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GaAs SURFACE PASSIVATION FOR DEVICE APPLICATIONS

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Development Center
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December 1981

Interim Report for period 10/01/80 through 03/31/81

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Avionics Laboratory
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Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This document is the interim report #5 which covers the period 10/01/80 through 03/31/81 for Contract No. F33615-78-C-1591 entitled "GaAs Surface Passivation for Device Applications." C-V and I-V measurements are reported for several GaAs (100) MIS samples. Both MBE and bulk grown GaAs samples were studied; several of the MBE grown samples had $Al_{1-x}Ga_xAs$ layers between the GaAs and insulator. Insulators formed by plasma oxidation of the $Al_{1-x}Ga_xAs$ layers and by deposition of silicon nitride were investigated. A novel As capping technique has been developed to transfer MBE grown $Al_{(1-x)}Ga_{x}As$ samples in air into another vacuum system without surface contamination.

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SUMMARY

Efforts to reproduce the reported MIS results on thermally oxidized $Al_{1-x}Ga_xAs$-GaAs MBE grown structures have produced insulators which are excessively leaky. To improve this situation while still preserving the hoped for benefits of the heterojunction concept, two additional methods of insulator fabrication have been tried. Plasma oxidation of $Al_{1-x}Ga_xAs$ layers has produced good insulators, however, the MIS structures exhibit both large hysteresis and flatband shifts which indicate the presence of large interface-state densities. The results suggest the possibility that the $Al_{1-x}Ga_xAs$-oxide interface may be a source of interface states which are difficult to isolate from the GaAs. Si_xN_y has been deposited on GaAs surfaces by a plasma deposition process. In some cases reasonably good insulating properties of the deposited films were obtained. The C-V results on MIS structures formed on these samples suggest that exposure of the GaAs surface to the plasma may increase the interface state density. With the current experimental apparatus it is difficult to exclude substantial amounts of oxygen from the Si_xN_y films; this oxygen may also be associated with the large interface-state densities which are observed.

A technique has been developed to transfer MBE grown samples in air into another vacuum system while avoiding surface contamination. For samples of the $Al_{1-x}Ga_xAs$ system, the technique involves coating the samples with elemental arsenic which is subsequently removed by heating to about 300°C. The technique should make it possible to transfer samples between systems in a

simple manner to permit further processing. For example, if an insulator can be deposited on a GaAs surface within a high vacuum system, this technique could minimize possible oxygen contamination of the interface. It is expected that the technique will be generally applicable to many material systems in addition to $Al_{1-x}Ga_xAs$.

SECTION I

INTRODUCTION

This is the fifth interim report for contract No. F33615-78-C-1591 which is entitled "GaAs Surface Passivation for Device Applications." The time period covered by this report is 10/1/80 to 3/31/81. A goal of this program is to develop a dielectric-GaAs interface which has properties suitable for a practical MIS technology.

Two approaches are being followed to find a practical dielectric-GaAs interface for surface passivation applications. The first involves attempts to utilize the heterojunction concept of Tsang et al.[1] Layers of $Al_{1-x}Ga_xAs$ are grown epitaxially on GaAs to produce a low defect $Al_{1-x}Ga_xAs$-GaAs interface. In the original work of Tsang et al,[1] the dielectric was formed by thermal oxidation of an outer AlAs layer. We have found that the dielectric formed by thermal oxidation of AlAs is quite leaky. Therefore efforts are being made to replace this dielectric with one formed either by plasma oxidation of an $Al_{1-x}Ga_xAs$ layer or by deposition of a good quality dielectric onto a $Al_{1-x}Ga_xAs$-GaAs heterojunction. The second approach is to prepare GaAs surfaces with known composition on which a dielectric is deposited or formed. The correlation of interface composition with electrical properties may make it possible to optimize MIS characteristics. Current-Voltage (I-V) and Capacitance-Voltage (C-V) measurements are the primary electrical measurements used to characterize the MIS samples prepared in this work. X-ray photoemission spectroscopy (XPS) is the primary analytical technique used to determine interface composition.

Section II describes the preparation of samples utilized during this reporting period. Several molecular beam epitaxy (MBE) grown samples were prepared as described in Section II-1. A novel elemental As protective coating technique was developed to transfer samples in air from an MBE system into another vacuum without surface contamination; this technique is described in Section II-2. The development of techniques to prepare insulators by plasma oxidation and by silicon nitride deposition is discussed in Sections II-3 and II-4. The principal sample characterization measurements (Section III) involved I-V and C-V measurements. These measurements on MIS samples studied during this reporting period are presented in Section III-1. A few preliminary XPS surface-potential measurements are given in Section III-2.

During this six month period, two papers based on work supported in part by this contract have been submitted for publication. Both papers, which are currently in press, are reproduced in the Appendix.

SECTION II

SAMPLE PREPARATION

In this section we describe the MBE preparation of several samples which were utilized in this program. A method to transfer these samples in air into another vacuum system without contaminating the surface is presented. Two additional techniques used to fabricate insulators on the MBE grown samples are also discussed.

1. MBE Samples

Two samples (No. 594 and No. 595) were grown by MBE for subsequent use with Si_xN_y deposition. These samples were grown in our MBE apparatus in Thousand Oaks, which has been described in previous reports. Two important modifications have been made to this MBE apparatus since the last interim report. The first is the addition of an antechamber with a heated substrate stage. This allows substrates to be degassed before their introduction into the growth chamber which significantly reduces the amount of water vapor introduced to the growth chamber with each new substate. The second modification was the use of a newly designed Ga oven, which has contributed significantly to improved material quality. Both of these modifications should have improved the quality of the $Al_{1-x}Ga_xAs$ material.

Sample No. 595 was a 1.5 μm thick p-type GaAs layer, doped with Be to 3×10^{16} cm^{-3}, grown on a p^+ GaAs substrate, and capped with an arsenic layer for passivation of the surface. The GaAs layer was grown at 580°C, our standard substrate temperature. The arsenic overlayer was condensed by cooling the substrate to below room temperature in the arsenic beam used for epilayer growth. This overlayer was estimated to be several thousand angstroms thick. The As overlayer has been found to be resistant to oxidation, and to leave a clean, well-ordered GaAs surface when desorbed at ~ 350°C in ultrahigh vacuum (UHV) (see Section II-2).

Sample No. 594 was a 1.5 μm thick p-type GaAs layer, doped with Be to 1×10^{16} cm^{-3}, covered with 2000 Å of $Al_{0.5}Ga_{0.5}As$, and then capped with an arsenic passivating layer. Substrate temperature was about 620°C for this run, in an attempt to decrease the impurity content of the $Al_{0.5}Ga_{0.5}As$.[2] The structure of samples No. 594 and No. 595 is shown schematically in Fig. 1.

Sets of (100) and (110) oriented GaAs samples were prepared in MBE growth run No. 588 to be used for XPS surface-potential measurements. Initial plans were to dope the samples p-type in the mid 10^{16} range with Be. Unfortunately technical difficulties caused the Be flux to be considerably less than expected and as noted in Section III-2, metal point contact measurements made on a (100) sample from this growth run suggest that the sample may have been n-type.

Several GaAs and AlAs samples were grown by MBE on GaAs substrates to test the protective elemental As capping technique which was developed to transfer MBE samples into other vacuum systems without surface contamination (see Section II-2). Samples were prepared with both thin (~ 25 Å) and thick (> 1000 Å) GaAs or AlAs outer layers to test the technique.

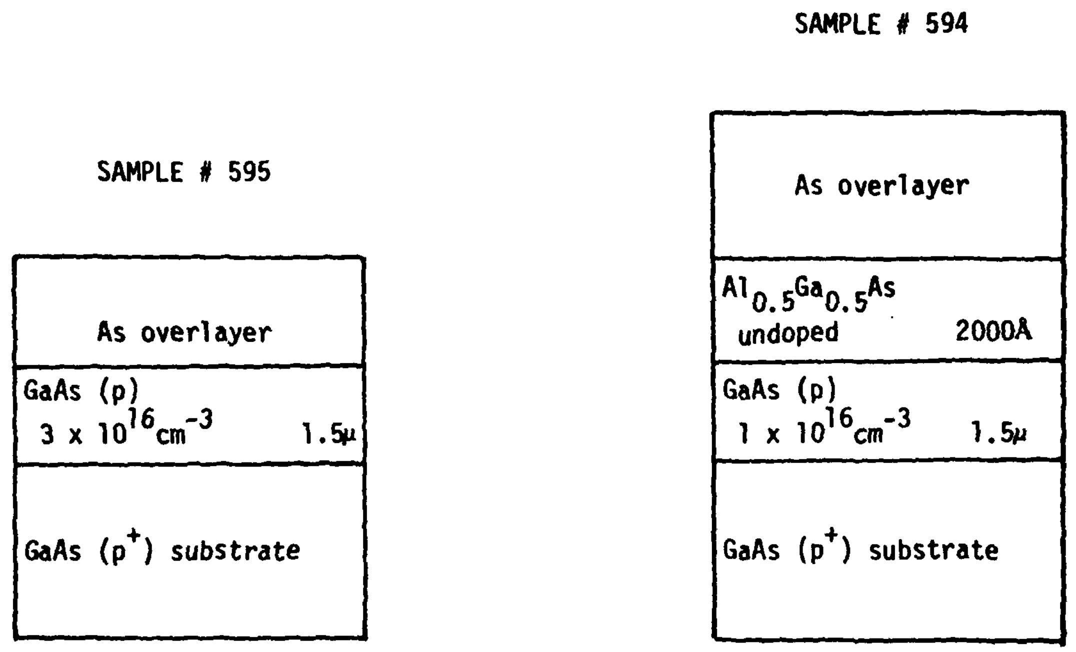

Fig. 1 Schematic illustration of structure for two MBE samples.

2. Arsenic Coating Technique

MBE is a powerful technique for the growth of epitaxial layers. Among the advantages of MBE is that the growths are carried out in UHV ambient and under well controlled growth conditions. A variety of novel and potentially useful epitaxial structures can be grown by MBE. One major problem in surface studies of MBE growths is how to transfer the growths from a MBE system to another vacuum system through air without oxidation and/or contamination. We have developed a novel and simple method for transferring samples from either of the Rockwell MBE systems to our HP5950A XPS spectrometer. The method is based on the use of a protective elemental As overlayer. This technique did not require any modification of the existing MBE system. The transfer procedure was tested on a variety of MBE grown specimens, with both AlAs and GaAs epilayers. The AlAs is extremely reactive to oxygen and thus provides a rather stringent test case.

The technique consists of growing the desired semiconductor layer in the conventional manner. Next, the key step of depositing the protective layer of elemental As is carried out. Arsenic is condensed on the surface of the epitaxial layers as rapidly as possible following the epilayer growth. This As comes from the arsenic beam used during the growth of the epilayers, and consists of As_4 derived from the sublimation of elemental arsenic. The metal (Ga and/or Al) and dopant sources are abruptly shuttered to terminate the layer growth, while the As_4 beam remains impinging on the surface of the wafer. At typical MBE growth temperatures (550-650°C), no condensation of As occurs (As has a very low sticking coefficient to itself at these temperatures) but the As_4 beam prevents surface decomposition. At the conclusion of the epilayer growth, the substrate heater is turned off and the edge of the substrate holder is brought into contact with the MBE system's liquid nitrogen cooled shroud to speed cooling of the holder. The substrate remains within the central portion of the As_4 beam. After the temperature falls below ~ 450°C, the As_4 flux is reduced by ~ 90%. This step is not necessary but is used to conserve the As charge. The specimen is cooled to slightly below room temperature. Such a temperature is necessary to condense a sufficiently thick As overlayer. This layer is approximately 100-1000 Å thick although layers as thin as ~ 15 Å thick have been successfully used. The sample is next transferred to the XPS system through air. This step takes about 15 min. Once the sample is again in a UHV ambient, the "as-grown" surface is regenerated by heating the sample to ~ 300-350°C to desorb the As overlayer. This yields an atomically clean and ordered surface as determined by XPS and LEED.

This technique has been successfully employed to protect a number of both thin (≈ 25 Å) and thick (≈ 1000 Å) epilayers which include AlAs and GaAs. Figure 2 shows typical results from an AlAs growth. The As overlayer itself is remarkably resistant to oxidation as can be seen from the very small As oxide peak noted in the figure. Samples have been stored in air for 5 days without oxidation of the epilayer and with almost neglible oxidation of the As cap.

