NASA Technical Memorandum 88937

AlGaAs Growth by OMCVD Using an Excimer Laser

Joseph D. Warner, David M. Wilt,
John J. Pouch, and Paul R. Aron
Lewis Research Center
Cleveland, Ohio

(NASA-TM-88937) AlGaAs GROWTH BY OMCVD USING AN EXCIMER LASER (NASA) 11 p Avail: NTIS HC A02/MF A01 CSCL 20B

N87-23304

Unclas
H1/76 0076798

Prepared for the
Fall Meeting of the Materials Research Society
Boston, Massachusetts, December 1-5, 1986

AlGaAs GROWTH BY OMCVD USING AN EXCIMER LASER

Joseph D. Warner, David M. Wilt, John J. Pouch, and Paul R. Aron
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

E-3379

SUMMARY

AlGaAs has been grown on GaAs by laser assisted OMCVD using an excimer laser, wavelength 193 nm, and a Cambridge OMCVD reactor. Films were grown at temperatures of 450 and 500 °C with the laser beam either parallel to the surface or impinging onto the surface at 15° from parallel. The samples were heated by RF coils when the laser beam was perpendicular to the gas flow. Typical gas flow parameters are 12 slm of H_2, 15 sccm of H_2 through 0 °C $Ga(CH_3)_3$, 13 sccm of H_2 through 0 °C $Al(CH_3)_3$, and a pressure of 250 mbar. The initial energy density of the beam at the surface was 40 mJ/cm^2, the pulse rate was 20 pps, and the growth time was 7 min. The films were analyzed by Auger electron spectroscopy for the aluminum concentration and by TEM for the surface morphology.

INTRODUCTION

The laser-assisted organo-metallic chemical vapor deposition (LA-OMCVD) process has the potential to be able to grow high quality III-V compound semiconductors at low temperatures. This process is expected to give the control needed to grow films with monolayer transitions of doping levels and/or composition, and should permit the growth of films such as undoped GaAs on p-AlGaAs or n-GaAs on p-GaAs. Excimer lasers have been used in the past to grow insulator and metallic films (ref. 1). Longer wavelength lasers have been used to grown gallium arsenide by heating either the substrate or the deposition gases (refs. 2 to 5). Donnelly et al. have demonstrated the growth of epitaxial single crystal InP films using an excimer laser (ref. 6).

In this paper we report preliminary results on the growth of AlGaAs films by LA-OMCVD and the aluminum concentration, impurities, and crystal quality of the films. Auger electron spectroscopy (AES) and transmission electron microscopy (TEM) were used for analysis. The films were grown on GaAs at temperatures of 450 and 500 °C using 193 nm light. The films were grown with the laser beam impinging on the substrate at an angle of 75° from normal or parallel to the substrate. During each of the runs a film was grown on a substrate which was located upstream and outside of the laser beam path. The three methods of film growth are compared.

Professor George Collins at Colorado State University helped with his discussion on laser-assisted CVD.

EXPERIMENT

Aluminum gallium arsenide films were grown in a Cambridge MR 100 OMCVD RF reactor modified with a fused silica window located on the side of the quartz reaction chamber. The laser, Lambda Physik model 102-ES, was operated at

20 pulses/sec at an energy of 250 mJ at 193 nm (ArF laser). The laser beam, with dimensions 6 by 20 mm, impinged on the GaAs wafer either at angle of 75° from normal, or was parallel to the wafer and making grazing contact. Films were grown on two samples during each run. The position of the samples relative to the laser beam is shown in figure 1. The exposed sample has the beam either parallel to or impinging on its surface. The "unexposed" sample is 25 mm upstream of the exposed sample. Also, for each set of growth parameters there was a control run made without the laser on. Films were grown at two temperatures: 450 and 500 °C.

