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ROCKWELL INTERNATIONAL THOUSAND OAKS CA ELECTRONICS--ETC F/6 20/12
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JUL 80 R W GRANT, J R OLIVER, S P KOWALCZYK F33615-78-C-1591

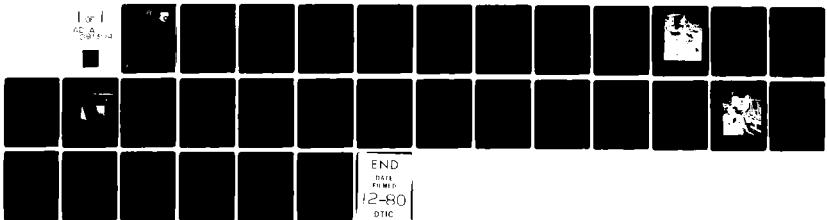
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**GaAs SURFACE PASSIVATION
FOR DEVICE APPLICATIONS**

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July 1980

TECHNICAL REPORT AFWAL-TR-80-1104
Interim Report for Period 12/03/79 through 03/31/80

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9 Interim rpt. no 3
3 Dec 79-31 Mar 80

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER 18 AFWAL-TR-80-1104	2. GOVT ACCESSION NO. AD-A091304	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) 6 GaAs Surface Passivation for Device Applications.		5. TYPE OF REPORT & PERIOD COVERED Interim Report #3 12/3/79 to 3/31/80	
7. AUTHOR(s) 10 R. W. Grant J. R. Waldrop J. R. Oliver D. L. Miller S. P. Kowalczyk		14. PERFORMING ORG. REPORT NUMBER ERC41651.15IRT	15. CONTRACT OR GRANT NUMBER(s) 15 F33615-78-C-1591
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rockwell International Corporation Electronics Research Center 1049 Camino Dos Rios, Thousand Oaks, CA 91360		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS 12 32		12. REPORT DATE 11 July 1980	13. NUMBER OF PAGES 34
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Avionics Laboratory Air Force Wright Aeronautical Laboratories Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		15. SECURITY CLASS. (of this report) Unclassified	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Same as block 16.			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Gallium arsenide XPS Oxidation Gallium Aluminium arsenide Insulation Surface passivation			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This document is the Interim Report #3 which covers the period 12/03/79 through 03/31/80 for Contract No. F33615-78-C-1591 entitled, "GaAs Surface Passivation for Device Applications." Preliminary C-V results are reported for several oxidized Al _{1-x} Ga _x As layers grown on n-type GaAs(100) by MBE. An XPS study of Al deposition and oxidation on a high temperature thermally oxidized GaAs(100) surface is also reported.			

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SUMMARY

Three samples of MBE grown graded $\text{Al}_{(1-x)}\text{Ga}_x\text{As}$ epitaxial layers on GaAs have been prepared. The initial oxidation procedure used on these samples produced only a superficial oxide layer as determined by SAM analysis. C-V and G-V results have been obtained for the initial oxidized specimens and for a specimen of sample #411 which was given a subsequent additional oxidation treatment. During the next reporting period a systematic C-V study as a function of oxidation conditions will be carried out.

An initial attempt to deposit an aluminum oxide layer by evaporating Al in an oxidizing atmosphere was unsuccessful which suggests that a much more oxidizing ambient (perhaps a plasma discharge) needs to be utilized if this approach is to be pursued.

SECTION I
INTRODUCTION

This report summarizes results obtained during the first four months of the redirected program for Contract No. F33615-78-C-1591 which is entitled "GaAs Surface Passivation for Device Applications." The initial contract called for the development of a practical dielectric for GaAs surface passivation by the preparation of an amorphous GaPO_4 layer produced by thermal oxidation of a heavily implanted phosphorous layer. The results obtained with this approach did not yield a dielectric with sufficiently good GaAs/dielectric interface properties to warrant proceeding into the device development phase of this program. Consequently, a major redirection of the program has been undertaken.

Recent progress has been reported in the development of dielectric layers for GaAs MIS devices by three different approaches. The first utilizes thermal oxidation of $\text{Al}_{1-x}\text{Ga}_x\text{As}$ epitaxial layers grown by molecular beam epitaxy (MBE).¹ The second employs a plasma oxidation process to form dielectric layers on GaAs (see e.g., Refs. 2 and 3) with particularly good C-V results being reported by R.P.H. Chang et al.⁴ A third approach which makes use of a novel two-step anodic oxidation process has also produced promising C-V results.⁵

The major emphasis of the redirected program will be to pursue the approach which utilizes thermal oxidation of MBE grown graded $\text{Al}_{1-x}\text{Ga}_x\text{As}$ epitaxial layers. Capacitance voltage (C-V) measurements of MIS structures have been interpreted¹ to demonstrate the achievement of inversion behavior and a fixed interface charge density of less than $2 \times 10^{10} \text{ cm}^{-2}$, however, results for more complex structures which involve carrier transport parallel to the

semiconductor/dielectric interface have not yet been reported. If promising C-V results are obtained, a goal of this program will be to fabricate simple FET-type device structures to evaluate charge transport characteristics parallel to the passivated GaAs interface.

The second interim report (AFWAL-TR-80-1018) associated with this contract and dated March 1980 summarizes all progress obtained on the initial ion implantation passivation approach. This third interim report covers progress on development of the MBE approach from 12/3/79 through 3/31/80. In Section II the MBE preparation of samples is outlined. Section III presents initial C-V analyses of these samples. Section IV discusses an attempt to prepare an Al oxide layer dielectric by deposition of Al in an oxidizing ambient.

SECTION II
MBE PREPARATION OF SAMPLES

Three structures were grown by MBE to investigate MIS performance in the system GaAs-Al_{1-x}Ga_xAs-AlAs (oxidized). These structures were grown by MBE using the apparatus shown in Fig. 1, which was designed and constructed in 1977 at ERC, Thousand Oaks, for the growth of GaAs and Al_{1-x}Ga_xAs. This MBE machine has extensive LN₂ cryoshrouding to maintain excellent vacuum conditions during epitaxy, a cryogenic 10K sorption pump to provide a high pumping speed for CO, and an airlock substrate insertion system. This airlock was also used in these experiments to provide an initial oxidation of the samples in an H₂O-free O₂ atmosphere.

The three structures are illustrated schematically in Fig. 2. All three were grown in an identical manner except for the Al_{1-x}Ga_xAs layer between the n-type GaAs and the AlAs layer. The substrate in each case was n⁺ Se-doped GaAs grown at ERC. This was prepared by using a Br-methanol etch on a rotating felt pad. The substrate was then soldered to the Mo MBE substrate holder heating block with indium metal, followed by a 10 sec etch in flowing H₂O/H₂O₂/NH₃OH (10:1:1). This substrate preparation procedure typically leads to an oxidized GaAs containing a trace of carbon, as seen by Auger Electron Spectroscopy.

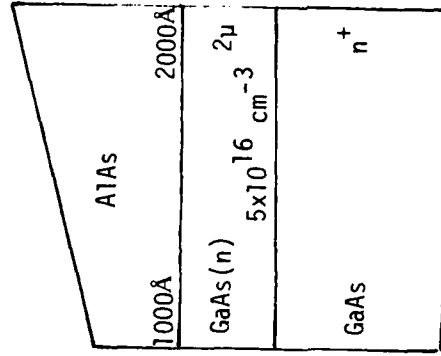
The oxide was removed from the GaAs substrate by heating the substrate in about 10⁻⁶ torr of As₄ (from elemental 6N As) to 580°C for 10 minutes.