This technique may be important for combining MBE with other technologies for device fabrication (e.g., after a MBE growth, another processing

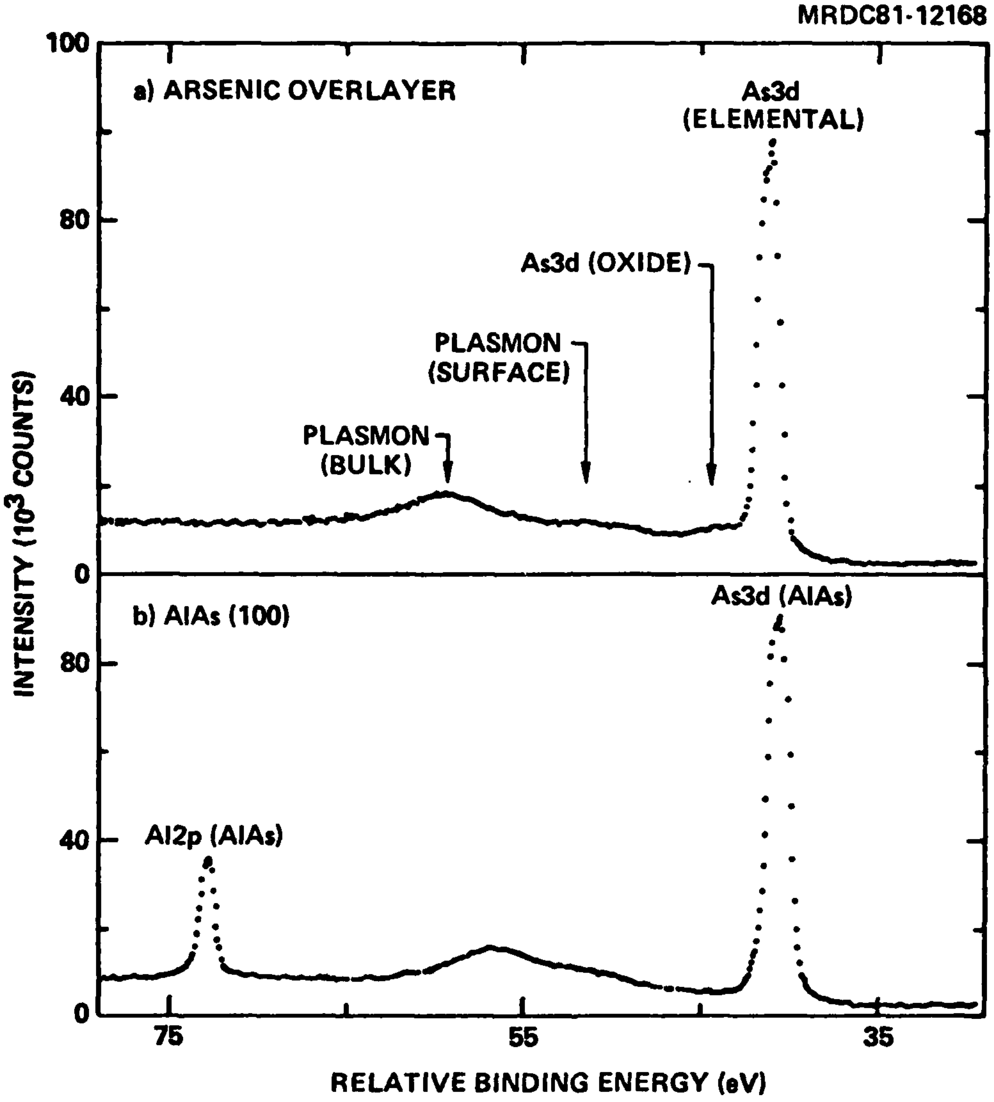

Fig. 2 (a) XPS spectrum of As3d core level from the protective elemental As overlayer for an AlAs sample that had been stored in air for 5 days. (b) XPS spectrum of Al2p and As3d core levels from the underlying AlAs epilayer after the protective As overlayer had been desorbed.

step such as ion implantation, MO-CVD epitaxial growth etc. could be carried out in another vacuum system). Also this technique should not be limited to the $Al_{1-x}Ga_xAs$ system, but may include other III-V and II-VI compounds. Instead of As, the appropriate volatile non-metallic component of the desired compound could be used as the cap material (see Table 1 for a partial list of possibilities).

Table 1
Partial List of Materials Which Could Employ
The Protective Capping Technique

	Materials			Protective Layers
	AlAs	GaAs	InAs	As
III-V	AlSb	GaSb	InSb	Sb
	AlP	GaP	InP	P
	ZnS	CdS	HgS	S
II-VI	ZnSe	CdSe	HgSe	Se
	ZnTe	CdTe	HgTe	Te

Ternaries and Quaternaries such as $Al_{1-x}Ga_xAs$, $Hg_{1-x}Cd_xTe$ and $InAs_{1-x}Sb_x$ are also possibilities.

3. Plasma Oxidation Development

The dielectric formed by thermally oxidized $Al_{1-x}Ga_xAs$ was found to be leaky and subject to breakdown making interpretation of the C-V measurements difficult. A dielectric with better insulating properties is needed. As a result we developed and investigated the properties of plasma oxidized

GaAs surfaces for this purpose. Plasma oxides have been reported with relatively low interface state densities and low leakage currents.[3]

Oxides were grown in a modified LFE PDS/PDE301 barrel etcher. Oxygen gas flowed through the etcher so that the net pressure ranged from 1 to 5 torr. A discharge was provided by an rf generator with a power of 100-300 watts. The sample was placed on an electrically grounded aluminum plate. No oxide growth was observed on an insulating plate. It was found that the rate of oxide growth was only weakly dependent on substrate bias but was strongly dependent on sample temperature and consequently on rf induced heating. The thickness of the film was generally self-terminating between 1000 Å and 2000 Å as determined by color charts previously published.

Oxide films formed in this manner had low leakage (less than 10^{-10} amps for 2×10^{-3} cm^2 area at 10 V forward bias for films ~ 1000 Å thick. Under these conditions the current in thermally oxidized samples was normally $> 10^{-6}$ amps.

4. Si_xN_y Deposition Development

We also investigated the use of Si_xN_y as a deposited insulator on the $Al_{1-x}Ga_xAs$ layers as opposed to a dielectric grown by oxidation of the $Al_{1-x}Ga_xAs$. The LFE PDS/PDE plasma etcher was modified to be compatible with either plasma oxidation or with Si_xN_y growth. Si_xN_y films were formed by leaking 1% silane diluted by argon into the discharge of an ambient gas which was either high purity nitrogen, forming gas (10% H_2, 90% N_2) or ammonia.

Similar results were obtained for all three gases. The power dissipated during the discharge was typically 100-300 watts. The partial pressures used were typically 2-10 torr for the SiH_4 + Ar mixture and 1-3 torr for the forming gas, nitrogen, or ammonia. The growth rate was very sensitive to the partial pressure of the silane mixture. Films obtained from this system have very low leakage currents typically less than 10^{-9} amps at 10 V across a 1000 Å thick film in a MIS capacitor with an area of 2×10^{-3} cm^2.

Figure 3 compares the I-V curves for three deposited insulators from our laboratory. These are sputtered SiO_2, sputtered Si_xN_y, and plasma CVD Si_xN_y. The SiO_2 films (~ 1000 Å thick) are quite leaky compared to the Si_xN_y films shown in the figure. Although it is difficult to compare the two Si_xN_y films because they have different thicknesses, the sputtered film appears to show greater leakage. The current levels in the plasma CVD Si_xN_y are near the sensitivity limit of the instrument. Thus the plasma CVD Si_xN_y film appears to be the best insulator of those investigated.

A heater was added to the system in order that the sample could be heated prior to deposition. Such a procedure is necessary to take advantage of the As coating technique described in Section II-2. With this technique an As overlayer is deposited on a sample *in situ* within the MBE growth chamber. This overlayer can subsequently be removed at a low temperature by heating the sample in the Si_xN_y deposition chamber prior to Si_xN_y deposition. In this way, the formation of native oxide on the surface can be minimized. The production of this native oxide is thought to produce a large density of

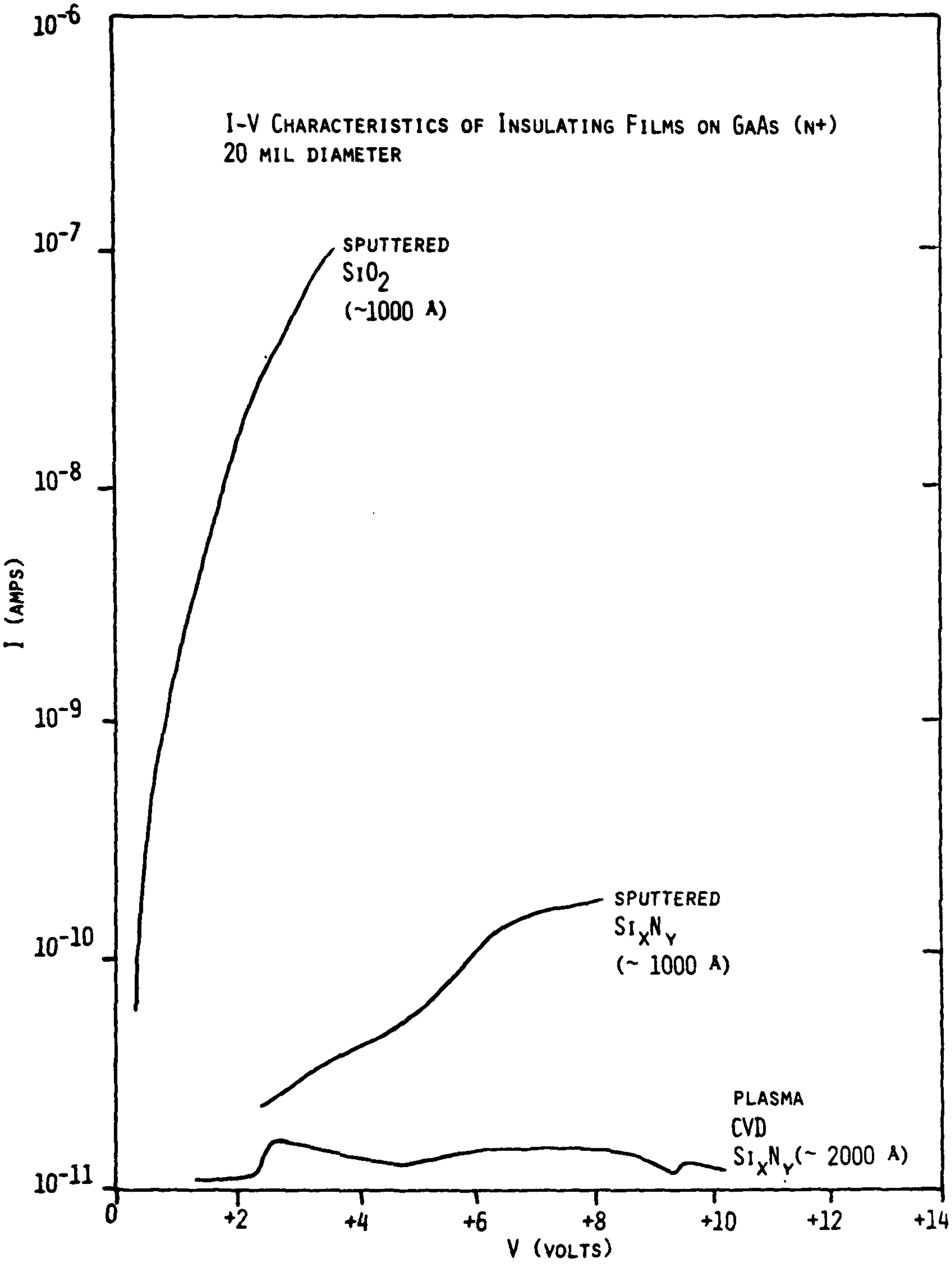

Fig. 3 I-V characteristics for three deposited insulators.

interface-states. Hopefully by eliminating the native oxide we will be able to produce a structure with low interface state density.

Initial results indicated that the arsenic was removed in part by the reaction of a forming-gas plasma with the coated substrate. After the initial reaction a residue remained which was not attacked by the plasma and which could only be removed by subsequent heating to temperatures above 400°C. Due to the residual film Si_xN_y layers formed without the subsequent heating showed poor morphology and were filled with pinholes resulting in devices with large leakage currents. Films formed by heating above 400°C had much lower leakage curents ($\sim 4 \times 10^{-10}$ amps at 10 V with area = 2×10^{-3} cm^2).

SECTION III

SAMPLE CHARACTERIZATION

In this section, I-V and C-V measurements to characterize MIS structures prepared as described in Section II are discussed. Preliminary XPS surface-potential measurements on MBE grown GaAs samples are also presented.

1. I-V and C-V Measurements

I-V and C-V measurements on samples studied during this reporting period are presented here. All C-V measurements were carried out at 1 MHz with sweep rates of 1.1 V/s and with samples at room temperature.

a. Plasma Oxidized Samples

As described in Section II-3 plasma oxidation of the $Al_{1-x}Ga_xAs$ was used to improve the insulating properties of the dielectric for oxide-$Al_{1-x}Ga_xAs$-GaAs structures. We found these films to have superior insulating properties compared to the thermal oxide formerly used. We used this technique on sample No. 412 which was described previously.[4] The AlAs layer was removed on this sample leaving a layer of $Al_{0.5}Ga_{0.5}As$ on n-type GaAs. The surface was plasma oxidized producing a highly resistive oxide layer on the remaining $Al_{0.5}Ga_{0.5}As$ layer.

The device showed leakage currents $< 10^{-10}$ amps at forward bias of 10 V for a 2×10^{-3} cm^2 area device. C-V curves for this structure are shown in Fig. 4. The device shows large hysteresis (~ 4 V) and a large flatband

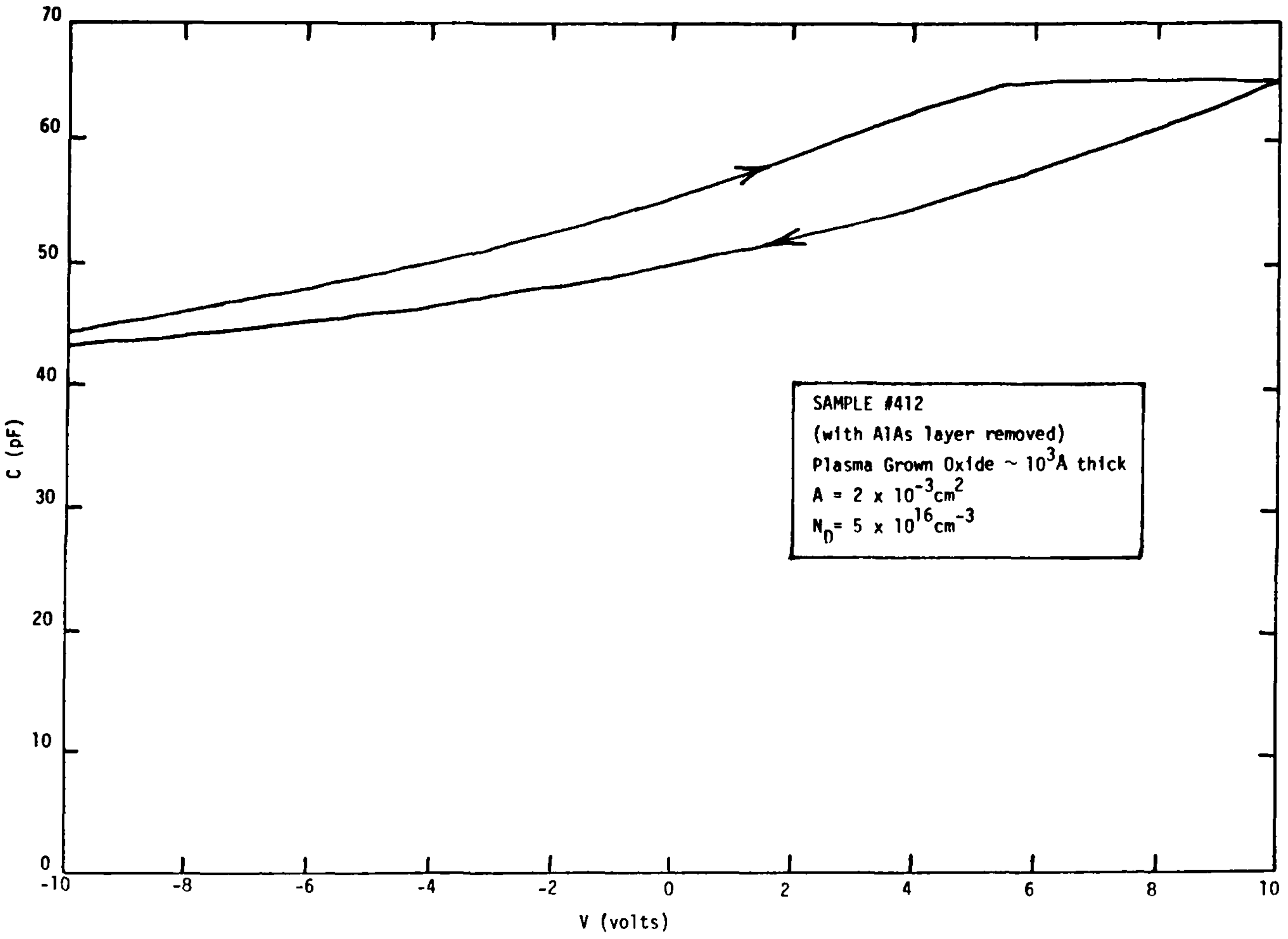

Fig. 4 C-V for plasma-grown oxide on sample No. 412 (which had AlAs layer removed).

voltage shift like that observed for the thermally oxidized devices. We do not see any indication of inversion but rather a deep depletion curve.

