates were obtained in 99.9999% purity from Eagle Picher. Substrates were degreased in boiling dichlorodifluoroethane, acetone, and methanol, and were subsequently etched in a room temperature 10:1 solution of $\text{H}_2\text{O}:\text{HF}$ followed by an etch in a room temperature 5:3:1 solution of $\text{H}_2\text{O}:\text{HNO}_3:\text{HF}$. Freshly etched substrates were immediately mounted with In on the sample holder and placed in vacuum. Prior to admitting any reactive gas to the reaction chamber, the substrate temperature was raised briefly to 600°C to desorb any oxide from the surface.

RESULTS AND DISCUSSION

GaAs deposition

Significant differences in film composition were observed as a function of laser wavelength, laser fluence, and orientation of the laser pulses with respect to the substrate. Best results were obtained when 193 nm pulses were directed parallel to the substrate. Under these conditions smooth, reflective and stoichiometric deposits were obtained.

Depositions performed at 248 nm using the GaAs adduct and a substrate temperature of 25°C resulted in films which were As deficient. Only in the cases of the highest adduct partial pressure used (0.4 Torr), or where excess TMAs was added to the adduct in the reactor (TMAs/TMGa:TMAs = 11 and 17), was any As detected in the films by AES analysis. This is in marked contrast to the results of our static cell experiments, described previously. However, the static cell experiments were performed at the equilibrium vapor pressure of the adduct, ~7 Torr at 25°C. We suggest that the difference between our static cell and low pressure MOCVD experiments is explained by the increasing dissociation of the adduct as its partial pressure is reduced below its equilibrium vapor pressure. Using available thermodynamic data [6], we calculate that the adduct is 100% dissociated at $10^{-2}$ Torr partial pressure. The addition of excess TMAs to the adduct in the gas phase will shift the equilibrium in the direction of the associated adduct.

The As:Ga ratio in the deposited films as determined by AES analysis is plotted as a function of associated adduct pressure in Fig. 3. The data show that the As content of the films increases as the pressure of associated adduct in the gas phase is increased. This is consistent with the hypothesis that for the
majority of the adduct partial pressures used in our low pressure MOCVD experiments the adduct is completely dissociated. The resultant films are As deficient because TMAs is a weak absorber at 248 nm. Considering that stoichiometric films were deposited in the static cell experiments, these results also suggest that absorption of 248 nm photons by the associated adduct molecules does not result in the release of ground state TMAs alone. In addition, photodissociation of the adduct must result in a product (e.g., an excited state or fragment of TMAs) which either absorbs at 248 nm or adsorbs on the substrate surface.

We have studied the effect of increasing laser fluence at 248 nm on film stoichiometry in a set of experiments in which the adduct partial pressure was on the order of $10^{-2}$ Torr, the substrate temperature was 25°C, and the laser beam was oriented perpendicular to the substrate. As the laser fluence was increased above 140 mJ/cm², the As/Ga ratio in the films was observed to increase. At the highest laser fluence used (200 mJ/cm²) the As/Ga ratio was 0.17. We have calculated the transient surface temperature rise during the laser pulse using an approximate solution to the heat flow equation, which is appropriate when the light absorption length is small compared with the heat diffusion length [8]. At 140 mJ/cm² the transient temperature rise is on the order of 400°C, which places the substrate surface at the threshold temperature for thermal decomposition of TMAs. Therefore, the increased As content of the films at higher laser fluences may occur as a result of pyrolysis under these conditions.
Depositions were performed at 193 nm using the GaAs adduct at a partial pressure of \(2 \times 10^{-2}\) Torr and a substrate temperature of 300°C. The As/Ga ratio as a function of laser fluence is presented in Fig. 4, for both parallel and perpendicular irradiation conditions. In the case of irradiation perpendicular to the substrate, the films were nonstoichiometric. Temperature calculations indicated that the substrate surface was being heated to a temperature (>600°C) at which desorption of As from the surface could be occurring. A competition between photodeposition and desorption is suggested which would adversely affect film stoichiometry.

In marked contrast to the results obtained using perpendicular irradiation, in the case of parallel irradiation, a stoichiometric film was obtained. SEM examination of the deposited layer showed that the surface was smooth on a micron scale. In addition, this stoichiometric film was deposited with a gas phase III/V ratio of only 1:1.