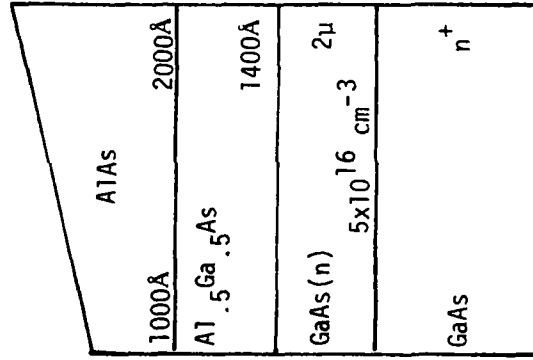
Figure 1 Photograph of MBE apparatus.

MBE SAMPLES

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412



SAMPLE # 411

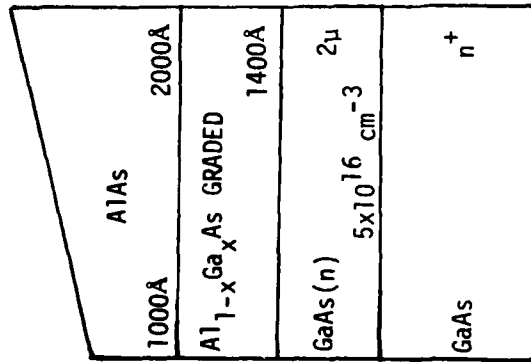


Figure 2 Schematic illustration of structure for the three MBE samples.

Epilayer growth was done with a substrate temperature of approximately 580°C,* growth rate of 1.0 μm/hr, and ratio of As₄ to Ga partial pressures of 20:1, as measured by a movable ion gauge. Tin was used to dope the GaAs layer to 5 x 10¹⁶/cm³. The n-type GaAs layers were 2 μm thick.

Al_{1-x}Ga_xAs intermediate layers were grown on two of the three samples. For sample #411, the Al content was initially set at x = 0.5 by opening the Al source shutter with the Al flux set equal to the Ga flux. The composition was then graded linearly to x = 1.0 over a 1400Å thickness by gradually reducing the Ga source temperature. For sample #412, the Al content remained at x = 0.5 during the entire 1400Å intermediate layer growth. Sample #413 had no intermediate Al_{1-x}Ga_xAs layer. Substrate temperature for the Al_{1-x}Ga_xAs intermediate layer growth, and for growth of the top AlAs layer, was increased to about 620°C.* This substrate temperature has been used most successfully in the MBE growth of low threshold double-heterostructure lasers⁶ and leads to a lower density of traps and recombination centers in Al_{1-x}Ga_xAs than more conventional MBE substrate temperatures of 550-580°C. The Al_{1-x}Ga_xAs intermediate layers were not intentionally doped, and therefore are expected to be semi-insulating.

Following the Al_{1-x}Ga_xAs intermediate layer (or the n-type GaAs layer in sample #413), undoped AlAs was grown epitaxially at 620°C by shutting the Ga shutter, leaving the Al and As₄ fluxes unchanged. The thickness of the AlAs layer was varied linearly along the length of the samples by using a Mo shutter to gradually cover a portion of the grown layer. In this way, the AlAs

*Later calibrations suggest that the actual substrate temperature may have been as much as 30°C lower than this value.

thickness was varied from about 1000Å to about 2000Å across each sample. Due to the difference in index of refraction between GaAs and AlAs, this grading shows up clearly as series of interference fringes across the sample. Variations in the intensity of reflected light due to the AlAs thickness variation can be seen in Fig. 3.

Following growth of the AlAs top layer, each sample was cooled to 450°C* and withdrawn into the MBE chamber airlock. Cooling during the transfer process resulted in the temperature dropping to about 400°C by the time the sample was within the airlock. Pure O₂ was then used to backfill the airlock to about 0.1 atmos., and the sample and Mo block were allowed to cool in O₂ to room temperature, which took about 30 min.

*Later calibrations suggest that the actual substrate temperature may have been as much as 30°C lower than this value.

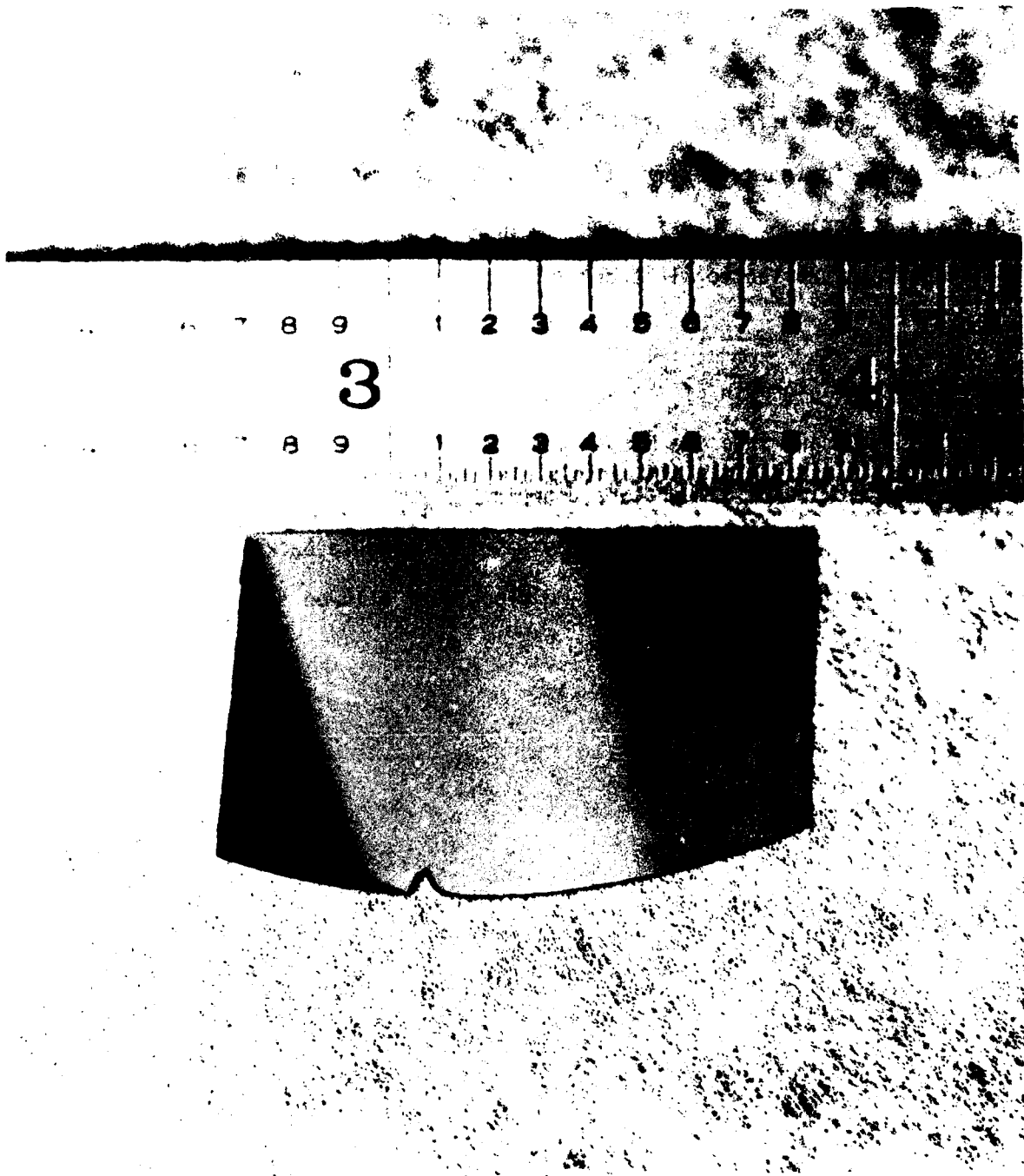


Figure 3 Photograph of MBE Sample 413. Scale in inches.