Such results indicate a large density of states ($\approx 10^{12}$ cm^{-2}) at one (or both) of the interfaces in this system. The interface between the plasma oxide and the $Al_{1-x}Ga_xAs$ is the likely site for these states as the $Al_{1-x}Ga_xAs$-GaAs interface should be relatively defect free. Annealing in N_2 did not change the C-V curves appreciably but did result in an increase in the leakage current through the oxide.

These results suggest that the inherent problem of having a large density of interface states may not be removed by the two-insulator approach. The problems associated with the large density of interface states may be transferred away from the GaAs-oxide interface to a region in the dielectric (the $Al_{1-x}Ga_xAs$-oxide interface). As a result it may be still difficult to change the interface potential and large hysteresis due to charge transfer between these states and the GaAs may be still observed.

b. Deposited Insulators

In an effort to improve the properties of samples made in the XPS system by photochemically deposited SiO_2 on a GaAs surface,[5] selected samples have been annealed under various conditions.

It has been found that by annealing in forming gas (a dilute H_2 in N_2 mixture) hysteresis in the C-V curves of the deposited SiO_2 samples can be appreciably reduced. As an example, Fig. 5 shows a typical C-V curve of an

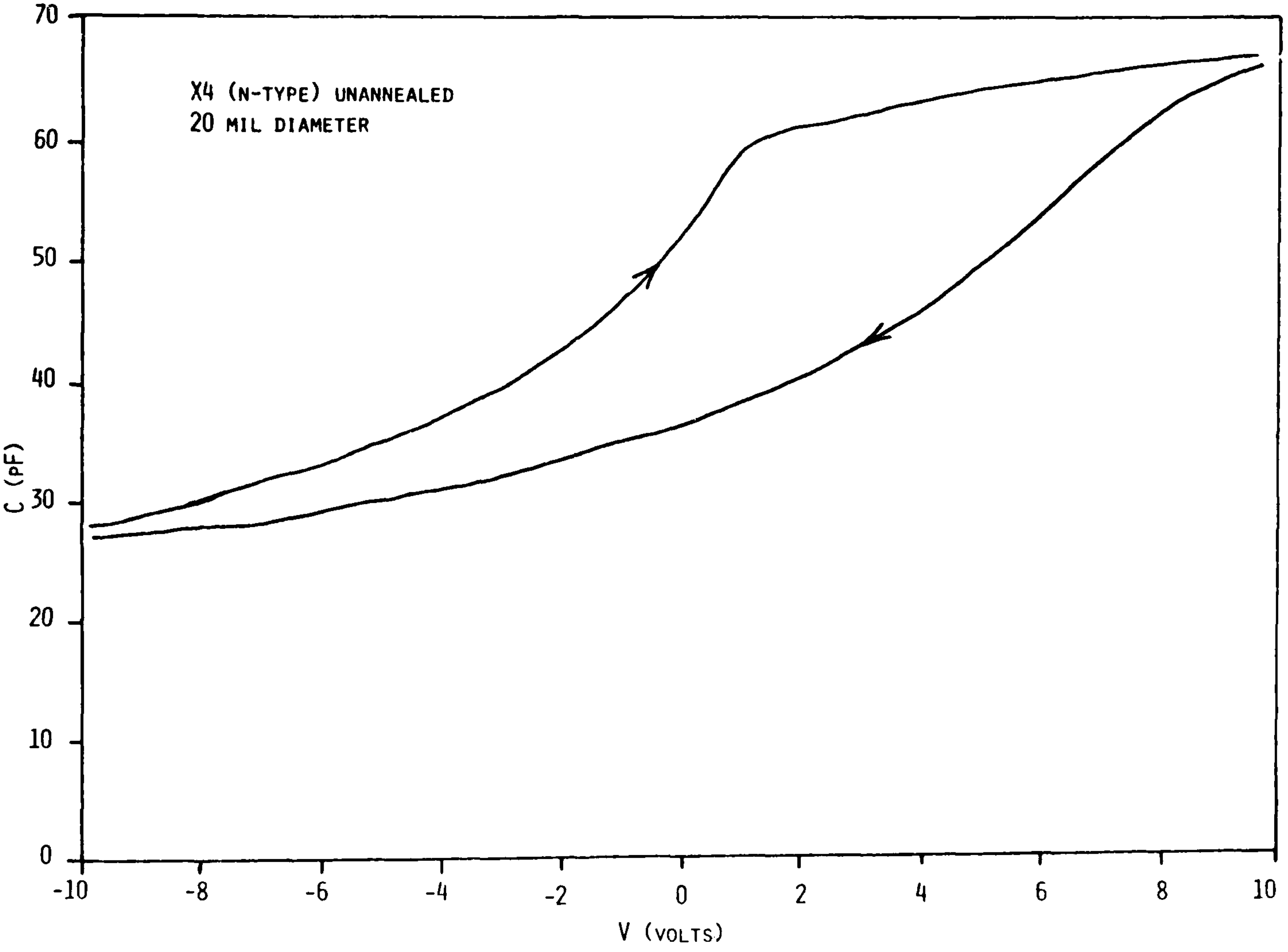

Fig. 5 C-V for sample X-4.

unannealed n-type sample, X4. Hysteresis of 5 or 6 volts is observed near the flatband region. Figure 6 shows results of C-V measurements on the same sample after a forming gas anneal at 400°C. It is observed that hysteresis in the C-V curves has been reduced to less than 1 V.

In spite of the reduction in hysteresis, the C-V curve indicates that there is a large flatband voltage shift indicative of a large density of interface states. In addition, the anneal is observed to have a detrimental effect on the dielectric properties of the device showing increased leakage current through the oxide. Such an increase in the leakage current may be responsible for the decreased hysteresis.

As mentioned in Section II-4 deposited Si_xN_y films had good I-V characteristics. Under the optimal conditions the Si_xN_y insulator has leakage currents of less than 10^{-9} amps for 2×10^{-3} cm^2 devices.

C-V curves for three samples are shown in Figs. 7, 8, and 9. The data in Fig. 7 correspond to a sample which was given an HF etch prior to insulator deposition. In Fig. 8, the sample was left in a forming-gas plasma for 10 min before deposition. For Fig. 9, the sample was left in the forming gas plasma for 30 min prior to deposition.

All three of these samples (Figs. 7-9) show flatband-voltage shifts consistent with a large density of interface states. For the sample with no plasma pretreatment (Fig. 7), the lowest interface-state density occurs with a flatband voltage $\approx$ 5 V. For the other two samples the shift is large enough

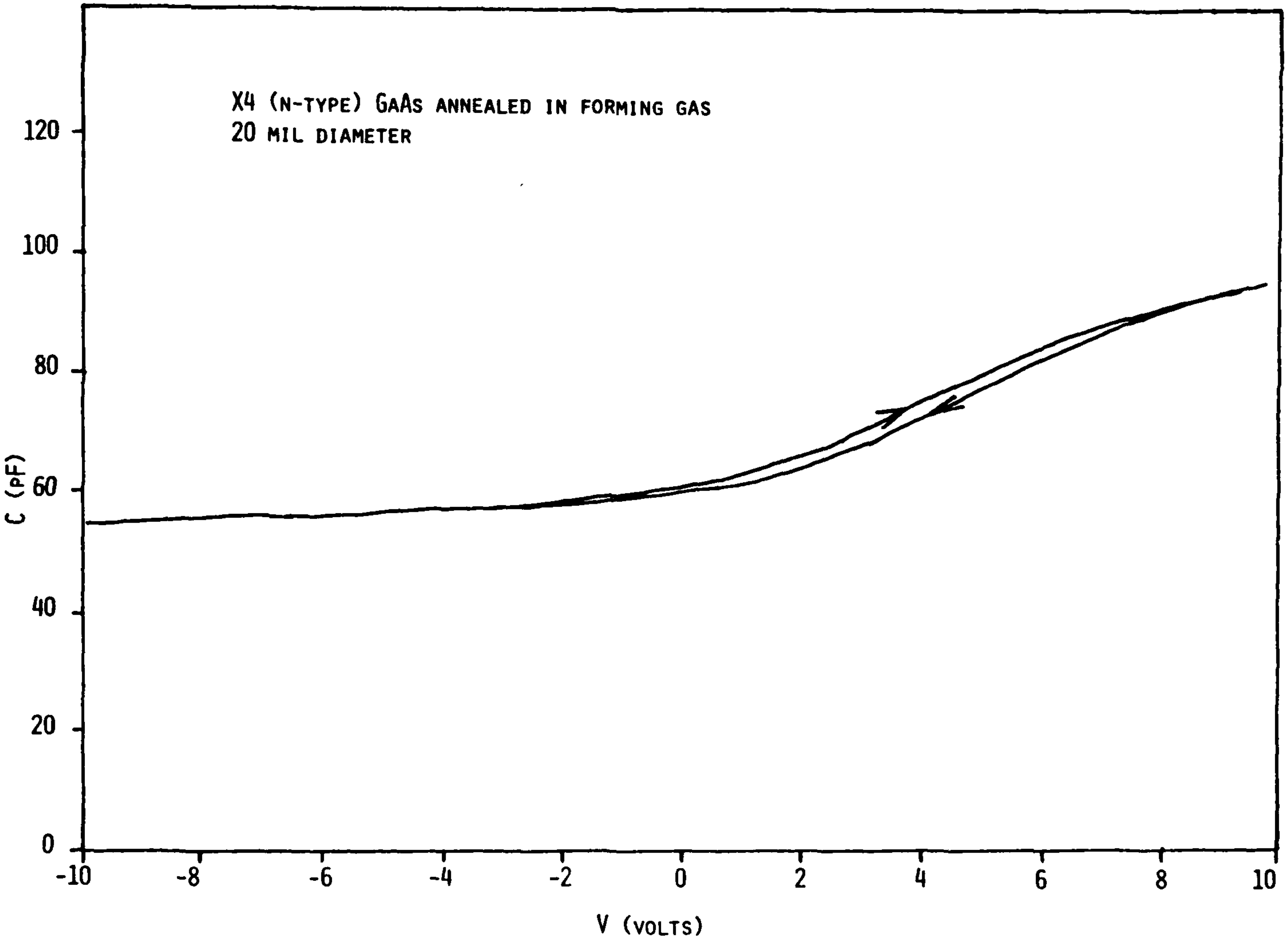

Fig. 6 C-V for sample X-4 which was annealed in forming gas at 400°C.

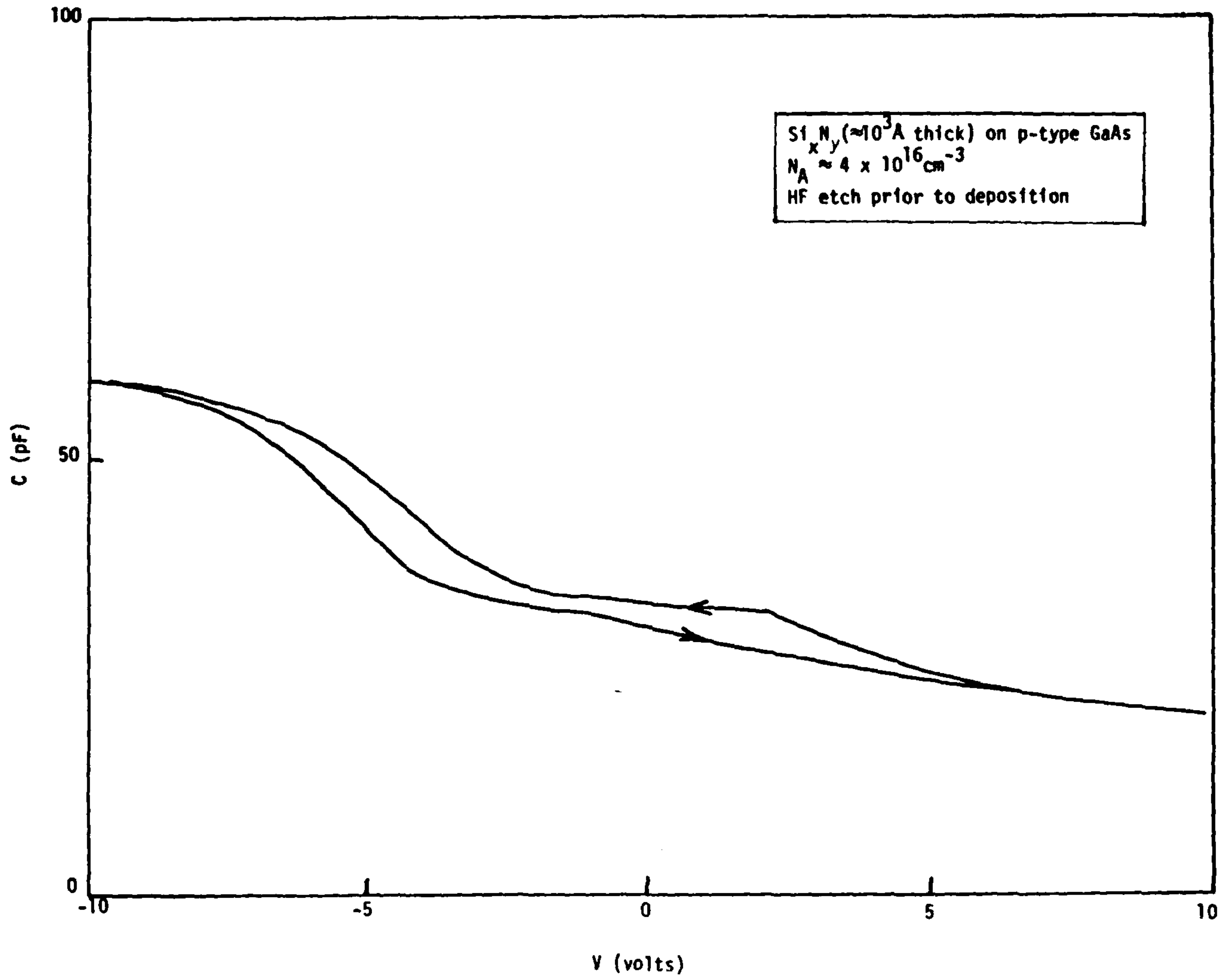

Fig. 7 C-V for Si_xN_y deposited on p-type GaAs which had been etched in HF just prior to deposition.