Prior to the deposition, the wafers ((100) orientations) were cleaned in boiling propanol, and etched with sulfuric acid and $H_2SO_4/H_2O_2/H_2O$ solution. The wafers were then placed in the reactor on a silicon carbide-coated graphite susceptor as seen in figure 1. The mass flow controllers were set at 12 slm for hydrogen, 230 sccm for 10 percent AsH_3 in H_2, 13 sccm of H_2 through 0 °C $Al(CH_3)_3$ (TMAl), and 15 sccm of H_2 through 0 °C $Ga(CH_3)_3$ (TMG). The chamber was purged for 2 hr in flowing hydrogen. Subsequently, the temperature was raised to 375 °C at a pressure of 250 mbar. The temperature was measured using a thermocouple imbedded in the susceptor. At 375 °C to prevent loss of arsenic from the surface, the arsine was turned on and then the temperature was raised to the deposition temperature. The laser was then turned on for 1 min with arsine flowing. After the laser was turned off the TMAl and the TMG were introduced. After 30 sec the laser was turned back on for 7 min during which time the growth proceeded. At the end of the run the window was coated with AlGaAs because no purge gas was directed to the windows. The laser and the metal alkyl sources were then turned off. The temperature was lowered to 375 °C and the arsine was turned off, and finally the temperature was lowered to room temperature. The time sequence for the events occurring during the growth of the films is given in figure 2.

A focused, 3 keV Ar ion beam was rastered over an area on the order of 3 by 3.5 mm for the AES depth profiling studies. The O(KLL), Al(KLL), C(KLL), Ga(LMM), and As(LMM) Auger peaks were monitored using a 3 keV electron beam. The average sputtering rate was approximately 45 A per minute.

RESULTS

Typical AES depth profiles (fig. 3) are shown for the films grown at 450 °C with laser impinging. Graph A is for the sample grown without exposure of the substrate to the light, and graph B is for the beam impinging onto the wafer at 15°. In all the films there was no carbon detected in the bulk. The aluminum peak was due to a pressure spike from the TMAl bottle when the gas was turned on. The aluminum peak associated in graph B with the interfacial oxygen peak is seen in all samples with interfacial oxygen. This aluminum peak also occurred in the control sample. The As signal was continuous across the interface for all samples.

The aluminum content in the bulk of the film, the oxygen content at the interface, and the sputtering time to the interface were determined by AES. The results are summarized in table I. In table I, I represents the case of the impinging beam, P represents the case for the parallel beam, and C represents the control sample with no light exposure. All three cases I, P, and C were at the same position on the substrate. The aluminum content (X_{Al}) is defined as one minus the ratio of the peak to peak height of the gallium in the bulk of the film (G_f) to the peak-to-peak height of the gallium in the substrate (G_b).

$$X_{Al} = \left(\frac{1-G_f}{G_b}\right) \tag{1}$$

The oxygen content (X_O) at the interface is defined as the ratio of the maximum peak-to-peak height of the oxygen signal at the interface (O_i) to the peak-to-peak height of the gallium signal in the substrate. The sensitivity factor for Ga was taken to be constant with changing Al percentage. This gives a ±0.04 uncertainty in the Al content as determined by our measurements on reference AlGaAs as samples.

$$X_o = \left(\frac{O_i}{G_b}\right) \tag{2}$$

The thickness is determined by the amount of time it takes to sputter to the maximum of the aluminum peak.

As seen from table I the oxygen content decreases when the light is impinging on the wafer (I) versus either for the parallel case (P) or for the control sample (C). At 500 °C for case I there was no oxygen found while at 450 °C only a slight amount of oxygen was found. The sensitivity for oxygen is estimated to be 0.5 percent. This is to be compared with the control film (C) or with the film for case P where a large amount of oxygen is found. This suggests that oxygen is being removed from the substrate by the laser beam prior to deposition.

As seen from table I, the films grown at 450 °C are 1/2 to 1/3 the thickness of the films grown at 500 °C. There appears to be an enhancement of the growth rate for the impinging case I versus the parallel case P or the control case C at 500 °C. At 450 °C the films are too thin for an accurate determination of growth enhancement. The aluminum content was lower for samples I and P than for the control sample C at 500 °C, but at 450 °C there is no statistical difference.

The TEM results are shown in Figs. 4 and 5. Figure 4 shows the diffraction pattern of the film grown at 500 °C with the laser beam impinging. It is single crystal as seen from the characteristic (100) diffraction pattern. Figure 5 shows the surface morphology after thinning with an ion beam. Vertical features that are typically 200 to 400 A apart are observed. The true morphology is expected to be at least as good as that shown in figure 5. The origin of these features has not been investigated. Optical microscopy shows no visible defects and the surface is smooth and mirrorlike.

SUMMARY

We have grown single crystal AlGaAs on GaAs at 500 °C using an OMCVD reactor and an ArF excimer laser. The films grown with 193 nm light impinging on the surface have no detectable amount, to the AES sensitivity limit, of oxygen or carbon in the film. Also, we have shown that the oxides on the substrate surface can be removed prior to deposition by exposing the wafer to the laser light.