SECTION III

C-V CHARACTERIZATION

C-V characteristics for the three samples were taken over the range of 1 kHz to 1 MHz. Comparative results are shown in Fig. 4 at 1 MHz; there was essentially no change in the characteristics at lower frequencies. Sample #412 showed the least amount of hysteresis, while #413 showed the largest. The degree of hysteresis for all three samples did not appreciably change with AlAs layer thickness. Hence, the hysteresis is probably due to energetically deep interface acceptor traps.

Figure 5 shows the 1 MHz C-V characteristic for sample #411 with a superimposed ideal characteristic (dashed line) for a donor density of $5 \times 10^{16} \text{ cm}^{-3}$. The experimental curve clearly does not show significant inversion at high reverse bias. Also evident is the shift in the C-V characteristic due to a net negative charge at the interface. Figure 6 shows the same curve in comparison with the C-V characteristic under white light illumination. The hysteresis in this case has been substantially decreased, indicating that some of the deep acceptors have been filled with holes. A similar decrease of the hysteresis can be obtained by further oxidation of sample #411 at 400°C for two hours, as shown in Fig. 7. This suggests that the deep acceptor states may lie at the interface between the AlAs and the $\text{Al}_{1-x}\text{Ga}_x\text{As}$ layers.

Figure 8 shows the G-V curves during white light illumination for sample #411 before and after oxidation. Similar results were obtained for sample #412, but the dark conductance of sample #413 was too high to show any conductance peaks. The conductance peaks for samples #411 and 412 appear only under

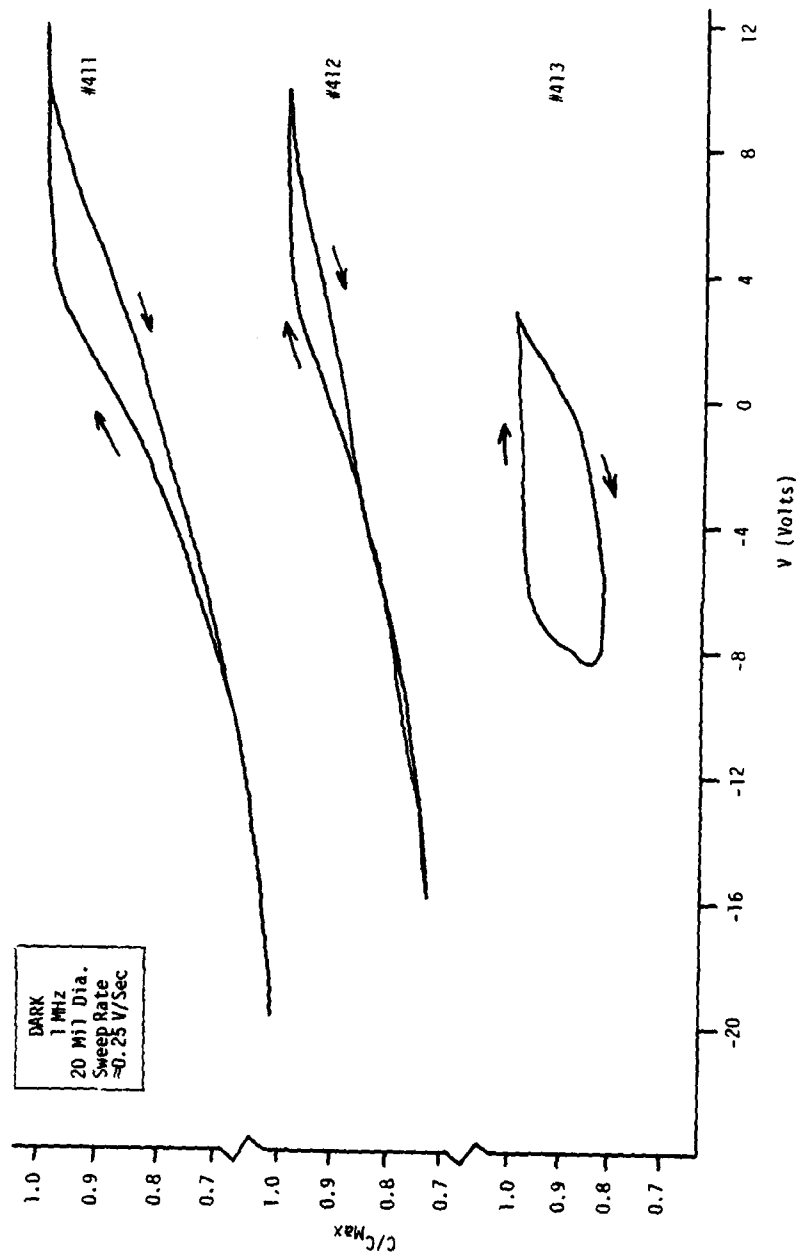


Figure 4 Typical C-V results for the three MBE samples.

$$\psi_s (\text{INV.}) = \frac{2kT}{q} \ln \frac{N_D}{n_i}$$

$$V = \psi_s \left(1 + \frac{\epsilon_s d}{\epsilon_{ox} W} \right)$$

$$N_D = 5 \times 10^{16} \text{ (n)}$$

$$\frac{\epsilon_{ox}}{d} = 2.3 \times 10^{-8} \text{ F/cm}^{-2}$$

$$(d \approx 2800 \text{ \AA}, \epsilon_{ox} \approx 7.3)$$

#411
DARK
1 MHz
20 mil Dia.

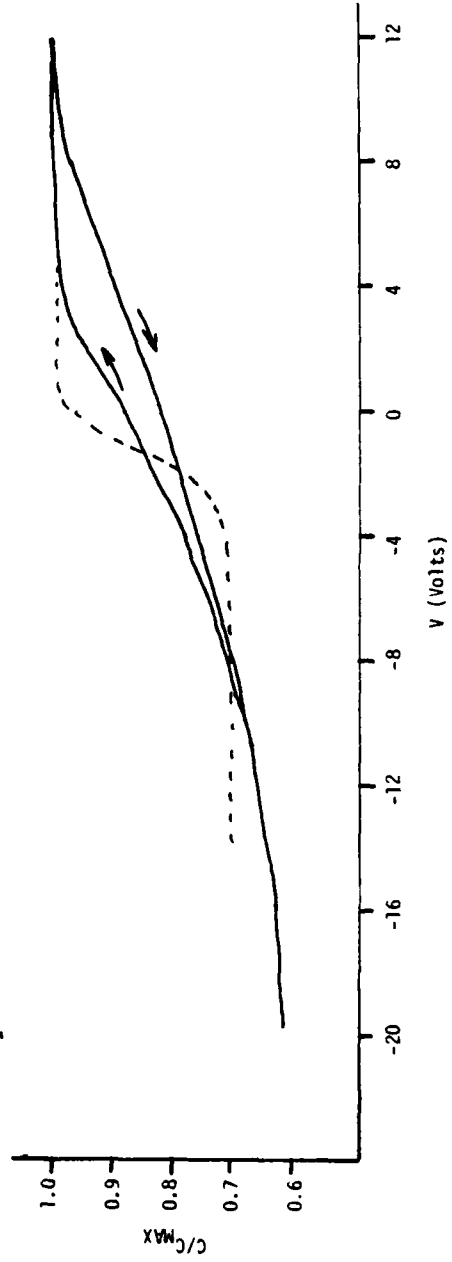
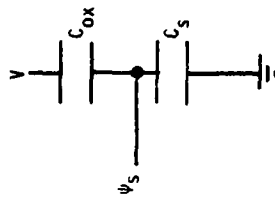


Figure 5 Observed and ideal (dashed curve) C-V for sample #411.