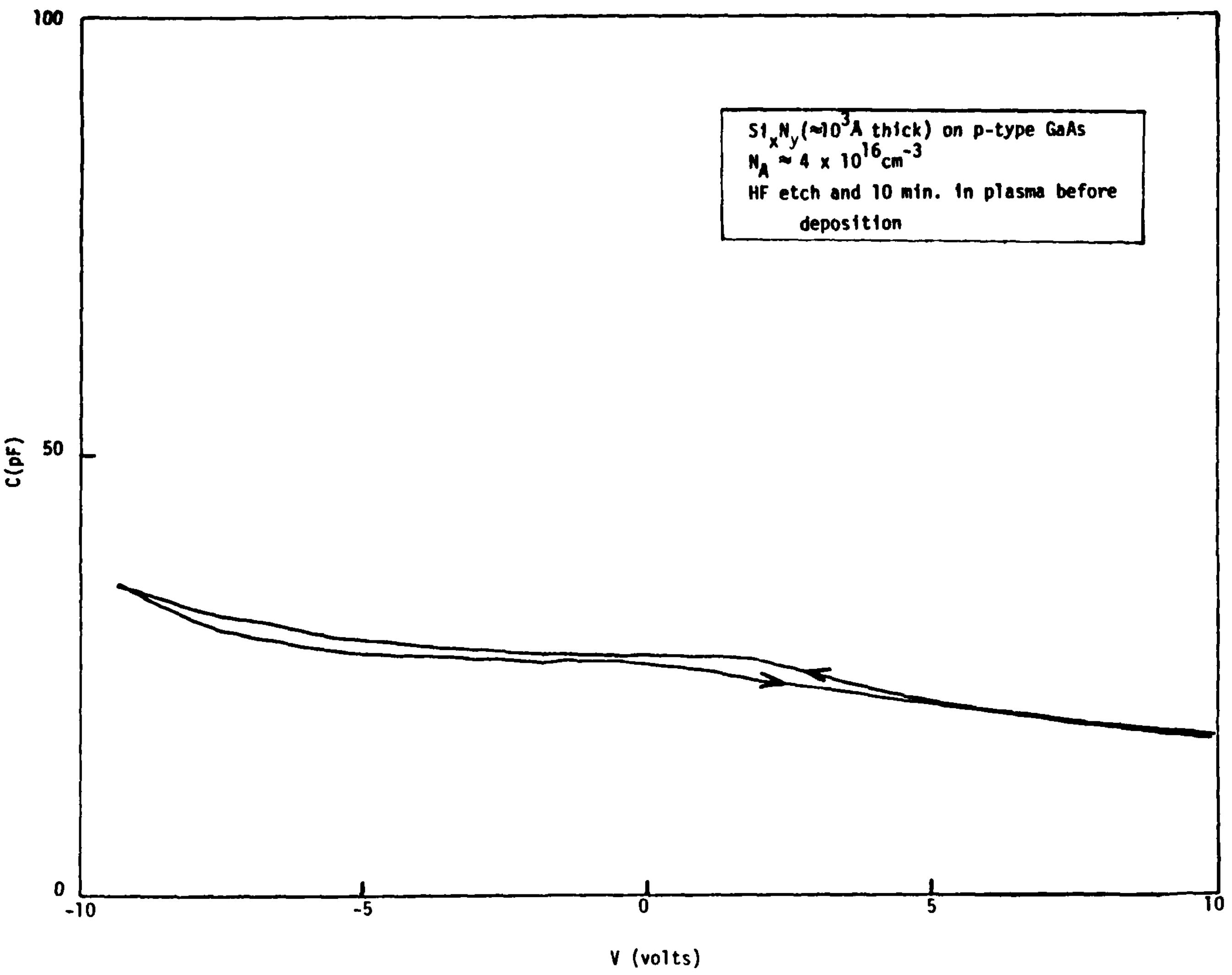

Fig. 8 C-V for Si_xN_y deposited on sample similar to that studied in Fig. 7 but which was exposed to a forming-gas plasma for 10 min prior to deposition.

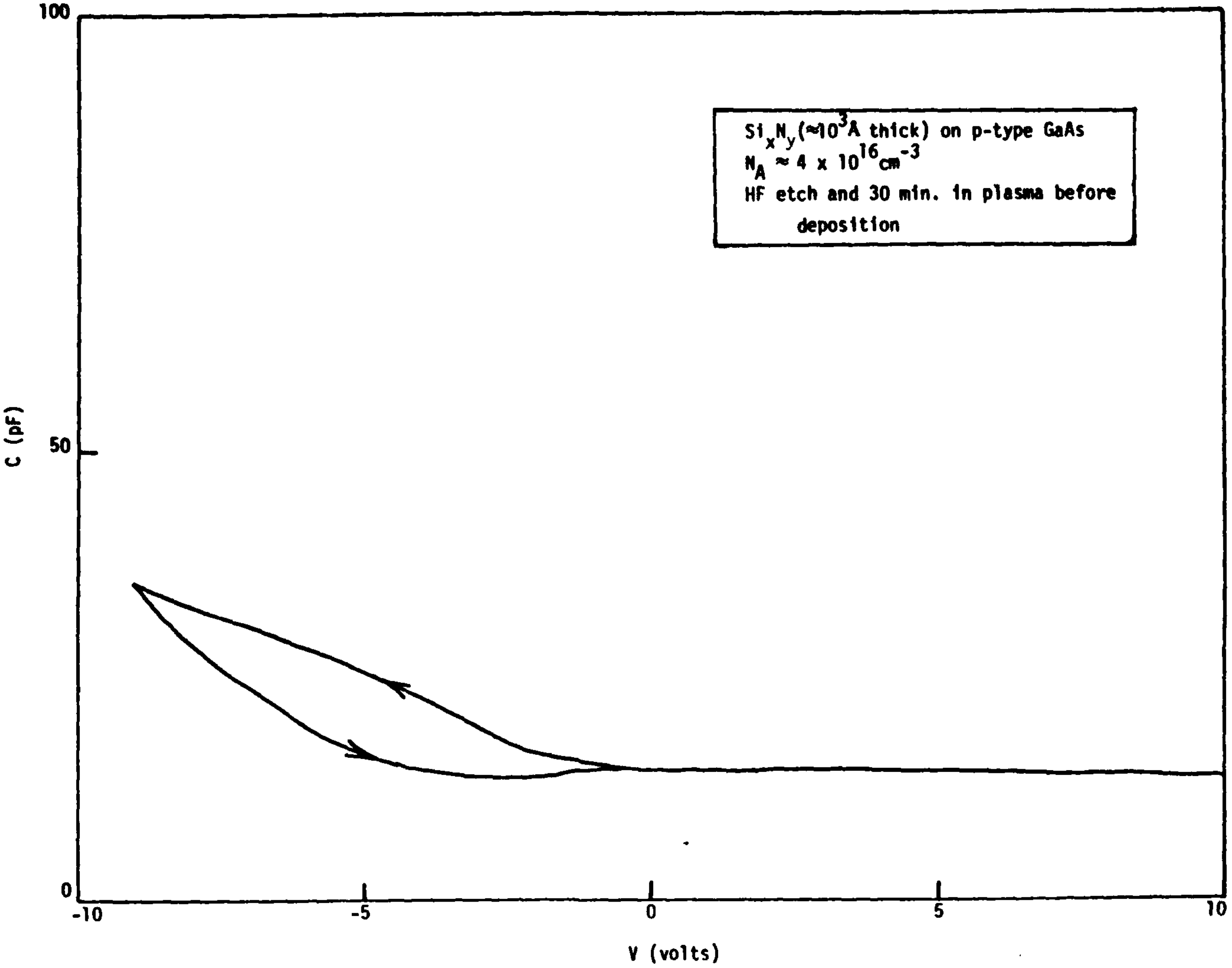

Fig. 9 C-V for Si_xN_y deposited on sample similar to that studied in Fig. 7 but which was exposed to a forming-gas plasma for 30 min prior to deposition.

to effectively pin the Fermi level. As a result it seems desirable to minimize the time of exposure of the semiconductor surface to the plasma.

Samples No. 491 and No. 493 described in Ref. 5 were covered with a thin layer of Si_xN_y. These samples consisted of a graded $Al_{1-x}Ga_xAs$ layer on GaAs. C-V curves for these samples gave the same flatband voltages and hysteresis characteristically observed with the thermal oxide. This apparently resulted from a layer of oxidized AlAs or $Al_{1-x}Ga_xAs$ at the interface.

We also measured C-V curves for samples produced by deposition of Si_xN_y following removal of arsenic on samples prepared by MBE as described in Section II-1. The As overlayer is deposited on a sample in situ within the MBE growth chamber to minimize the formation of the native oxide. Afterwards the As is removed by evaporation. A C-V curve for a GaAs sample with deposited Si_xN_y is shown in Fig. 10. The Si_xN_y was produced in the LFE system. The C-V curve shows very strong pinning, in fact considerably more than observed in samples which were etched in HF with no other kind of surface treatment. For preparation of samples with low interface-state densities by the As overcoating technique a cleaner system may be necessary. The LFE system used is not capable of providing an ultraclean low oxygen environment. During the heating cycle the surface probably reacted with oxygen. Thus further effort is being concentrated on providing a high-vacuum environment for deposition of insulating films.

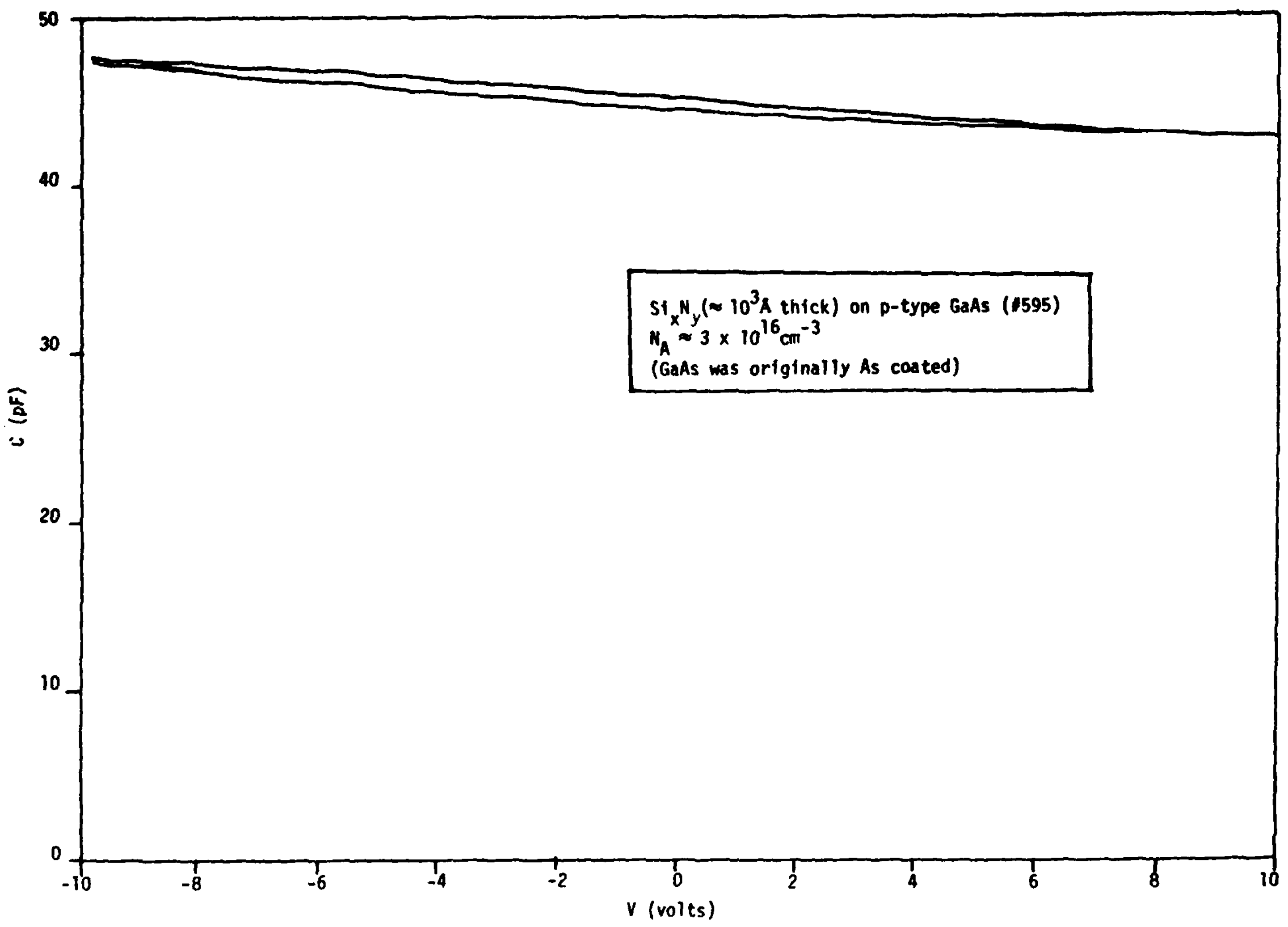

Fig. 10 C-V for Si_xN_y deposited on MBE grown sample No. 595 which had been protected by As° prior to deposition.