**AlAs deposition**

The AlAs adduct has been estimated to have a donor acceptor bond strength on the order of 25 kcal/mol [7], 15 kcal/mol stronger than the GaAs adduct. Although entropy data were not available for the AlAs adduct, we assumed a similar entropy as for the GaAs adduct, and calculated that there should be negligible dissociation of the AlAs adduct at 25°C and the pressures used for these experiments. Therefore, given this assumption, when the partial pressure of the AlAs adduct was reduced from its equilibrium vapor pressure (approximately 0.5 Torr) to the partial pressure typically used in the low pressure MOCVD system (approximately \(10^{-3}\) Torr), the adduct should have remained associated.

In support of this hypothesis, films deposited from the AlAs adduct onto a 25°C substrate using 248 nm laser pulses oriented perpendicular to the substrate contained significant amounts of As, even at low partial pressures of the AlAs adduct. The As:Al ratio as determined by AES analysis is plotted as a function of 248 nm laser fluence in Fig. 5, for both parallel and perpendicular irradiation. These films were still nonstoichiometric, suggesting either a partial dissociation of the adduct, and/or a competition between photodeposition and desorption.

![Fig. 5. Deposit stoichiometry as a function of laser fluence. Results from 248 nm irradiation of the AlAs adduct. P_adduct = 3 \times 10^{-3}\) Torr, T_s = 25°C.](image-url)
In the case of irradiation parallel to the surface, where surface heating could not be adversely affecting stoichiometry, no film was visible on the substrate. Auger analysis of the surface revealed only a small quantity of Al. The observation that a deposit results from direct irradiation of the surface, and no deposit results from non-surface irradiation, suggests that photodeposition from the AlAs adduct at 25°C results from photolysis of physisorbed layers of the adduct on the substrate surface.

The Al/As ratios in films deposited from the AlAs adduct at 193 nm for several pressures, substrate temperatures and laser fluences are presented in Table I. In all cases the deposited films were As deficient. In the case of irradiation parallel to the substrate, once again no deposit was observed, and AES analysis indicated only a trace amount of Al and As on the surface. We have evidence, which we will present in the next section, that at the highest substrate temperature (300°C), the AlAs adduct is dissociated in the vicinity of the substrate surface. This suggests that in the deposition of AlAs a surface nucleation step is required to initiate film growth by adsorption of Al, which necessitates direct surface irradiation. A strong surface component for the photolysis of TMAI in the deposition of Al films has previously been reported by Ehrlich et al. [9].

Table I. Conditions and results for the deposition of AlAs using 193 nm irradiation

<table>
<thead>
<tr>
<th>P_{add} (Torr)</th>
<th>T (°C)</th>
<th>Laser Fluence (mJ·cm⁻²)</th>
<th>As/Al (deposit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2×10⁻¹</td>
<td>207</td>
<td>20 (perpendicular)</td>
<td>0.36</td>
</tr>
<tr>
<td>2×10⁻¹</td>
<td>207</td>
<td>86 (perpendicular)</td>
<td>0.45</td>
</tr>
<tr>
<td>1×10⁻¹</td>
<td>305</td>
<td>73 (perpendicular)</td>
<td>0.36</td>
</tr>
<tr>
<td>1×10⁻¹</td>
<td>305</td>
<td>165 (perpendicular)</td>
<td>0.10</td>
</tr>
<tr>
<td>1×10⁻¹</td>
<td>305</td>
<td>306 (parallel)</td>
<td>0.16</td>
</tr>
</tbody>
</table>

[Al,Ga]As deposition

We have used combinations of the GaAs and AlAs adducts in the gas phase to deposit films at both 248 nm and 193 nm. A summary of the deposition conditions and resultant film compositions is given in Table II. No As was found in any of the films deposited at 248 nm at a substrate temperature of 300°C, and with the laser oriented perpendicular to the substrate. This led us to conclude that at 300°C the AlAs complex was dissociated in the vicinity of the substrate surface, releasing TMAs which did not absorb at 248 nm. In addition, the gas phase ratio of Ga/Al was not reflected in the deposit, suggesting a thermal loss of Ga.