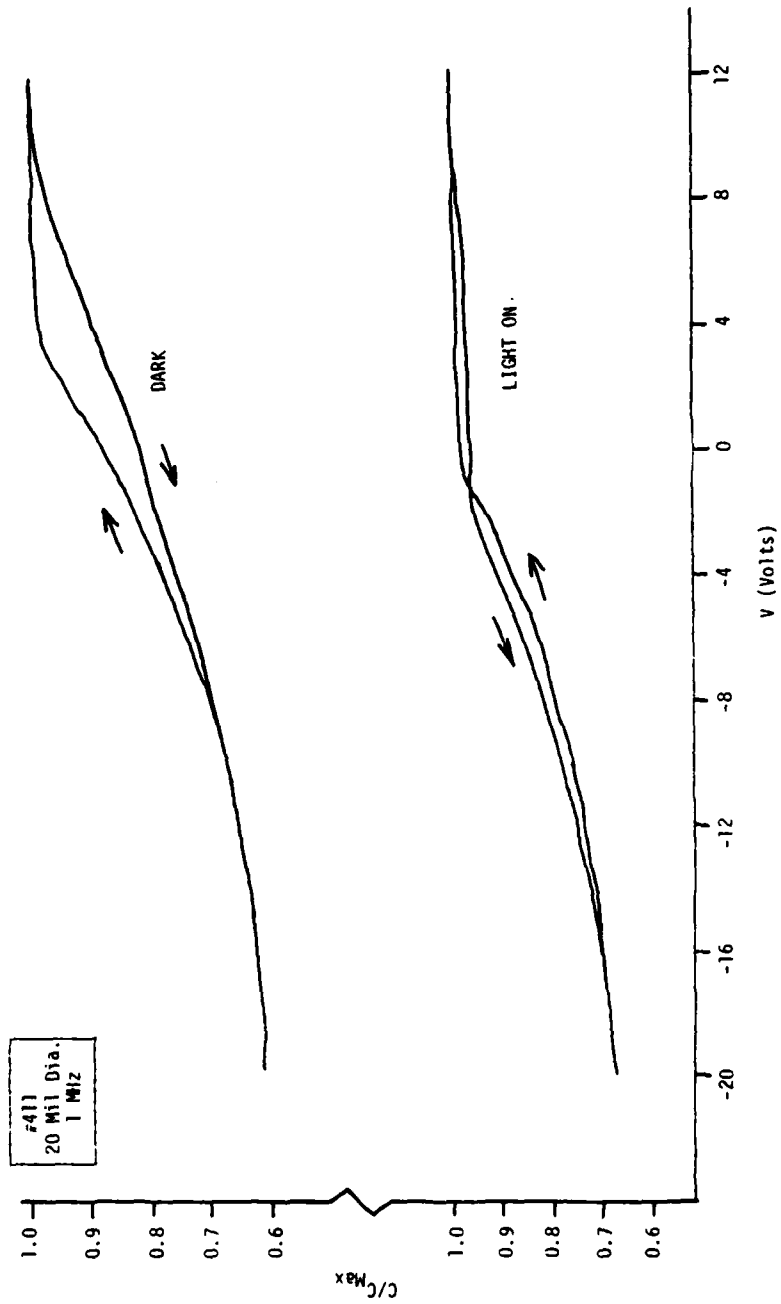


Figure 6 Effect of illumination on C-V for sample #411.

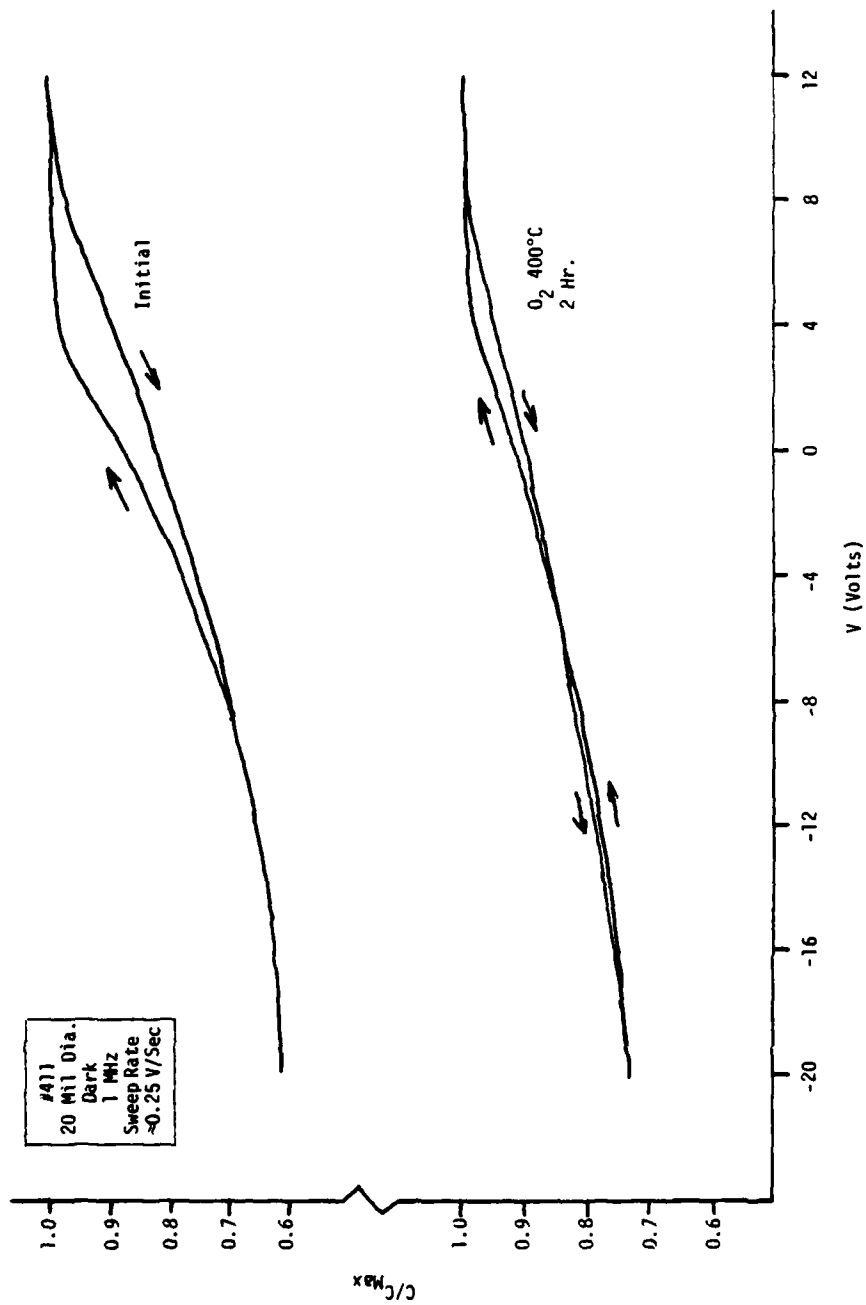


Figure 7 Effect of subsequent oxidation on C-V for sample #411.