Other AlGaAs films are being prepared at lower growth temperatures for comparison. The films in this paper and others will be analyzed for their impurity levels, and carrier concentration. The impurity levels will be determined by secondary on mass spectrometry. The carrier concentration will be determined by electrical transport measurements.

REFERENCES

1. P.K. Boyer, G.A. Roche, W.H. Ritchie, and G.J. Collins, Appl. Phys. Lett., 40, 716 (1982).

2. W. Roth, H. Krautle, A. Krings, and H. Beneking, in Laser Diagnostics and Photochemical Processing for Semiconductor Devices, ed. by R.M. Osgood, S.R.J. Brueck, and H.R. Schlossberg, North-Holland, NY (1983) pp. 193-198.

3. W. Roth, H. Schumacher, and H. Beneking, Electron. Lett., 19, 142 (1983).

4. C. Juang, S.K. Dubey, T.M. Wiseman, and K.A. Jones, J. Vac. Sci. Technol. A, 4, 728 (1986).

5. S.M. Bedair, J.K. Whisnant, N.H. Karam, M.A. Tischler, and T. Katsuyama, Appl. Phys. Lett., 48, 174 (1986).

6. V.M. Donnelly, M. Geva, J. Long, and R.F. Karlicek, Appl. Phys. Lett., 44, 951 (1984).

TABLE I. - THE THICKNESS OF THE AlGaAs FILMS IN SPUTTERING TIME (MIN) TO THE INTERFACE

[The aluminum content in the films (X_{Al}), and the amount of oxygen at the interface (X_O) for different temperatures and samples are given below. The samples: C represents the control sample (no laser interaction); P represents the beam parallel to the surface of the wafer; and I represents the beam impinging onto the wafer at 15° from parallel.]

Temperature, °C	Sample	Thickness, min	X_{Al}	X_O
500	C	23±.5	0.28±.04	0.11
500	P	27.5±.5	.17±.04	.10
500	I	37.5±.5	.17±.04	.00
450	C	13.0±.5	.11±.04	.24
450	P	-------	.13±.04	.20
450	I	10.0±.5	.13±.04	.06