2. XPS Surface Potential Measurements

XPS offers a convenient method to determine the surface potential of a sample. This method is described in Refs. 6 and 7. For convenience the method is illustrated briefly here. Figure 11 shows a schematic band diagram for GaAs. In this figure, all binding energies are referred to the Fermi level (E_F). The conduction-band minimum is E_C^{GaAs}, the valence-band maximum is E_V^{GaAs}, the As3d core-level binding energy is E_{As3d}^{GaAs}, the Fermi-level position relative to E_V^{GaAs} is Δ, and W is the depletion width. The (b) and (i) notations refer to bulk- and interface-quantities respectively. For a flatband condition $\Delta(b) = \Delta(i)$. The bulk doping characteristics determine $\Delta(b)$.

The perfectly cleaved (110) surface is the only GaAs surface that has been found to be unpinned.[8,9] As mentioned in Section II-2, a method has now been developed to transfer an MBE grown surface (which has been protected by an As° cap) into the XPS system without surface contamination. An XPS experiment was carried out to determine the surface potential of two MBE grown samples which had been protected by the As° capping method. During the MBE growth run No. 588, both (100) and (110) samples of GaAs were prepared. The samples were intended to be doped p-type (in the mid 10^{16} cm^{-3} range), however, as mentioned in Section II-1, the intentional doping was considerably lighter than expected. Subsequent metal point contact measurements suggested that the (100) sample was actually doped n-type while the measurements on the (110) sample gave an ambiguous result. XPS surface-potential measurements were carried out on these samples. The results are shown in Fig. 12 where E_{As3d}^{GaAs} and $\Delta(i)$ are plotted for several sequential surface treatments. The

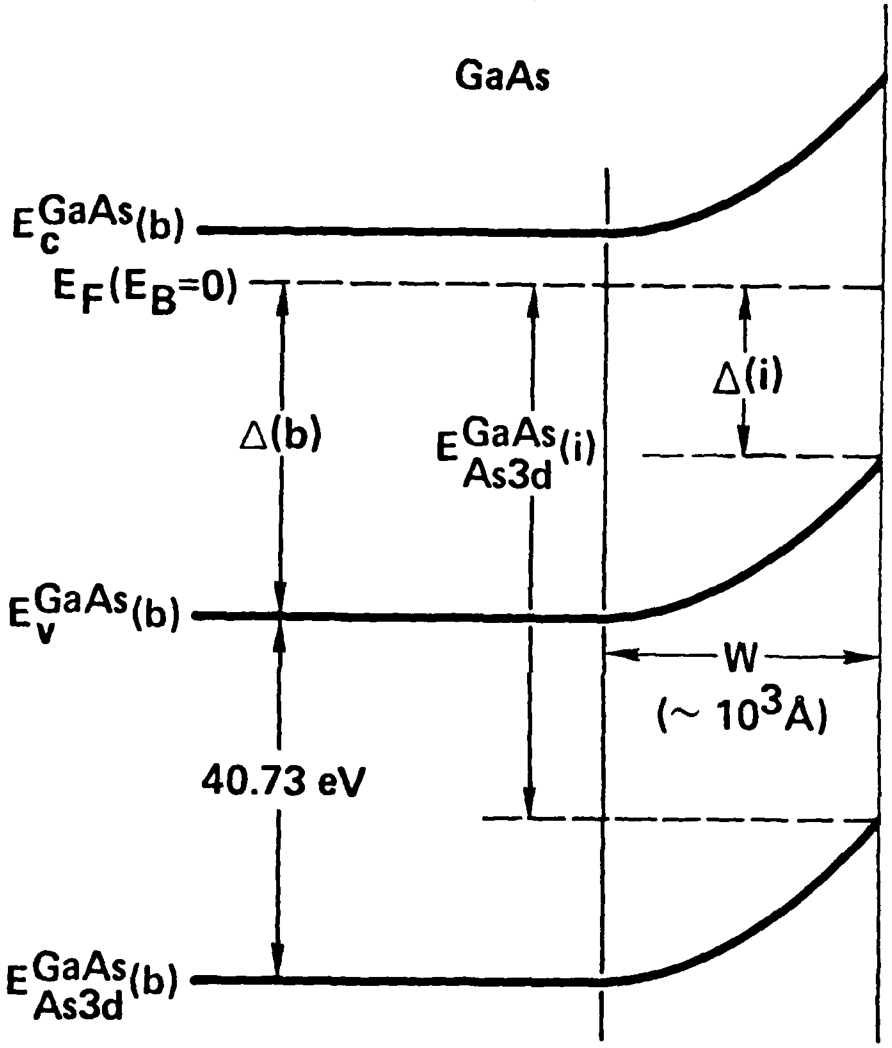

Fig. 11 Schematic energy-band diagram which illustrates the XPS measurement of interface Fermi level for GaAs.

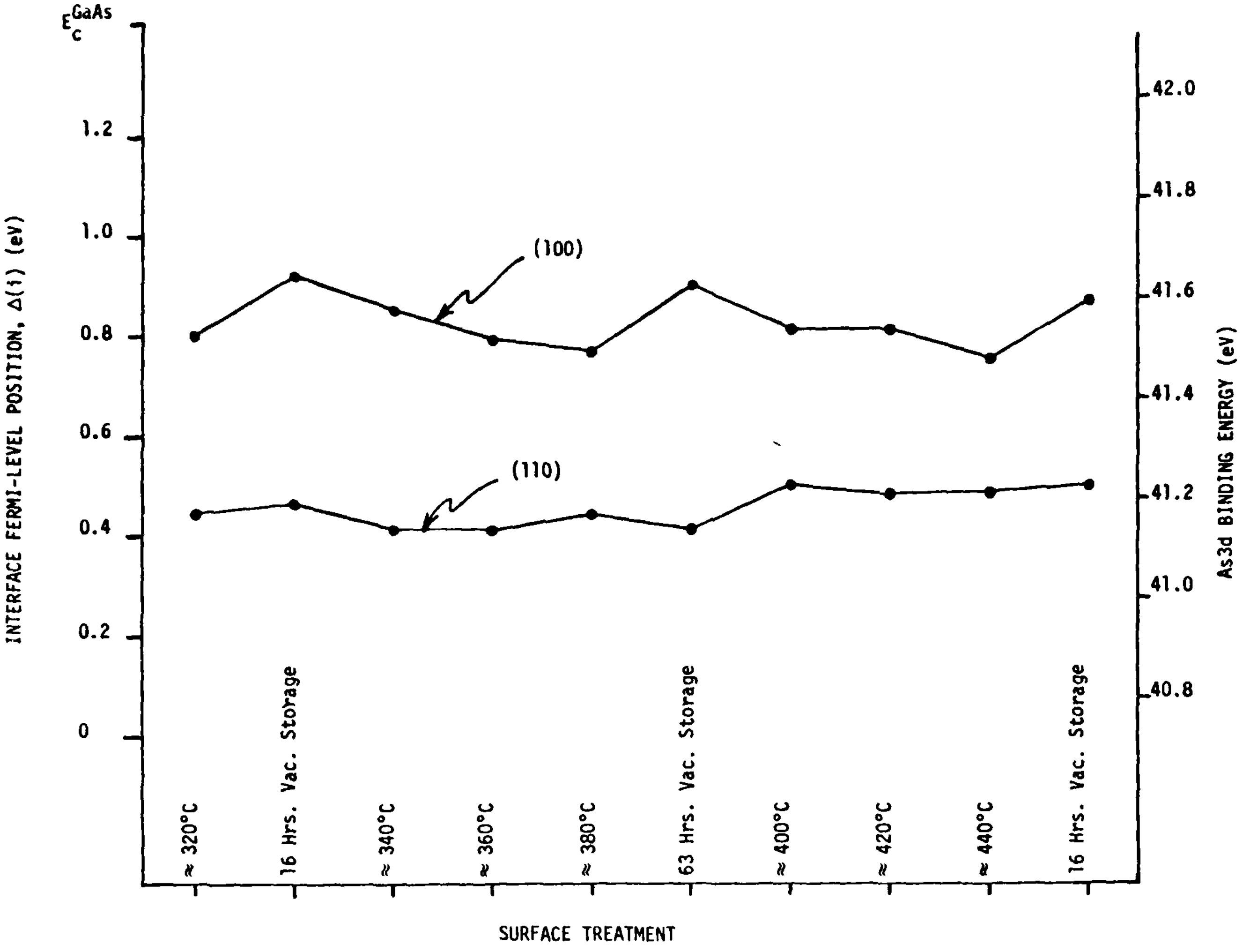

Fig. 12 Interface Fermi-level position and As3d binding energy in GaAs for (100) and (110) samples of MBE growth No. 588.

$E_{As\,3d}^{GaAs}$ values were determined as described in Ref. 10. The elemental As layer was removed from the surface by heating to ≈ 320°C. Subsequent thermal treatments and vacuum storage (in 10^{-9} torr) caused only small variations in $\Delta(i)$.

The results presented in Fig. 12 show that in all cases the E_F of these two samples was pinned. Previous studies[10] of thermally cleaned GaAs surfaces (cleaned at ≈ 550°C) have shown that n-type surfaces are pinned at about 0.75 eV above E_V while p-type surfaces are pinned at about 0.45 eV above E_V. By comparison with these previous results,[10] the data in Fig. 12 suggest that the (100) surface is n-type while the (110) surface is p-type. The observed surface band bending can be used to determine the surface charge and thus set a lower limit on the occupied surface-state density. Because the bulk doping characteristics of these samples were poorly known this was not done. We expect to repeat these experiments.

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APPENDIX (PUBLICATIONS)

In the appendix, two papers are reproduced which were based on work partially supported by this contract. Both papers will be published in the J. Vac. Sci. Technol. and are currently in press.

APPENDIX A

PROTECTION OF MOLECULAR BEAM EPITAXY GROWN $Al_xGa_{1-x}As$ EPILAYERS DURING AMBIENT TRANSFER

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ABSTRACT

A method for the protection of reactive compound semiconductor surfaces during transfer from a molecular beam epitaxy apparatus through ambient for further processing or experimental characterization is demonstrated for GaAs and AlAs. This method is likely to be applicable to other compound semiconductors.

Molecular beam epitaxy (MBE) has become a powerful technique for the fabrication of epilayers and abrupt heterojunctions of compound semiconductors [1] One of the most important compounds is the ternary $Al_xGa_{1-x}As$, which has such applications as solar cells, heterojunction lasers, and field-effect transistors. Surfaces of this material are especially reactive near x=1.0. It is of interest to investigate the surface properties of these materials, particularly the surface atomic geometry and the interfacial reactions which occur with deposited metals, insulators, or controlled gas exposure. MBE is an attractive epitaxial growth technique for the preparation of single crystal semiconductor surfaces because of the ultra-high vacuum (UHV) ambient. A typical MBE apparatus contains, however, a limited amount of surface analytical instrumentation. Although several systems designed to combine MBE growth with extensive analysis capabilities are available commercially, they are very expensive. Thus it is useful to have a simple procedure to transfer a MBE grown sample to another vacuum system through ambient while preserving its clean ordered surface. Two approaches to this type of sample transfer have been tried previously. One is the use of an UHV transfer device.[2] This presupposes compatibility of the transfer device with both the MBE system and the systems to which the sample is being transfered. Such a device can often be very complicated mechanically. Also for a sample such as AlAs, which is extremely reactive, the transfer device is required to operate in the 10^{-10} torr range. A second technique is to deposit a less reactive material as a protective coating; the coating is removed by ion milling after the transfer.[3,4] This technique is not suitable for studying very thin films of

~ 20 Å thickness, and may be difficult to apply to very reactive materials. For some applications, sputter damage of the resulting surface may be a complication.

In this communication, we report a relatively simple technique for transferring reactive compound semiconductor samples from an MBE system to other UHV systems through air while preserving the as-grown surface. This technique did not require addition to or modification of the MBE system. We have demonstrated this technique for AlAs, GaAs and for AlAs-GaAs and GaAs-AlAs heterojunctions. The method we have developed is based on the use of a protective elemental As overlayer. The semiconductor layers are grown by MBE on GaAs substrate material in the conventional manner.[1] The GaAs substrates are mounted with In to Mo plates which are then clamped tightly to our standard MBE substrate holders by using Ta screws. This allows the samples to be demounted from the MBE holder without heating to melt the In solder. After growth of the desired semiconductor layer, a protective layer of elemental As is deposited. The thickness of this layer is usually greater than 100Å, although we have successfully used an As layer as thin as ~ 25Å. The sample is then transferred from the MBE apparatus through air to another apparatus. In our case, about ten samples have been transferred from an MBE system (constructed at Rockwell International) to an x-ray photoelectron (HP5950A) spectrometer - LEED system. This step takes about 15 minutes. Once the sample is under the desired vacuum conditions (for AlAs, in the 10^{-10} torr range), the specimen is heated gradually to ~ 300-350°C to desorb the As overlayer. This yields an atomically clean and ordered AlAs surface as determined by XPS and LEED.

The key step of this protective method is the growth of the As overlayer. Arsenic is condensed on the surface of the epitaxial layers as rapidly as possible following the epilayer growth. This As comes from the arsenic beam used during the growth of the epilayers, and consists of As_4 derived from the sublimation of elemental arsenic. The metal (Ga and/or Al) and dopant sources are abruptly shuttered to terminate the layer growth, while the As_4 beam remains impinging on the surface of the wafer. At typical MBE growth temperatures (550-650°C), no condensation of As occurs (As has a very low sticking coefficient to itself at these temperatures) but the As_4 beam prevents surface decomposition. At the conclusion of epilayer growth, the substrate heater is turned off and the edge of the substrate holder is brought into contact with the MBE system's liquid nitrogen cooled shroud to speed cooling of the holder. The substrate remains within the central portion of the As_4 beam. After the temperature falls below ~ 450°C, the As_4 flux is reduced by ~90%. This step is not necessary but is used to conserve the As charge. The specimen is cooled to slightly below room temperature. Such a temperature is necessary to condense a sufficiently thick As overlayer.