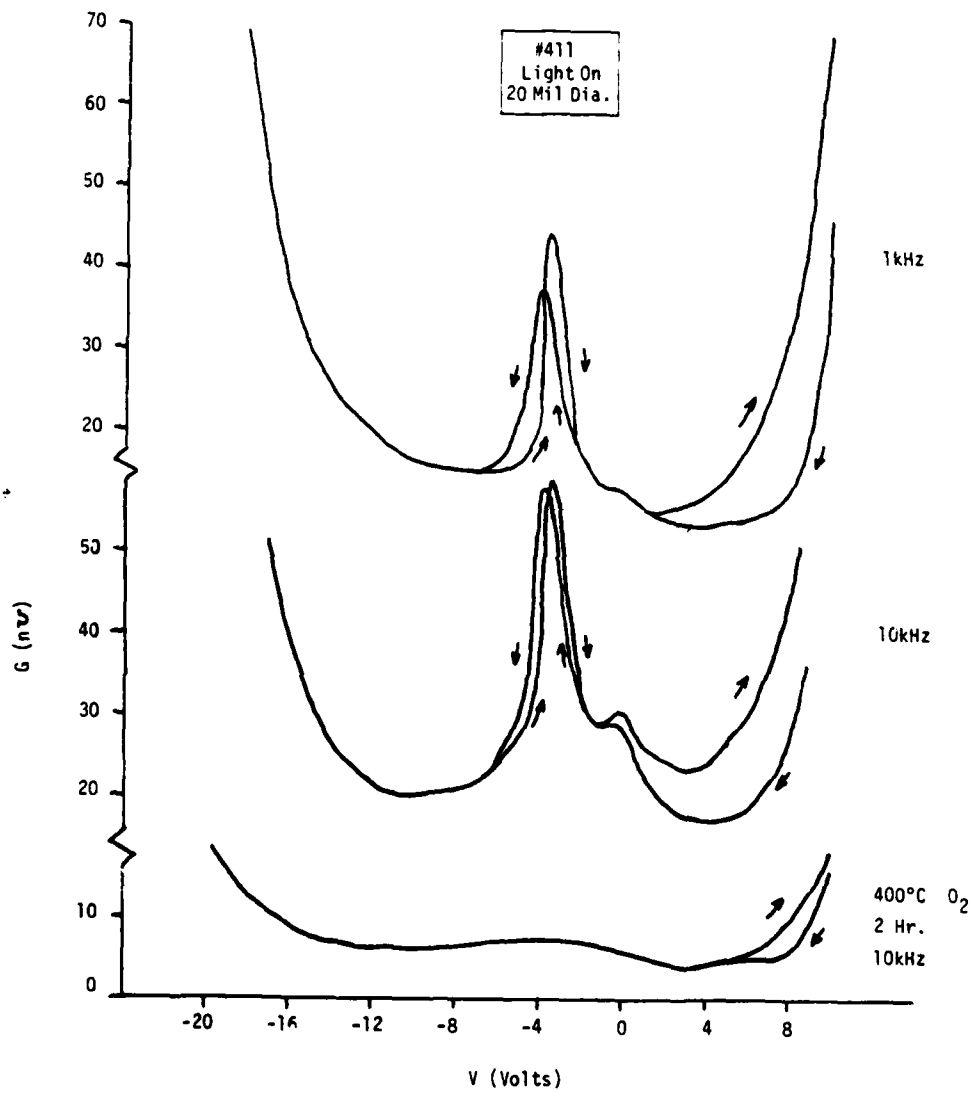


Figure 8 G-V measurements for sample #411.

illumination, a further confirmation that these are due to minority carrier (acceptor) traps which lie below mid-gap. Note that after oxidation these traps disappear, consistent with the C-V results in Fig. 7.

The fact that the conductance peaks in Fig. 8 do not shift in voltage with changes in frequency indicates that these peaks are due to discrete trap levels in the bandgap. It would be useful to calculate the energy and density of the major trap level at -4 volts based on the results of Fig. 8. We will assume that this trap level is completely filled as a result of the illumination. For an interface state capacitance C_s , the conductance at the maximum is given by

$$G = \frac{C_s \omega^2 \tau}{1 + \omega^2 \tau^2} \quad (1)$$

where τ is the reciprocal of the trap emission rate and ω is the signal frequency. Comparing the results at 1 kHz ($G = 45 \text{ nV}$) and 10 kHz ($G = 65 \text{ nV}$) using Eq. (1), we obtain a time constant of $\tau = 2.3 \times 10^{-4}$ seconds. The interface state density N_{ss} is given by

$$N_{ss} = \frac{C_s}{qA} \quad (2)$$

where A is the contact area. By using the calculated value for τ and the measured conductance in Eq. (1), C_s is found to be 15.3 pF, and hence from Eq. (2), $N_{ss} = 4.8 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. An estimate of the trap energy can be made from the relation

$$E_a = \frac{kT}{q} \ln (N_v \bar{v} \tau \sigma_p) \quad (3)$$

where N_v is the valence-band density of states, \bar{v} is the thermal velocity, and σ_p is the hole capture cross section. Assuming a typical value of $\sigma_p = 10^{-14} \text{cm}^2$, E_a is estimated to be ~ 0.4 eV above the valence band.

3.1 SAM Profile Analysis

Following MBE growth of the AlAs/ $\text{Al}_{1-x}\text{Ga}_x\text{As}$ /GaAs structures the top layer of AlAs was exposed to dry O_2 in a auxiliary chamber on the MBE system as described in Section II. Initial estimates of oxidation rates suggested that this procedure would fully oxidize the AlAs top layer. To assess the actual effect of the above procedure, a piece of sample #411 was analyzed in a Scanning Auger Microprobe (SAM) which is equipped with an Ar-ion sputter gun. A chemical analysis depth profile was obtained by a series of sputter-Auger analysis steps. In Fig. 9 we show the result of sputtering for 180 min. The sputter time axis is proportional to depth, with the sputter rate $\approx 30 \text{ \AA}/\text{min}$.

From the sputter profile it is apparent that the initial oxidation procedure resulted in only a superficial AlAs oxidation, the top layer remained essentially pure AlAs. However, the sputter profile also reveals that the $\text{Al}_{1-x}\text{Ga}_x\text{As}$ middle layer was graded in the desired manner, going from 100% Al to 50% Al at the GaAs interface. Thus as mentioned in Section III, a portion of sample #411 was reoxidized at 400°C for 2 hrs in O_2 with the intent of increasing the oxide thickness. This procedure had a substantial effect on C-V and G-V results (Section III); a SAM analysis of this sample has not yet been performed.