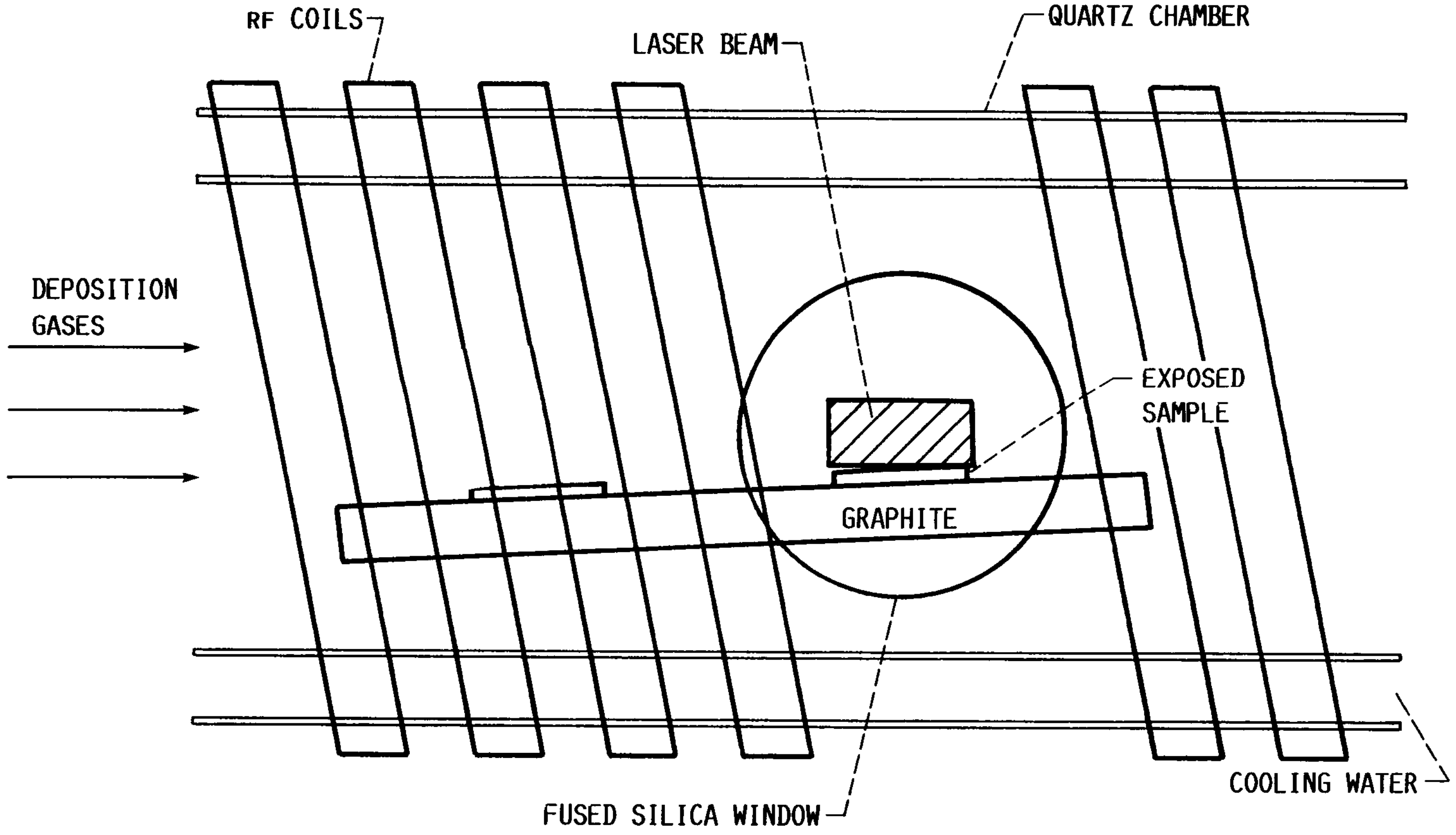


FIGURE 1. - OMCVD QUARTZ CHAMBER MODIFIED FOR LASER ASSISTED OMCVD (LA-OMCVD) GROWTH OF ALGAAS.