A typical sample structure which has been transfered between MBE and XPS systems is shown in Fig. 1. These samples were used for studies of the valence band of AlAs[5] and GaAs-AlAs heterojunction band discontinuities.[6] Figure 2 shows XPS core-level spectra in the region of Al 2p and As 3d lines. This sample had been stored in air for 5 days before insertion into the XPS system. The upper spectrum in the figure is from the As overlayer.

We observe elemental As and a trace amount of As_2O_3. After heating the sample to ~300-350°C, the spectrum of clean AlAs is obtained (lower portion of Fig. 2). No O, C or other contaminant could be detected, and good LEED patterns were obtained from the samples prepared by this technique.

In summary, we have developed and demonstrated a simple method for the protection of reactive $Al_xGa_{1-x}As$ surfaces. With this technique a surface prepared by MBE can be transfered in air to another vacuum system for either experimental studies, characterization or further processing. While this method has been demonstrated for GaAs, AlAs and AlAs-GaAs heterojunctions, it should be applicable to other III-V or II-VI binary (and ternary or quaternary) systems as well. The method consists of the deposition at or slightly below room temperature, of a protective elemental overlayer (~ 100-1000 A) of the higher vapor-pressure phase, non-metallic component of the semiconductor. Thus As was used for GaAs and AlAs and could presumably be used for other arsenides. It seems likely that Sb, S, Se, and Te can be used for some antimonides, sulfides, selenides and tellurides, respectively. The condensed overlayer protects the surface from contamination and oxidation during transfer between UHV systems. After transfer, the protective layer is easily removed by low temperature annealing to yield clean and oriented surfaces. This technique may also be applicable for other growth techniques such as metal-organic chemical vapor deposition.

ACKNOWLEDGEMENT

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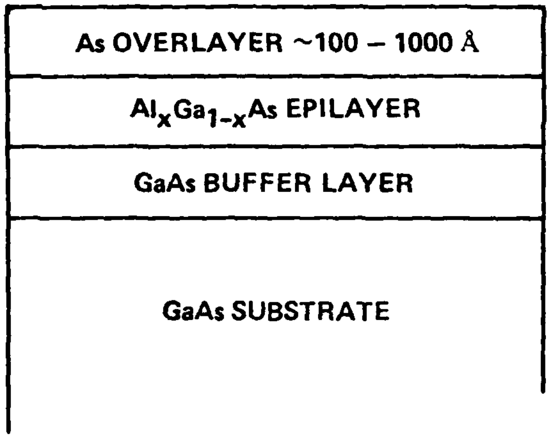

Fig. 1 A typical structure grown by MBE in this study and successfully transferred to an XPS apparatus without contamination of the $Al_xGa_{1-x}As$ surface.

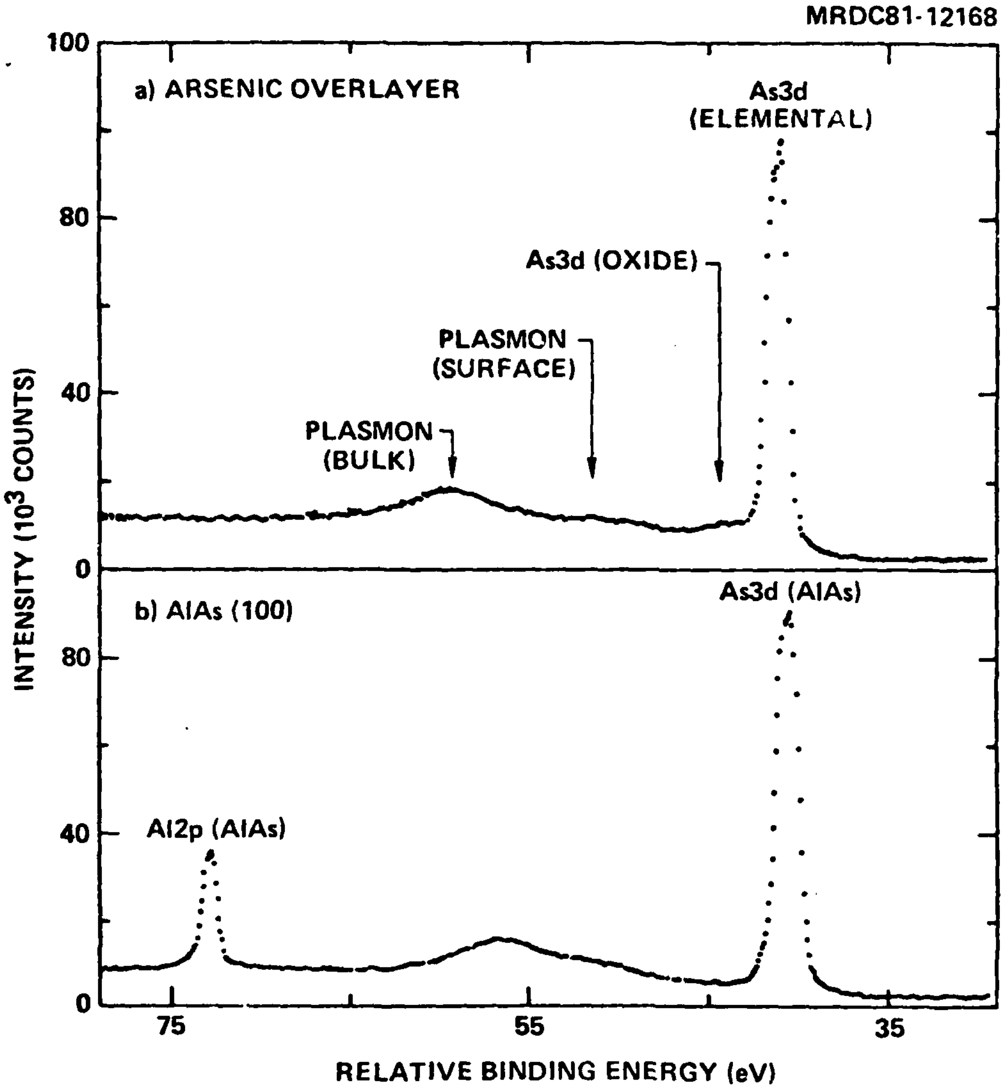

Fig. 2 a) XPS spectrum of As 3d core level from the protective elemental As overlayer for an AlAs sample that had been stored in air for 5 days.

b) XPS spectrum of Al 2p and As 3d core levels from the underlying AlAs epilayer after the protective As overlayer has been desorbed. The binding-energy scale is relative to the AlAs valence-band maximum.

APPENDIX B

INTERFACIAL CHEMICAL REACTIVITY OF METAL CONTACTS WITH THIN NATIVE OXIDES OF GaAs

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ABSTRACT

X-ray photoemission spectroscopy (XPS) was used to investigate the chemical reactivity and band-bending variation of native oxide covered surfaces of GaAs (100) during Schottky-barrier formation. The GaAs surfaces prior to metal deposition had thin ~ 10Å overlayers of either As_2O_3 and Ga_2O_3 or only Ga_2O_3. A variety of metals, some chemically inert (Au, Cu, and Ag) and some chemically reactive (Al, Mg, Cr, and Ti), were studied on both types of oxide surfaces. The chemical reactions occurred at room temperature and were well predicted by bulk thermodynamic free energies of formation.

I INTRODUCTION

Metal-semiconductor contacts are ubiquitous in semiconductor electronics, with Schottky-barrier contacts being of particular fundamental and practical importance. To date the primary emphasis in surface science experiments applied to contacts has been to study the phenomena associated with ideal Schottky-barrier contacts, that is, metals deposited onto clean and ordered semiconductor surfaces under ultra-high vacuum conditions (see e.g. Refs. 1-4). When Schottky-barrier contacts are formed during the fabrication of a typical device, however, there is generally a thin native oxide film present on the surface of the semiconductor. Consequently, the modeling of Schottky-barrier contacts in devices usually assumes the existence of a 10-100Å thick insulating native-oxide film between the metal and the semiconductor.[5] The question naturally arises as to the interface chemistry during Schottky-barrier contact formation in the presence of a native oxide layer on a semiconductor. Furthermore, a current trend in the development of fast electronic circuits is to utilize very small devices, with active regions being envisioned as small as 50 to 200Å. The constraints imposed by small dimensions on reliably fabricating such devices make it incumbent to develop an understanding of the microchemical processes at various semiconductor interfaces. Presently, GaAs has received the most attention as the prototypical compound semiconductor for advanced high-performance electronic devices.

This paper reports the investigation, by x-ray photoemission spectroscopy (XPS), of the room temperature chemical reactions of the metals Au, Ag, Cu, Al, Mg, Ti, and Cr with thin native oxides on GaAs

(100) surfaces. The reactions were followed as a function of increasing metal thickness from submonolayer amounts to $\geqslant 25$Å. The metals were either inert (Au, Ag, and Cu) or reactive (Al, Mg, Ti and Cr), with the former leaving the native oxide layer intact and the latter causing removal of the native oxide by a chemical displacement reaction. In addition to chemical analysis, XPS was also used to observe changes in interface Fermi-level ΔE_F^i position (band-bending) during the early stages of Schottky-barrier formation.

II EXPERIMENTAL DETAILS

A HP5950 electron spectrometer was used for the XPS measurements. This system possesses a monochromatized Al$K\alpha$ ($h\nu$ = 1486.6 eV) x-ray source; the electrons from most of the core levels measured in these studies had escape depths of ~ 25Å. The features of this system include a custom ultra-high vacuum preparation chamber ($P \sim 1 \times 10^{-10}$torr), resistively heated metal evaporators, quartz crystal thickness monitor, sample heater, and LEED instrumentation.

The application of XPS for the detection of the chemical state of the component atomic species in solids is well established. The chemical-state information is easily obtained via the chemical shifts of core-level binding energies which are sensitive to the valence-electron distributions (e.g., the As 3d core-level binding energy in As_2O_3 is ~ 3.4 eV higher than it is in GaAs). Concurrently with monitoring the chemical state, XPS can be employed to monitor changes in E_F^i during interface formation. The ΔE_F^i can be measured because, for a semiconductor, changes in band bending rigidly shifts all core-level binding energies of a particular valence state with respect to the Fermi level (ΔE_F^i = final binding energy - initial binding energy). This aspect of XPS is more fully discussed by Grant et al.[6]

The samples were all bulk grown n-type (~ $5 \times 10^{16} cm^{-3}$) GaAs, which had been wafered and polished to give a (100) surface and 20 mil thickness.[7] All surfaces were given a sulfuric acid etch (4:1:1 - H_2SO_4, H_2O_2, H_2O) for approximately 1 minute, quenched and rinsed in H_2O, blown dry with N_2, mounted on molybdenum plates with indium, and inserted into the introduction chamber of the XPS system within several minutes. The XPS analysis of the relative peak intensities shows that this procedure yields an oxide surface of ~ 10Å thickness with a mixed composition of As_2O_3 and Ga_2O_3 and an associated large surface band bending of ~ 0.7 eV.[6,8,9] A second type of surface was prepared by heating the etched surface in a vacuum of ~ 5×10^{-9}torr for 5 minutes at ~ 450°C. This treatment results in the loss of As_2O_3 via the reaction

$$As_2O_3 + 2GaAs \rightarrow Ga_2O_3 + \frac{4}{x} As_x \uparrow . \qquad (1)$$

The surface is now covered with Ga_2O_3 and is associated with a low band bending; the difference in surface potential between these two types of surfaces can be as much as ~ 0.4 eV.[6, 8-10]

III RESULTS AND DISCUSSION

Characteristic spectra from our study of the interaction of metals with the native oxides of GaAs are given in Figs. 1-6. Fig. 1 illustrates several of the topics we wish to cover in this paper. This figure shows the various interfacial phenomenon which occur with increasing Al deposit on the Ga_2O_3 (low band-bending) surface of GaAs (100). We see from the Al 2p spectrum (Fig. 1b) that the initial Al reacts with the Ga_2O_3 via

$$2Al + Ga_2O_3 \rightarrow Al_2O_3 + 2Ga. \qquad (2)$$

After all the Ga_2O_3 is reacted, a metallic layer is formed (Fig. 1c-1d). Fig. 1c and 1d also show a shift of the metallic Al 2p core level to lower binding energy with increasing Al thickness. The As 3d core level exhibits no evidence of chemical change (Fig. 1a-d), however, between Fig. 1a and 1b there is evidence of a ΔE_F^i of several tenths of an eV, which indicates an increase of band bending with the first submonolayer deposit of metal. The Ga 3d spectrum of Fig. 1a shows the presence of two chemical forms of Ga, Ga_2O_3 (high binding-energy component) and GaAs (the more intense component). With the initial Al deposit, three observations can be made: 1) a gradual decrease of Ga_2O_3 with increasing Al (via Eqn. 2), 2) a potential shift (between 1a and 1b) which is the same as that seen with the As 3d core level, and 3) a new component to lower binding energy which is characteristic of Ga metal liberated by Eqn. 2. Finally, for the thickest coverages such that the GaAs interface cannot be sampled by XPS (see As 3d spectrum Fig. 1d), we observed out-diffused metallic Ga "floating" on the surface (see the Ga 3d spectrum in Fig. 1d). Figs. 2-6 illustrate these points in more detail for other metals.

Figs. 2 and 3 show spectra which illustrate the behavior of a reactive metal (Mg) compared to a non-reactive metal (Au) deposited on the Ga_2O_3 surface. In Fig. 2 the reduction of the Ga_2O_3 by Mg and the liberation of free Ga via the reaction

$$3Mg + Ga_2O_3 \rightarrow 3MgO + 2Ga \qquad (3)$$

can easily be seen by comparison of the two Ga 3d spectra of the upper panel. The initial small deposit of Mg has slightly reduced the high binding-energy shoulder due to Ga_2O_3 of Fig. 2a and a small low binding-energy shoulder indicative of free Ga is detectable. Further Mg deposit causes complete reduction of Ga_2O_3 and increased Ga. A concomitant potential shift of E_F^i which corresponds to higher band bending can be observed in both the As 3d and Ga 3d lines from GaAs in Fig. 2 (Ti and Cr depositions behave similarly to Mg). The potential shift is not due to chemical reactions with the native oxide as the potential shift is also present when there is no such chemical reaction, as for example, in the case of Au (Fig. 3) or Cu. On the Ga_2O_3 surface we have observed a significant increase of band bending even for the smallest submonolayer depositions of metals that we have studied, regardless of chemical reaction.