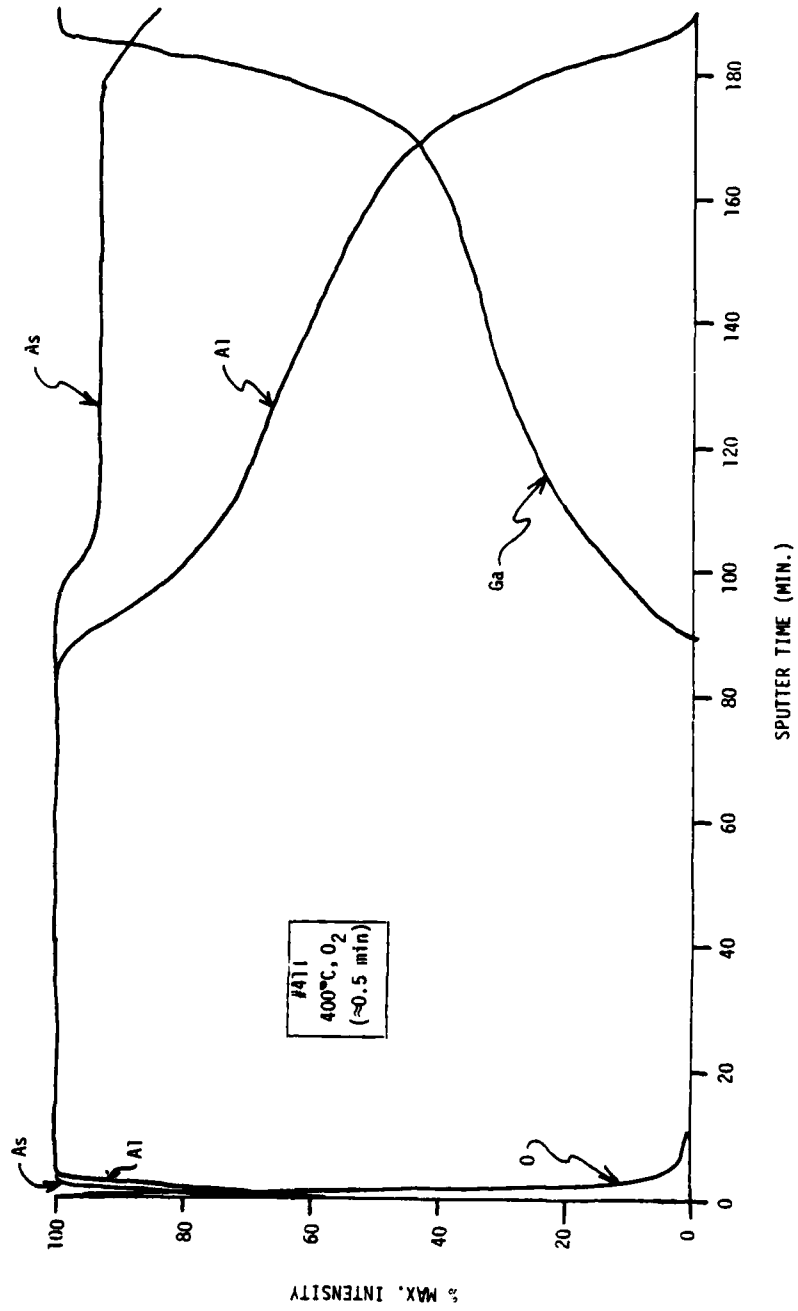


Figure 9 Depth profile obtained with SAM for sample #411.

SECTION IV

XPS STUDY OF DEPOSITION AND OXIDATION OF Al ON n-TYPE GaAs(100)

In a related Contract ("Effects of Surface Conditions on Carrier Transport in III-V Compounds," Contract #F33615-78-C-1532), XPS (X-ray Photoemission Spectroscopy) has been utilized to study the surface chemistry of GaAs(100) and to characterize the variation of surface potential with chemical and/or thermal treatments. The instrument used for these investigations is shown in Fig. 10, which is a Hewlett-Packard 5950A electron spectrometer modified to obtain ultra-high vacuum ($< 2 \times 10^{-10}$ torr) and provide various in situ specimen treatments (heat, molecular and atomic beam deposition, ion etching) and LEED analysis capabilities (see Fig. 11). Previously reported studies (Contract #F33615-78-C-1532, Interim Report #2) indicated that high temperature oxidation of a thermally cleaned n-GaAs(100) surface results in a surface which is covered with Ga_2O_3 (see Table 1 which summarizes the typical chemistry and surface potential variations of such a surface) and decreases surface band bending by ~ 0.2 eV. This suggests that a useful structure would be to grow a thin interfacial Ga_2O_3 oxide on GaAs and to deposit a thick dielectric layer on this surface. Thus, an initial attempt was made to grow an Al_2O_3 dielectric layer. The results are shown in Figs. 12-14. The lower portions of Figs. 12 and 13 show the Ga3d and As3d core-level spectral regions before Al deposition but after growth of the Ga_2O_3 layer which is indicated by the asymmetry to high binding energy of the Ga3d level. Aluminum oxide growth was attempted by slow ($\sim 1\text{\AA}/\text{sec}$) deposition of Al metal in an ambient of 1×10^{-4} torr O_2 . Figure 14 shows that a chemical reaction occurs upon deposition of submonolayer amounts of

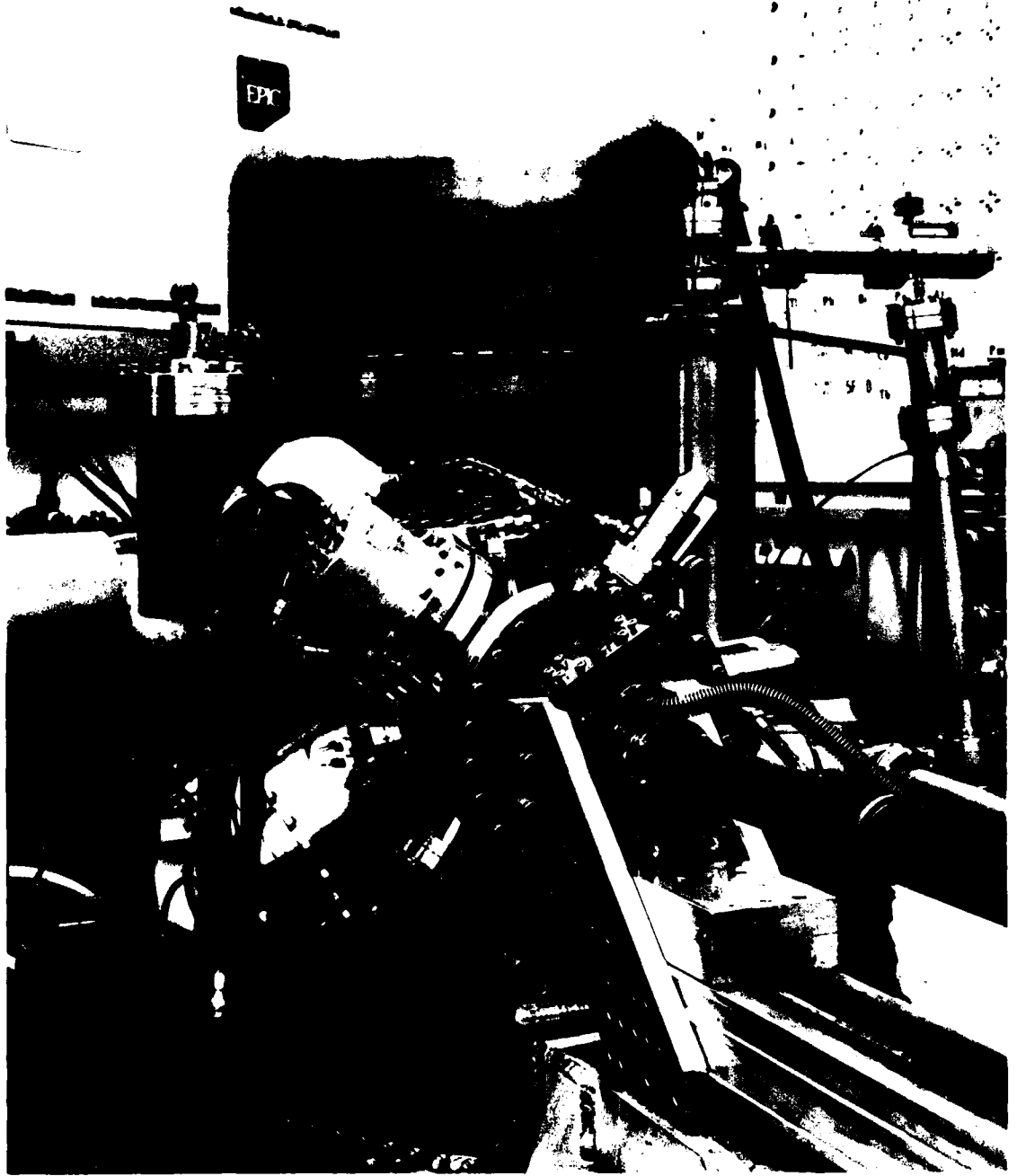


Figure 10 Photograph of XPS apparatus.