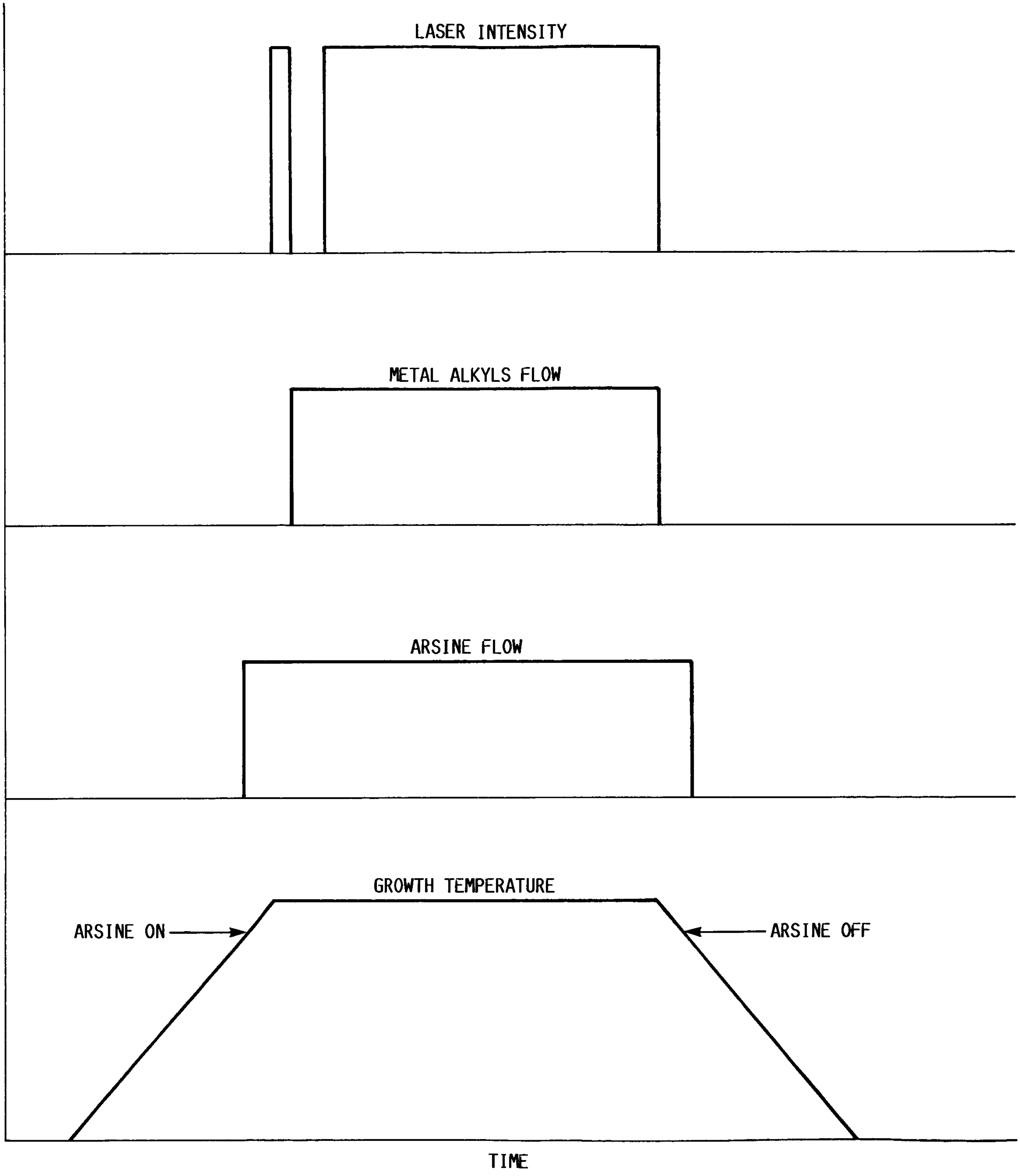
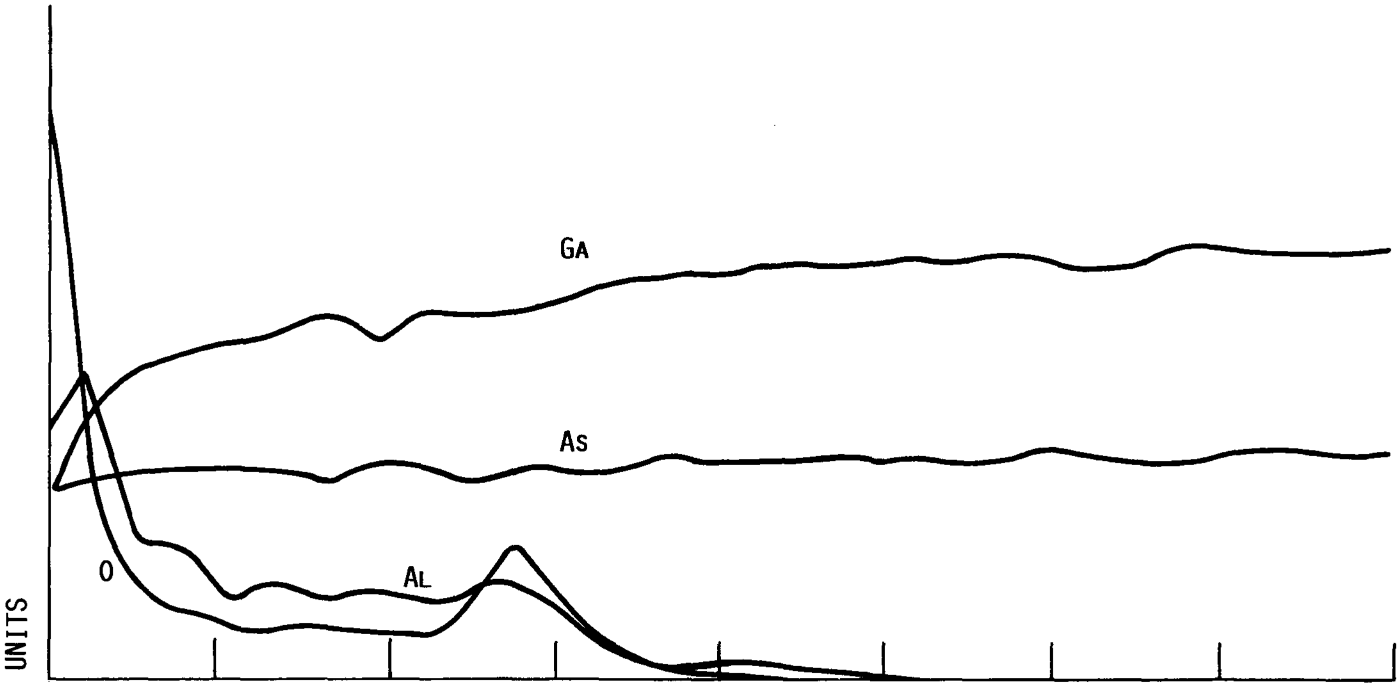