At 193 nm, with irradiation perpendicular to the substrate and a substrate temperature of 300°C, a similar trend was noted with the Ga/Al ratio in the gas phase and in the deposit. In this case, As was present in the films because TMAs absorbs at 193 nm. However, the films were nonstoichiometric. We attribute this to a competition between photodeposition and desorption, under the conditions studied. In the case of parallel irradiation the situation was greatly improved, as can be seen in Table II. Under these conditions the Ga/Al ratio in both the gas phase and deposit were comparable, and the films were stoichiometric. Once again, these films were deposited with a gas phase III/V ratio of only 1:1.

It is surprising that a stoichiometric film of [Al,Ga]As could be deposited with parallel irradiation when it was not possible to obtain any deposit of AlAs with parallel irradiation. A possible explanation for this may be that the [Al,Ga]As film was nucleated by Ga, and that the first few atomic layers were actually GaAs. Once this thin layer of GaAs was established, growth of [Al,Ga]As proceeded.
Table II. Conditions and results for the deposition of [Al,Ga]As

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>Laser fluence (mJ/cm(^2))</th>
<th>Ga/Al (gas)</th>
<th>Ga/Al (deposit)</th>
<th>III/V (deposit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>248</td>
<td>100 (perpendicular)</td>
<td>14</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>248</td>
<td>100 (perpendicular)</td>
<td>5</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>248</td>
<td>100 (perpendicular)</td>
<td>3</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>248</td>
<td>100 (perpendicular)</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>193</td>
<td>87 (perpendicular)</td>
<td>14</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>193</td>
<td>87 (perpendicular)</td>
<td>5</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>193</td>
<td>87 (perpendicular)</td>
<td>3</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>193</td>
<td>87 (perpendicular)</td>
<td>2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>193</td>
<td>320 (parallel)</td>
<td>17</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>193</td>
<td>320 (parallel)</td>
<td>5</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

Carbon content, growth rate, and film quality

A typical Auger profile for the films revealed the carbon content to be on the order of 5 atomic percent. There is some question as to the origin of the carbon which contaminates the film. One source of carbon could be the surface adsorption of radical hydrocarbon species generated as photolysis products during the deposition. However, in a recent study, carbon deposition was not observed on a GaAs substrate at 300°C when it was exposed to a methane plasma, where CH\(_2\) radicals were produced [10]. This suggests that in our experiments the carbon may still have been bonded to the metal atom when it adsorbed on the substrate surface. If this hypothesis is correct, then using highly focused beams in a parallel configuration, to increase the production of metal atoms versus molecular fragments, should result in the highest quality films.

The best growth rates obtained for the stoichiometric films were on the order of 0.03 Å/pulse. Higher growth rates should be obtainable by increasing the gas phase partial pressures of the adducts and by increasing the repetition rate of the laser.

Stoichiometric films were shiny and reflective. However, electron channeling studies of these deposits indicated that they were either amorphous, or had a high defect density. The high carbon content of these films is probably deleterious to epitaxial crystal growth. The addition of hydrogen in the gas phase as a hydrocarbon scavenger may improve this condition. In addition, the maximum substrate temperature used in this study, 300°C, may not be optimal for the growth of an epitaxial film.

SUMMARY AND CONCLUSIONS

We have successfully deposited stoichiometric films of GaAs and [Al,Ga]As with parallel irradiation, using a gas phase III/V ratio of 1:1. Our data suggest that in the case of perpendicular irradiation a competition between desorption and photodeposition adversely affects the production of stoichiometric films, under the conditions studied. All deposited films were either amorphous or had a high defect density. Work is currently in progress to establish the appropriate conditions to deposit high quality epitaxial films.

The results of this work indicate that unless the donor-acceptor bond of an adduct is sufficiently high it will dissociate into its Lewis acid-base components at low pressures as well as moderate temperatures. It is possible to strengthen the donor-acceptor bond by substituting more electronegative ligands on the group III atom or more electropositive ligands on the group V atom. Work is under way in our laboratory to synthesize such adducts and determine their utility as source materials for photodeposition.
ACKNOWLEDGMENTS

The authors wish to thank J.A. Roth and E.-H. Cirlin for valuable discussions, and R.F. Scholl, Jr. for his expert technical assistance. This work was supported in part by the Office of Naval Research.

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10. J.D. Warner, private communication.