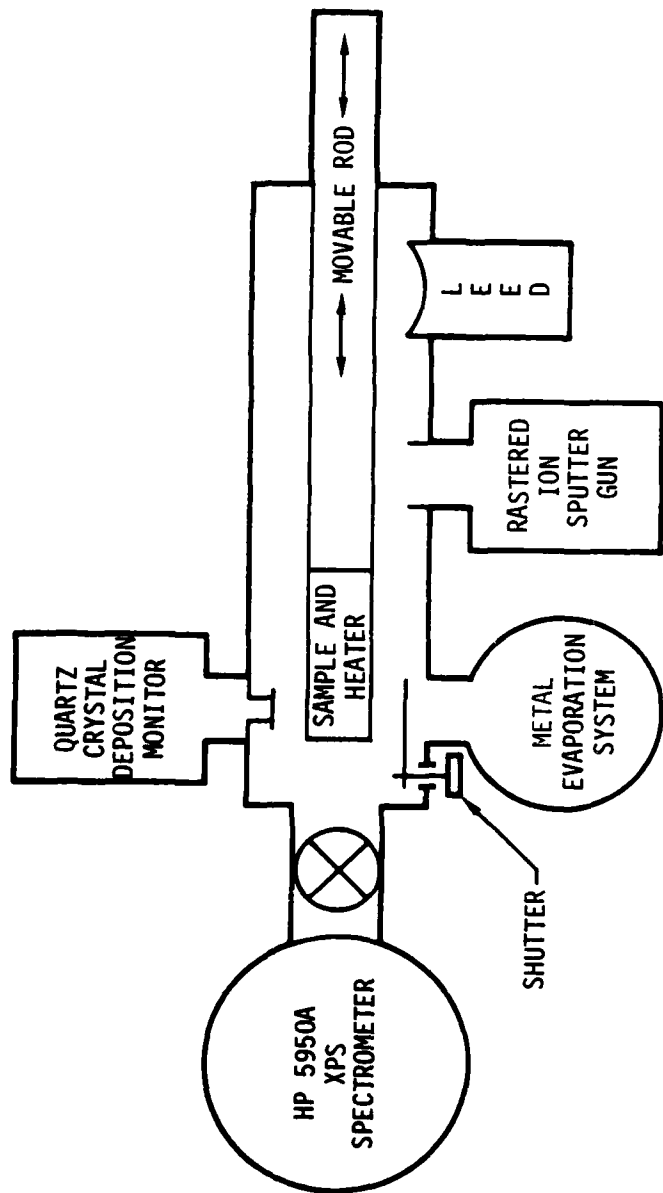


Figure 11 Schematic diagram of XPS apparatus.

Table 1
 XPS RESULTS FOR OXIDATION AND DEPOSITION OF Al ON GaAs(100)
 ($n = 2 \times 10^{17} \text{ cm}^{-3}$)

Treatment	Relative As3d Binding Energy in GaAs (eV)	Remarks
Chem. etch	+0.2	$\text{Ga}_2\text{O}_3 + \text{As}_2\text{O}_3$
710°C	0.0	Clean
$2 \times 10^4 \text{L O}_2$ at 575°C	+0.2	Ga_2O_3
Few monolayers Al deposited in 10^{-4} torr O_2 (25°C)	0.0	Ga3d asymmetric to low binding energy $\text{Ga}_2\text{O}_3 + 2\text{Al} + 2\text{Ga} + \text{Al}_2\text{O}_3$

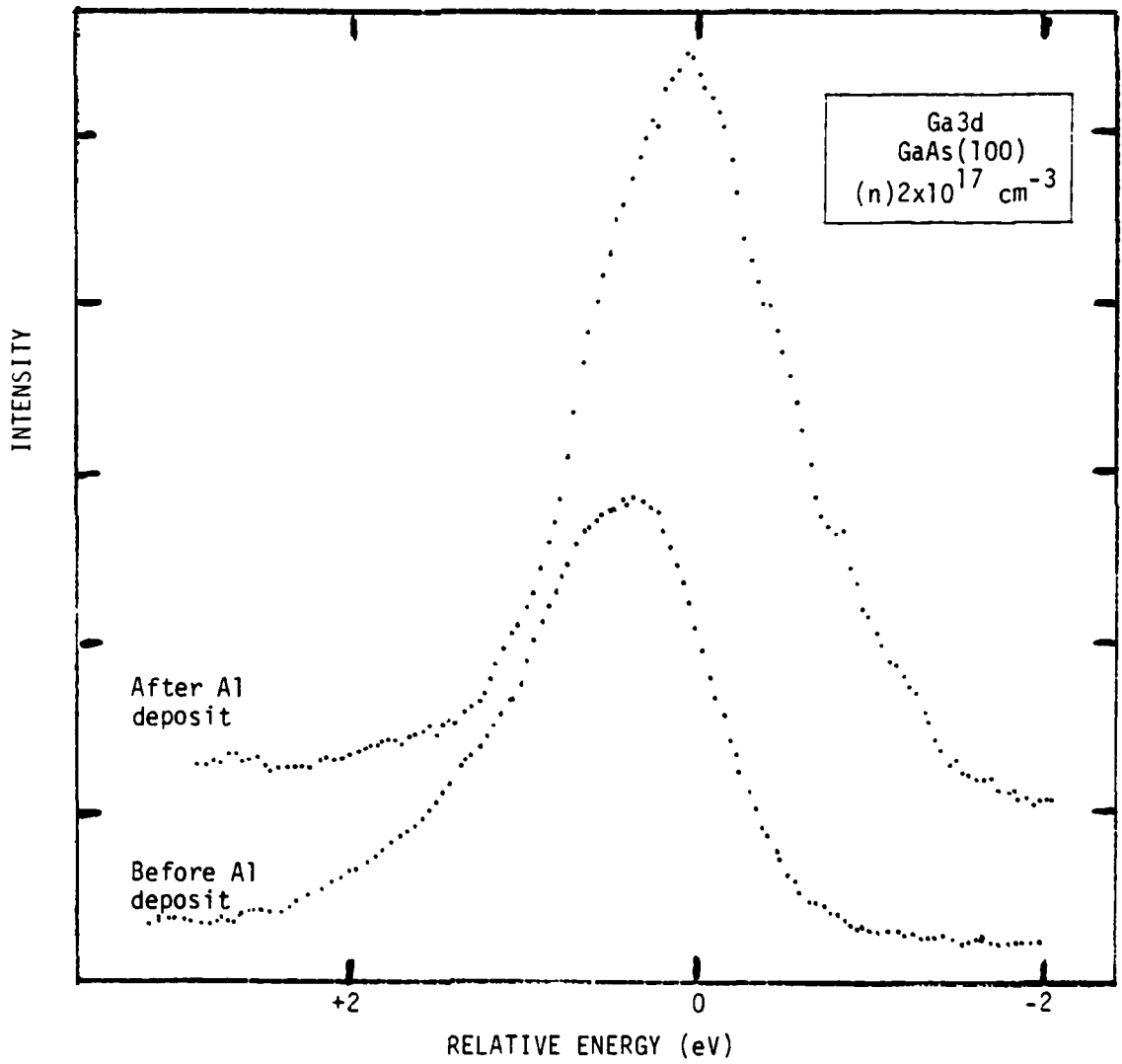


Figure 12 XPS spectrum which illustrates effect of Al deposition on Ga3d line shape. See Section IV.0 for details.