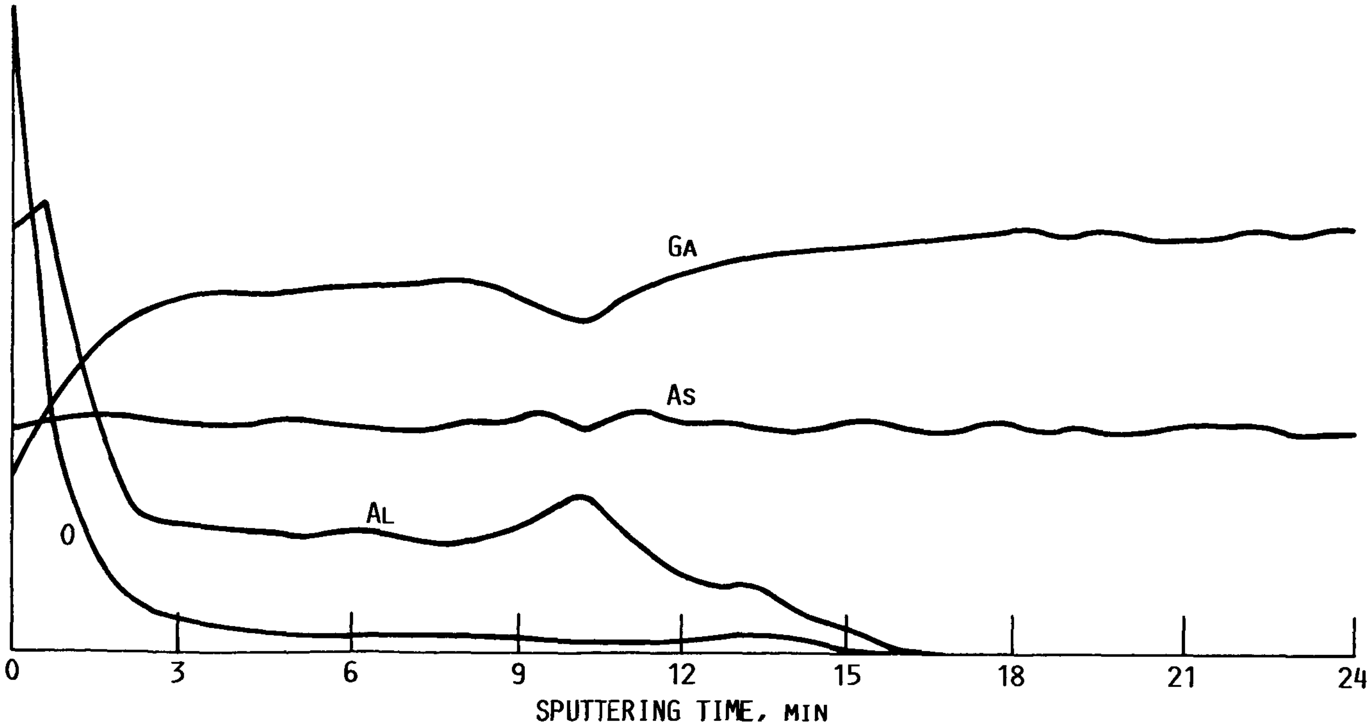