Figs. 4 and 5 (Cr and Ag deposition, respectively) show Ga 3d and As 3d spectra on the mixed As_2O_3-Ga_2O_3 surface where Cr is an example of a reactive metal and Ag of a non-reactive metal. Fig. 4 shows the decrease in both Ga_2O_3 and As_2O_3 with an initial deposit of Cr. Further deposit leads to complete reduction of the mixed native oxide and formation of a Cr oxide via

$$2M + N_2O_3 \rightarrow M_2O_3 + 2N \qquad (4)$$

where M = Cr and N is either Ga or As (Ti deposition acts similarly to Cr). In contrast, Al reacted sequentially, first with the As_2O_3, after the As_2O_3 was totally reduced, then it reacted to reduce the Ga_2O_3. Fig. 5 shows the result of the initial Ag deposit, there is no reduction of either oxide, only an attenuation of substrate signal with increasing Ag (Au and Cu behaved similarly to Ag on this surface). On the mixed oxide surface, no change of E_F^i independent of reactivity of deposited metal was observed.

The chemical reactivity results for both types of native oxide surface are summarized in Table I along with the effect of the deposited metal on the surface Fermi-level position. We note that the chemical reactivity of the metals for reducing the native oxide and producing a metal oxide can be simply and, in all the cases we have studied, reliably predicted by the change of free energy of formation ΔG.[11] We emphasize that these reactions occurred at room temperature.

Table II indicates our observations regarding outdiffusion of Ga or As from the native oxide covered samples; these observations are compared with results on atomically clean GaAs (100) surfaces.[2] This outdiffusion may be an indication of important processes occurring at interfaces, such as non-abruptness and the formation of defects.

An additional observation concerns a size effect on the metal core-level binding energies. As already seen in Fig. 1b for Al, after the reaction to form Al_2O_3 was complete the binding energy of the metallic Al 2p core level shifted to lower binding energy with deposition thickness (1c-1d). This effect is more easily observed for the metals which do not react and thus have no complications due to chemically shifted oxide components. Fig. 6 shows the evolution in shape and binding energy of the Cu $2p_{3/2}$, Ag $3d_{3/2}$, $_{5/2}$, and Au $4f_{5/2}$, $_{7/2}$ core levels with increasing metal coverages. We see dramatic shifts in core-level binding energies of the metals (Cu, Ag, Au, Al, Ti, Cr) to lower binding energy with increasing coverage until the bulk binding energy is attained.[12] The smallest deposits also show broadened linewidths (by almost 50% in some cases) in comparison to those of the thickest bulk-like films. We also have observed similar effects for Au and Pd deposited on clean n-type GaAs (100) surfaces.[13] For example, the Au $4f_{7/2}$ core level shifted from 85.02 eV for initial small sub-monolayer coverages to the bulk value of 84.00 eV[14] for thick bulk-like films. In the case of the Pd $3d_{5/2}$ level, a shift of ~ 1.45 eV has been observed.[12] S.T. Lee and co-workers have recently systematically studied the binding energy for vacuum deposited Au clusters on amorphous carbon, SiO_2, and Al_2O_3; they find a range of binding energies for the Au $4f_{7/2}$ from 85.0 eV for coverages of ~ 10^{13} atoms/cm^2 to 84.0 eV for ~ 10^{16} atom/cm^2 coverages.[15] Similar shifts have been observed for Ni, Cu, Ag, and Au ions implanted into inert matrices.[16] Size-effect shifts are due to a combination of electronic-structure changes[17] and extra-atomic relaxation[18] and are largely independent of substrate. The broadening at low coverages may be due to reduced electronic screening in the final state as proposed by Ascarelli et al[19] or a large range of characteristic sizes.

IV SUMMARY AND CONCLUSIONS

We have used XPS to study metal-contact interfacial chemical reactivity on two types of thin native oxide covered GaAs (100) surfaces. The contact metals examined were Al, Ti, Cr, Mg, Cu, Ag and Au. Both the interfacial chemistry and Fermi-level position were monitored during the contact formation and a number of observations were made:

1) For the metals Cu, Ag, and Au, $\Delta G > 0$ for the reduction of As_2O_3 and Ga_2O_3. These metals did not exhibit reduction of the native oxides.

2) For the metals Mg, Al, Ti, and Cr, $\Delta G < 0$ for the reduction of As_2O_3 and Ga_2O_3. Sufficient deposit of these metals at room temperature led to complete reduction of the native oxides and formation of a new metal oxide at the interface.

3) For the Ga_2O_3 + As_2O_3 (high band bending) surface, deposition of either reactive or non-reactive metal did not change E_F^i.

4) For the Ga_2O_3 (low band bending) surface, deposition of the smallest amounts of metal, either reactive or non-reactive, shifted E_F^i by several tenths of an eV which caused E_F^i for both types of native oxide surfaces to have the same Fermi-level position.

5) Outdiffusion of Ga and As from the native oxide covered surfaces was similar to that from atomically clean surfaces.

6) Metal core-level binding energies and the corresponding linewidths decrease with increasing metal coverages.

Our results are relevant to modeling of Schottky-barrier contacts in devices. For device contacts it is common to assume the presence of a distinct thin insulating native oxide film which acts to isolate the semiconductor from the metal at the metal-semiconductor interface.[5] We have shown that many metals chemically react to eliminate the initial native oxide film on GaAs to produce an interface region which consists of a non-insulating mixture of metal and metal oxide. Even when no gross chemical effect is observed, changes in band bending are still observed for the inert metals on Ga_2O_3 surfaces. Thus Schottky-barrier contacts to GaAs should not be modeled by assuming an insulating oxide interfacial layer. These observations support defect models of Fermi-level pinning of Schottky barriers on GaAs.[6,20] Since GaAs is a prototypical compound semiconductor, analogous interface phenomena can be expected for other compound semiconductors.

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TABLE I. Summary of interfacial chemistry and ΔE_F^i for several metals deposited on native oxide surfaces of GaAs.

Metal	$As_2O_3 + Ga_2O_3$ Surface		Ga_2O_3 Surface		Oxide Product	ΔG (K cal)[4-6]	
	Reacted	ΔE_F^i[7]	Reacted	ΔE_F^i[7]		Ga_2O_3 Reaction	As_2O_3 Reaction
Au	No	0.0	No	-0.2	Au_2O_3	+278	+177
Ag	No	0.0	[1]	[1]	AgO	+249	+148
Cu	No	0.0	No	-0.2	CuO	+149	+ 48
Al	Yes[2]	0.0	Yes	-0.2	Al_2O_3	-138	-239
Mg	[1]	[1]	Yes	-0.2	MgO	-169	-270
Ti	Yes[3]	0.0	Yes	-0.2	Ti_2O_3	-107	-208
Cr	Yes[3]	0.0	Yes	-0.2	Cr_2O_3	- 11	-112

[1] This surface was not studied.

[2] The metal-oxide reactions occurred sequentially, with As_2O_3 reacting first.

[3] Both oxides, Ga_2O_3 and As_2O_3 reacted simultaneously with the deposited metal.

[4] ΔG for the reaction $2M + 2N_2O_3 \rightarrow M_2O_3 + 2N$

(M = Au, Al, Ti, or Cr; N = Ga or As) or

$3M + N_2O_3 \rightarrow 3MO + 2N$ (M = Ag, Cu, or Mg; N = Ga or As).

It can be seen that the difference in ΔG for the As_2O_3 and Ga_2O_3 reactions is the difference in G for Ga_2O_3 and As_2O_3 (-101 K cal/mole).

[5] The free energies used to calculate the ΔG's were obtained from Handbook of Chemistry and Physics, 58th ed. R.C. Weast, Ed (CRC Press, Cleveland, 1977) and Lange's Handbook of Chemistry ed J.A. Dean, (McGraw-Hill Book Co., N.Y., 1979).

[6] Other possible oxide products were also considered (namely Ag_2O, Ag_2O_3, Cu_2O, TiO_2, TiO, Ti_3O_5, and Ti_4O_7). For a particular metal the sign of ΔG did not change for these alternative oxide products.

[7] ΔE_F^i was measured by the change of the As 3d binding energy upon the addition of ~ 1 monolayer metal. In the case of Cr, the Ga 3d level was used because of overlap between Cr 3p and As 3d levels.

TABLE II Summary of outdiffusion characteristics from GaAs (100) interfaces.[1]

METAL	As_2O_3 + Ga_2O_3 SURFACE	Ga_2O_3 SURFACE	CLEAN SURFACE (Ref. 2)
Au	As	As	Ga,[3] As
Ag	As	[2]	None
Cu	None	As[3]	[2]
Al	Ga	Ga	Ga
Ti	None	None	None
Cr	No Ga[4]	No Ga[4]	No Ga[4]

[1] These results are for coverages of ~ 50Å of metal.

[2] This surface was not studied.

[3] Thicker metal deposits (> 100Å) showed no surface concentration of this element.

[4] As outdiffusion was not investigated as the Cr 3p core level overlapped the As 3d core level.

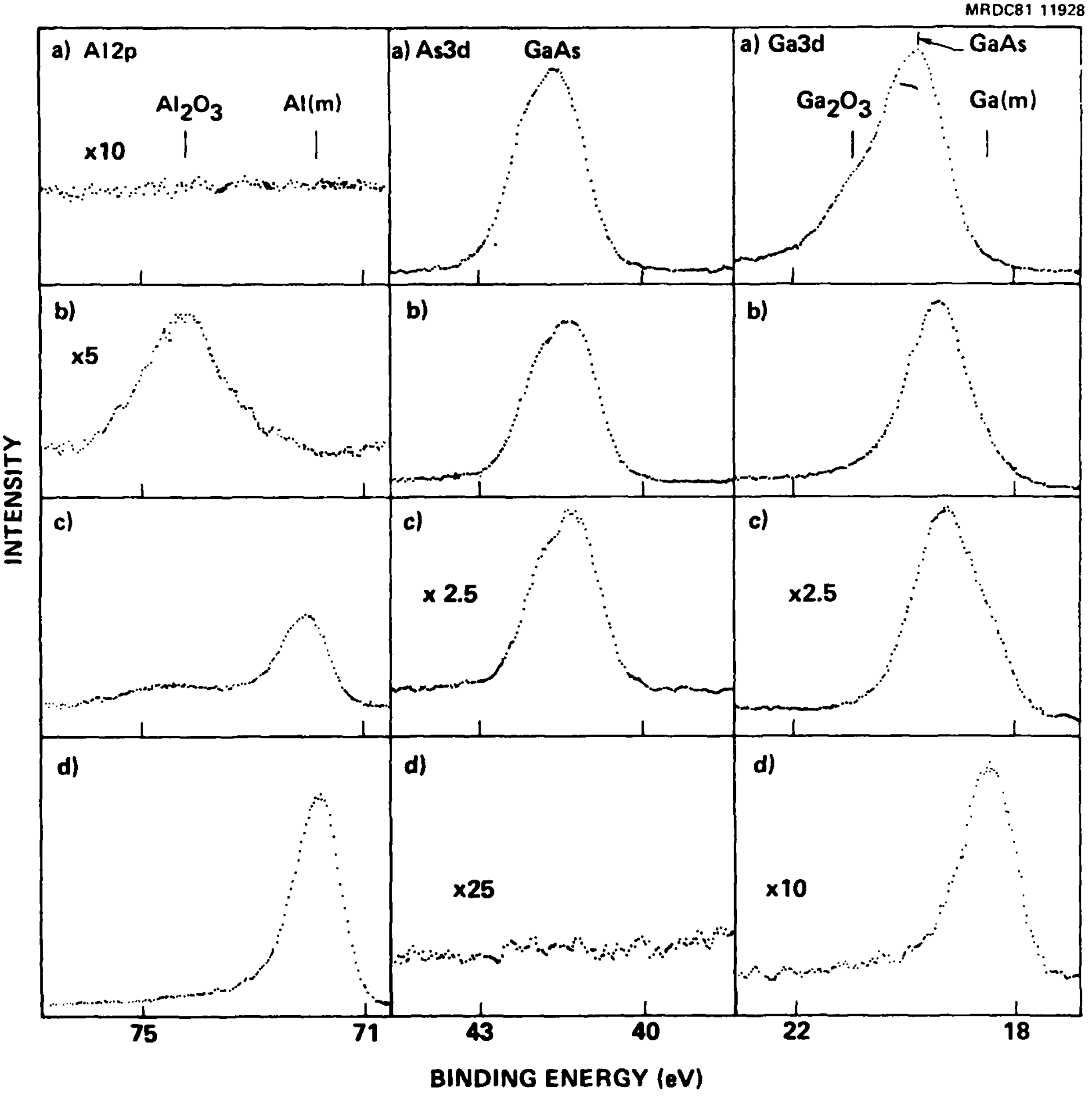

Fig. 1 XPS spectra of the Al 2p (left), As 3d (center), and Ga 3d (right) core levels for an increasing amount of an Al deposit (a-d) on a Ga_2O_3 covered GaAs surface. Al film thicknesses determined by assuming uniform coverages are 0, ~3, ~16, and >100Å for a-d, respectively.