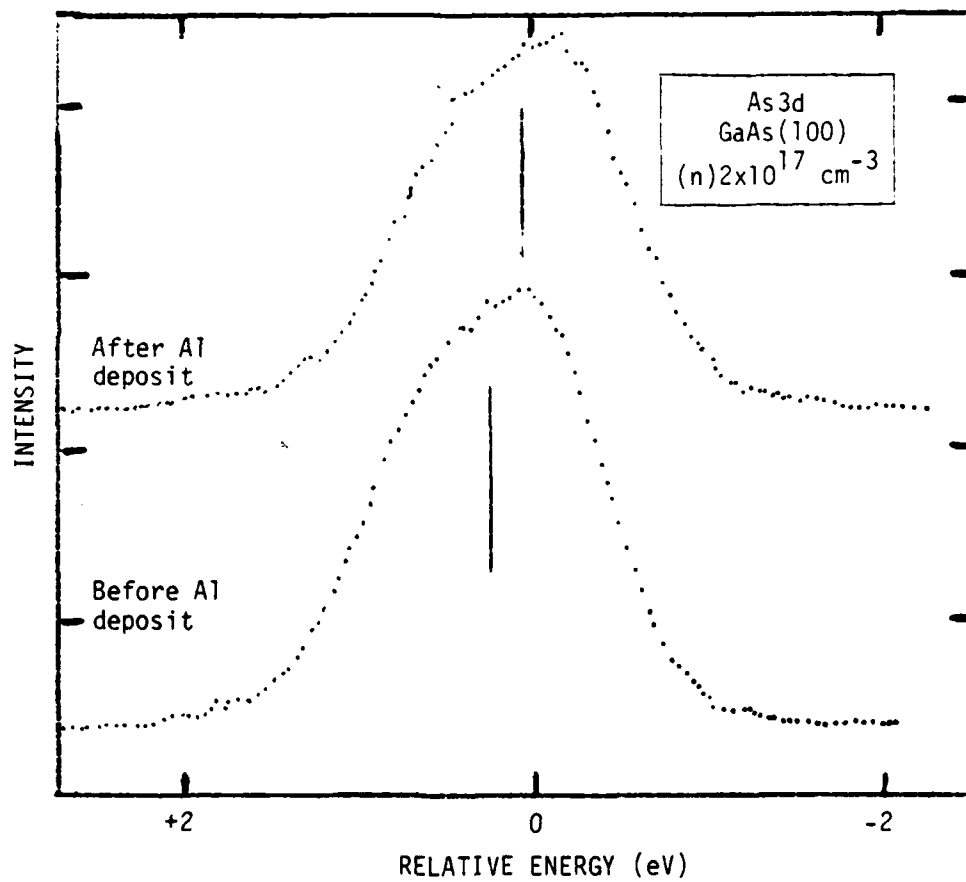


Figure 13 XPS spectrum which illustrates effect of Al deposition on As3d line shape. See Section IV.0 for details.

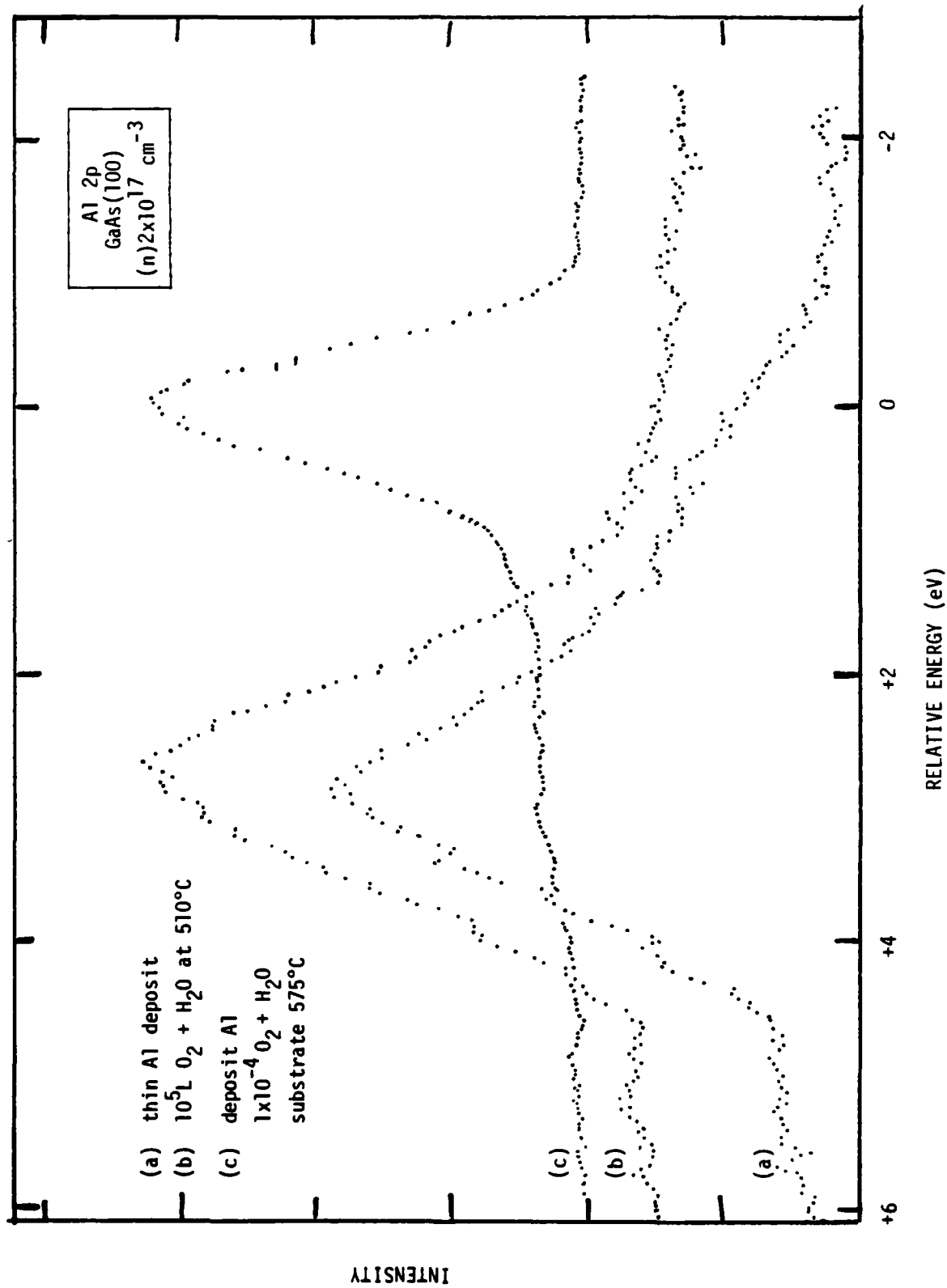


Figure 14 XPS spectrum in region of Al2p line for Al deposited on GaAs surface.

Al. First, the gallium oxide is reduced and, secondly, some Ga metal is produced as indicated by the Ga3d line asymmetry to lower binding energy. Figure 13 shows the potential shift as monitored by the As3d level. After the Al deposition the bands are pinned at the "clean" surface position. Figure 14a shows that Al oxide is formed. Further deposition of Al in an ambient consisting of water vapor and O₂ resulted only in a thick Al metal deposition (Fig. 14c) with no obvious difference from Al deposited under UHV conditions without O₂ ambient. Conclusions drawn from these experiments are:

- 1) There is a surface chemical reaction occurring, namely the reduction of gallium oxide by Al metal



This reaction might be expected from consideration of the relative heats of formation.

- 2) The Al, which getters the Ga₂O₃, pins the bands at the "clean" surface position.
- 3) Under the conditions employed here, after the oxygen available in the form of Ga₂O₃ is consumed, the Al deposit is metallic and not oxide.

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