FIGURE 2. - TIME SEQUENCES OF THE TEMPERATURE, OF THE GASES, AND OF THE LASER INTENSITY DURING AlGaAs GROWTH.



(A) FILM GROWN WITHOUT EXPOSURE TO THE LASER BEAM.



(B) FILM GROWN WITH EXPOSURE TO IMPINGING LASER PULSES FROM AN ARF LASER (193 NM AT 450 °C.

FIGURE 3. - AUGER ELECTRON SPECTROSCOPY DEPTH PROFILE OF ALGAAS ON GAAS SUBSTRATE GROWN AT 450 °C. GALLIUM (GA), ARSENIC (AS), ALUMINUM (AL), AND OXYGEN (O) PEAK-TO-PEAK HEIGHT IN ARBITRARY UNITS VERSUS SPUTTERING TIME.

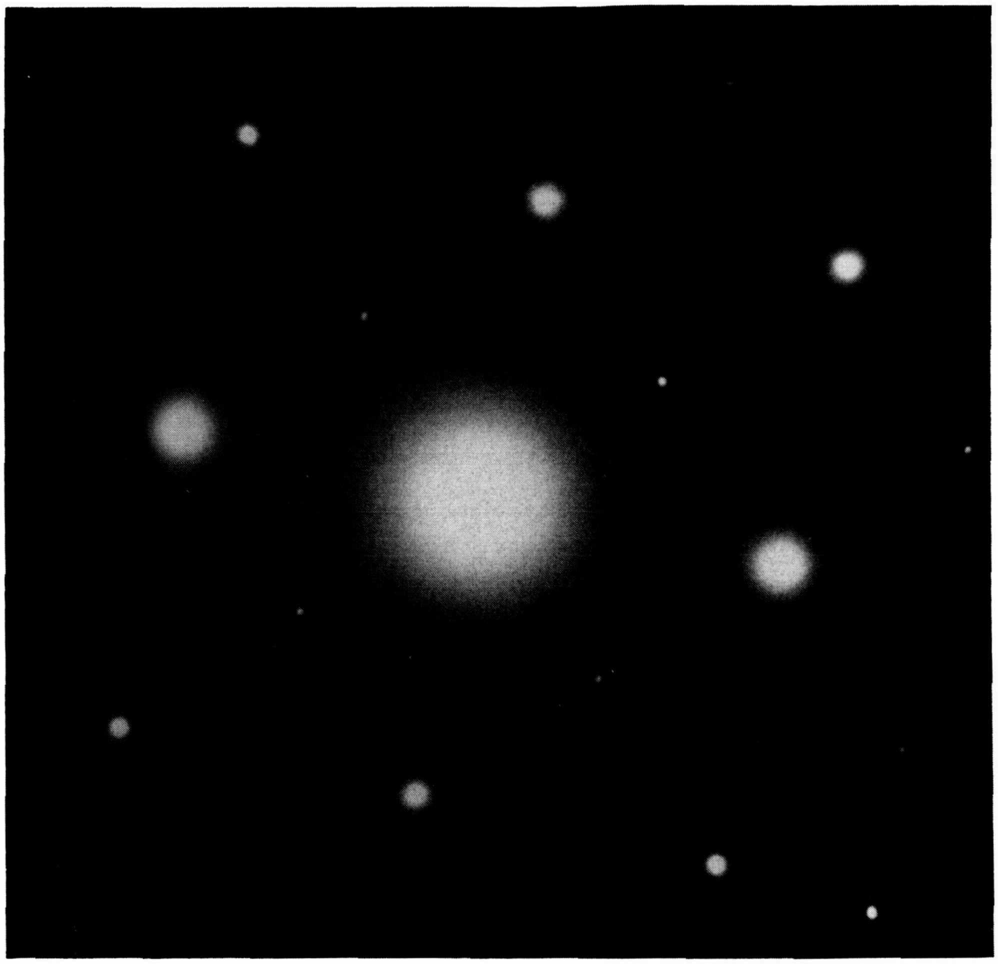


FIGURE 4. - TEM ELECTRON DIFFRACTION PATTERN OF ALGAAS GROWN AT 500 ^{0}C WITH THE LASER BEAM (WAVELENGTH 193 NM) IMPINGING.

ORIGINAL PAGE IS
OF POOR QUALITY

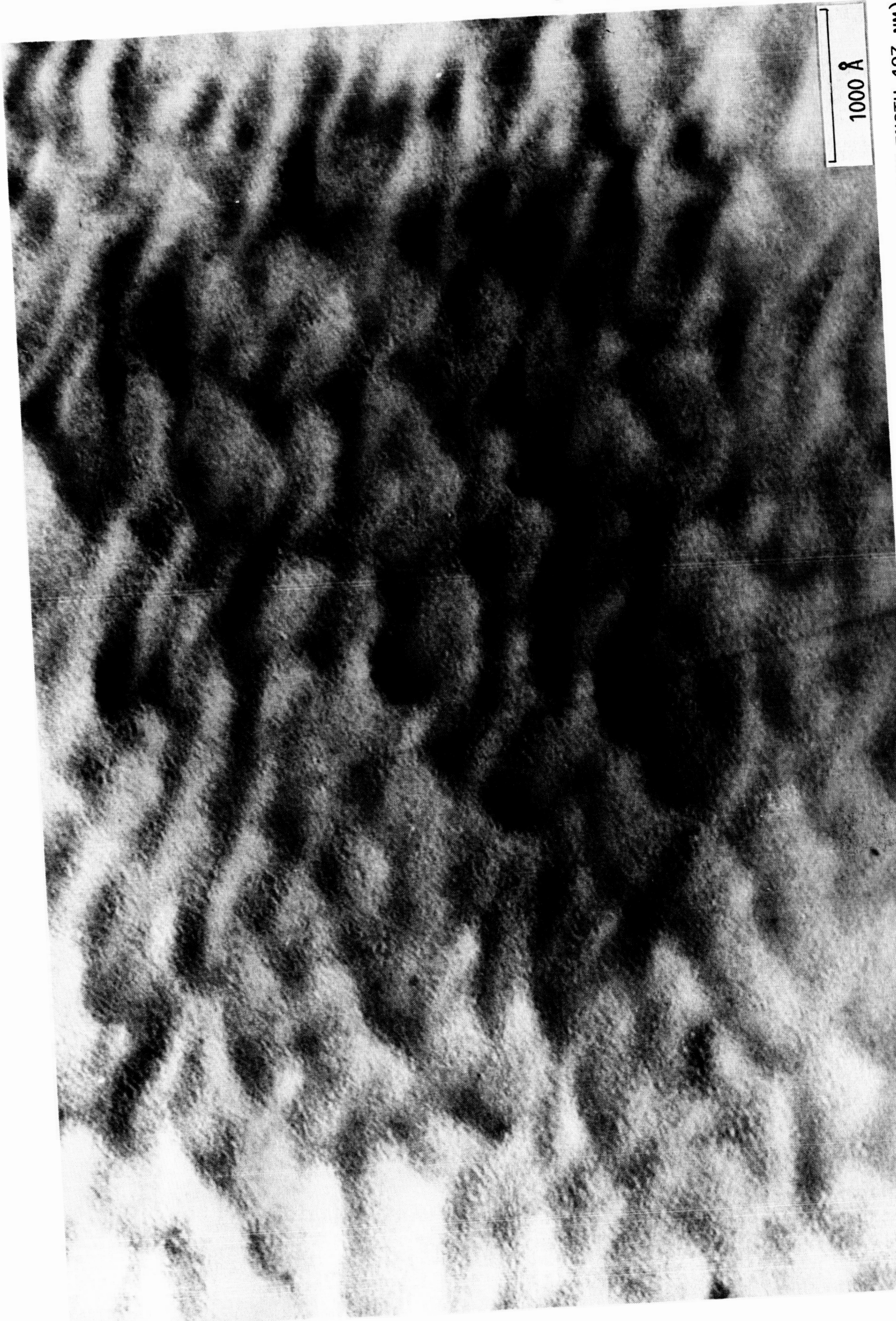


FIGURE 5. - TEM MICROGRAPH NORMAL TO THE SURFACE OF ALGAAS GROWN AT 500 °C WITH THE LASER BEAM (WAVELENGTH 193 NM) IMPINGING.

1. Report No.
NASA TM-88937

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
AlGaAs Growth by OMCVD Using an Excimer Laser

5. Report Date

6. Performing Organization Code
307-07-01

7. Author(s)
Joseph D. Warner, David M. Wilt, John J. Pouch, and
Paul R. Aron

8. Performing Organization Report No.
E-3379

10. Work Unit No.

9. Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11. Contract or Grant No.

13. Type of Report and Period Covered
Technical Memorandum

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes
Prepared for the Fall Meeting of the Materials Research Society, Boston, Massachusetts, December 1-5, 1986.

16. Abstract

AlGaAs has been grown on GaAs by laser assisted OMCVD using an excimer laser, wavelength 193 nm, and a Cambridge OMCVD reactor. Films were grown at temperatures of 450 and 500 °C with the laser beam parallel to the surface and impinging onto the surface at 15° from parallel. The samples were heated by RF coils while the laser beam was perpendicular to the gas flow. Typical gas flow parameters are 12 slm of H_2, 15 sccm of $Ga(CH_3)_3$, 13 sccm of $Al(CH_3)_3$, and a pressure of 250 mbar. The initial energy density of the beam at the surface was 40 mJ/cm^2, the pulse rate was 20 pps, and the growth time was 7 min. The films were analyzed by Auger electron spectroscopy for the aluminum concentration and by TEM for the surface morphology.

17. Key Words (Suggested by Author(s))
Excimer laser; CVD; VPE; Gallium arsenide; Aluminum gallium arsenide; Photolysis; OMCVD; MOCVD; OM-VPD; Epitaxial

18. Distribution Statement
Unclassified - unlimited
STAR Category 76

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified	10	A02

*For sale by the National Technical Information Service, Springfield, Virginia 22161