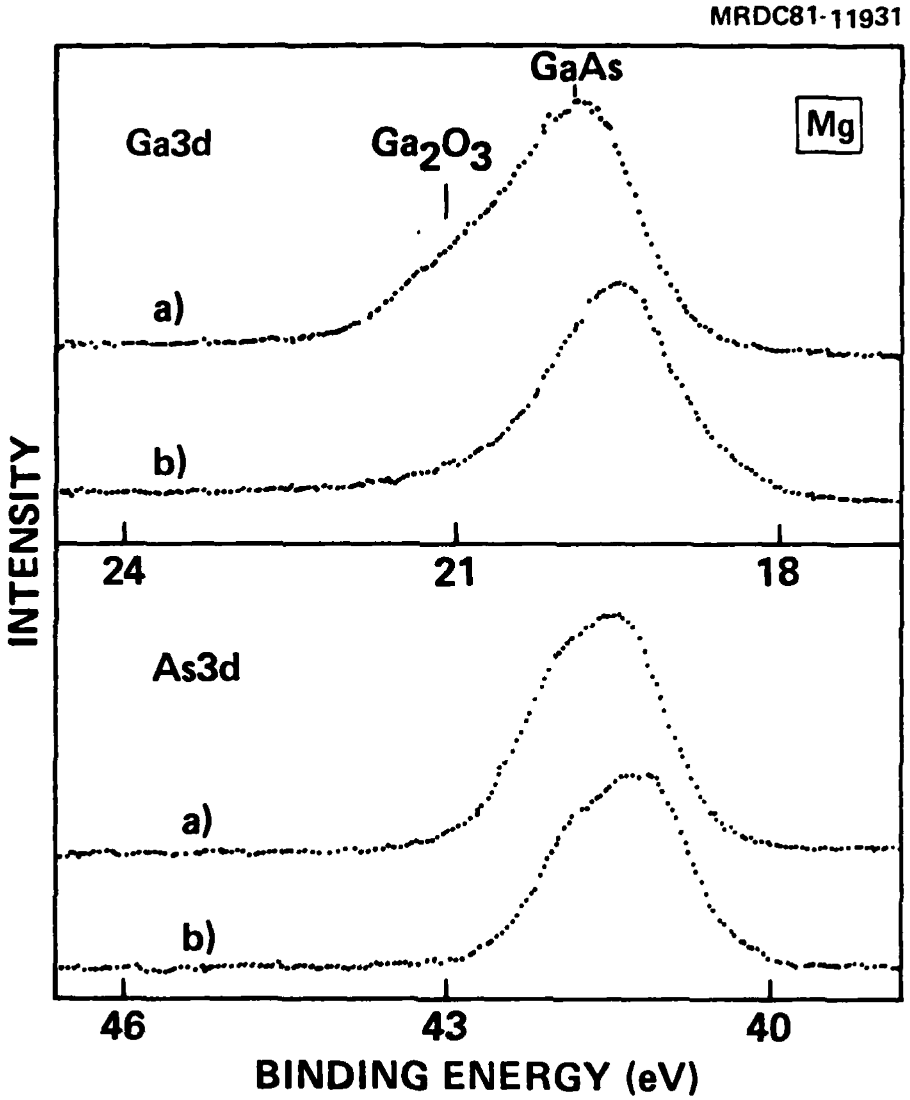

Fig. 2 XPS spectra from a Ga_2O_3 covered GaAs surface of Ga 3d (upper panel) and As 3d (lower panel) core levels;
a) before a submonolayer deposit of Mg.
b) after a submonolayer deposit of Mg.

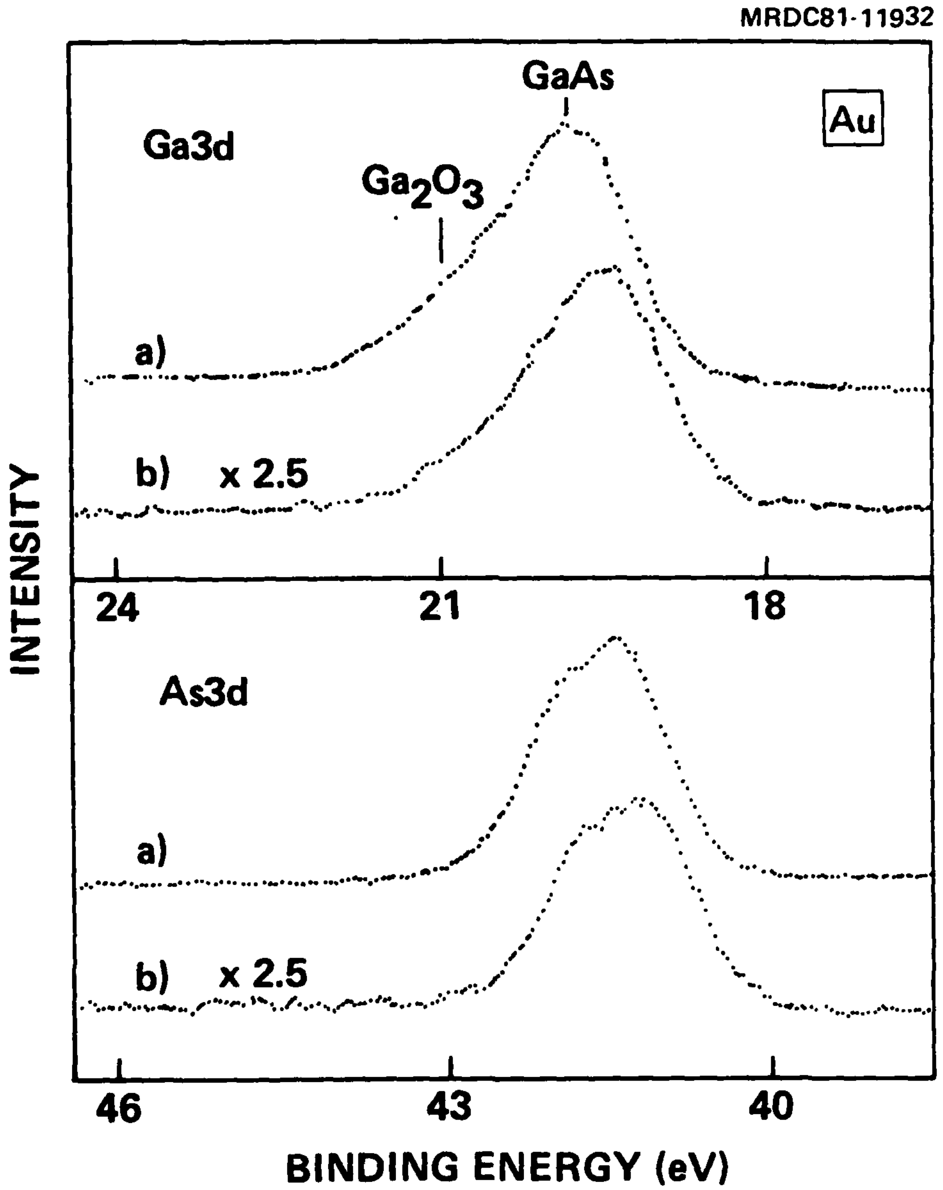

Fig. 3 XPS spectra from a Ga_2O_3 covered GaAs surface of Ga 3d (upper panel) and As 3d (lower panel) core levels;
a) before a Au deposit.
b) after a Au deposit.

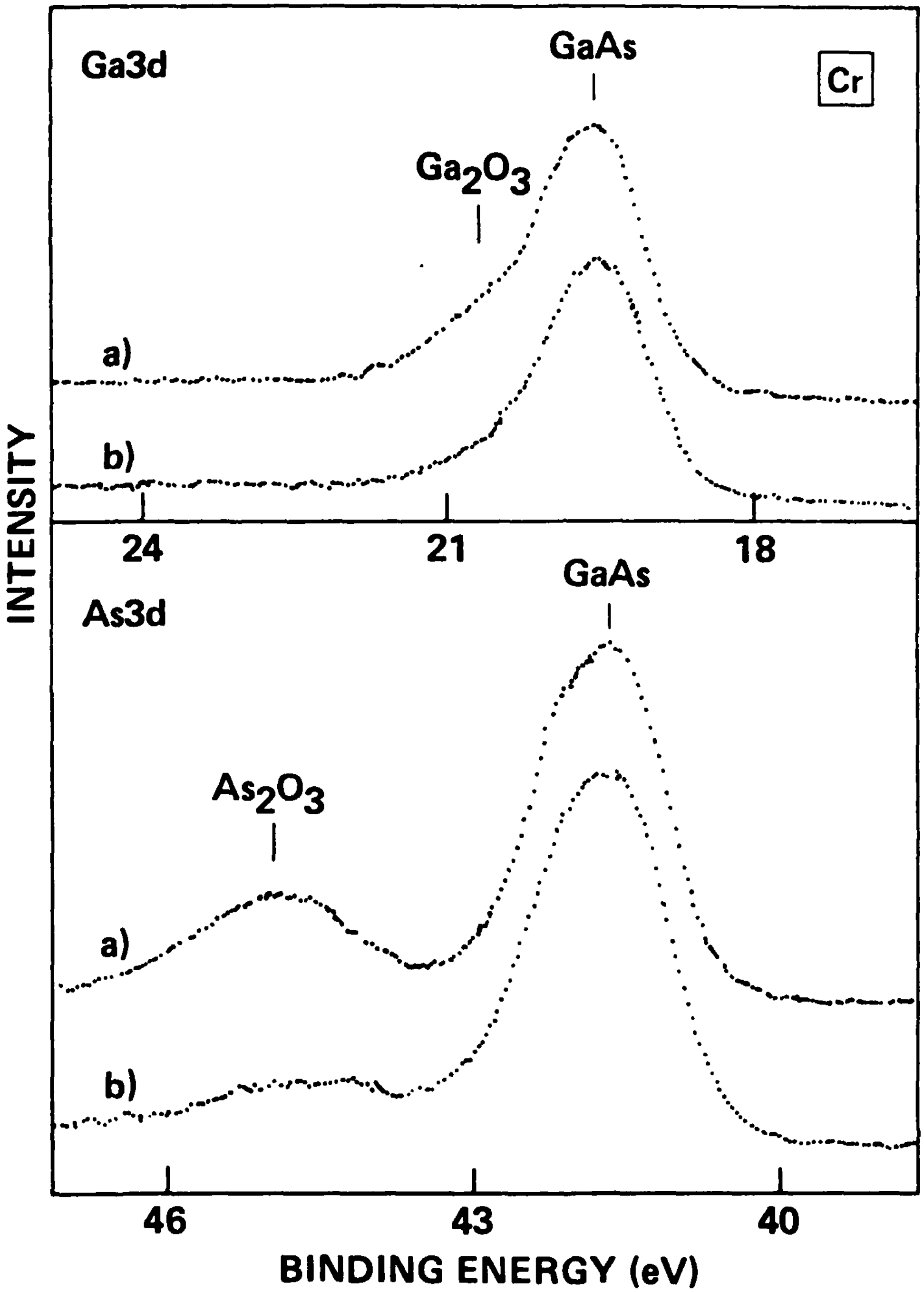

Fig. 4 XPS spectra from a As_2O_3-Ga_2O_3 covered GaAs surface of Ga 3d (upper panel) and As 3d (lower panel) core levels;
a) before a submonolayer Cr deposit.
b) after a submonolayer Cr deposit.

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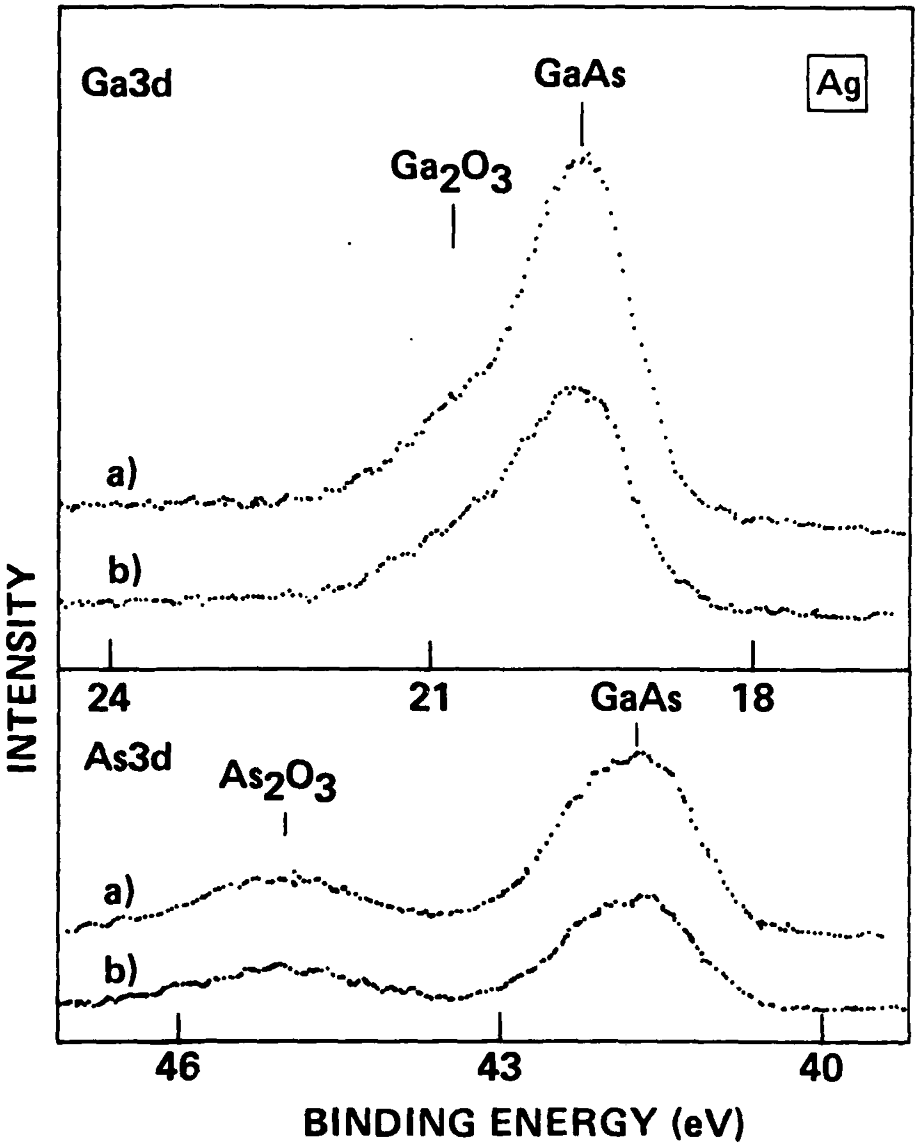

Fig. 5 XPS spectra from a As_2O_3-Ga_2O_3 covered GaAs surface of Ga 3d (upper panel) and As 3d (lower panel) core levels;

a) before initial Ag deposit.

b) after initial Ag deposit.

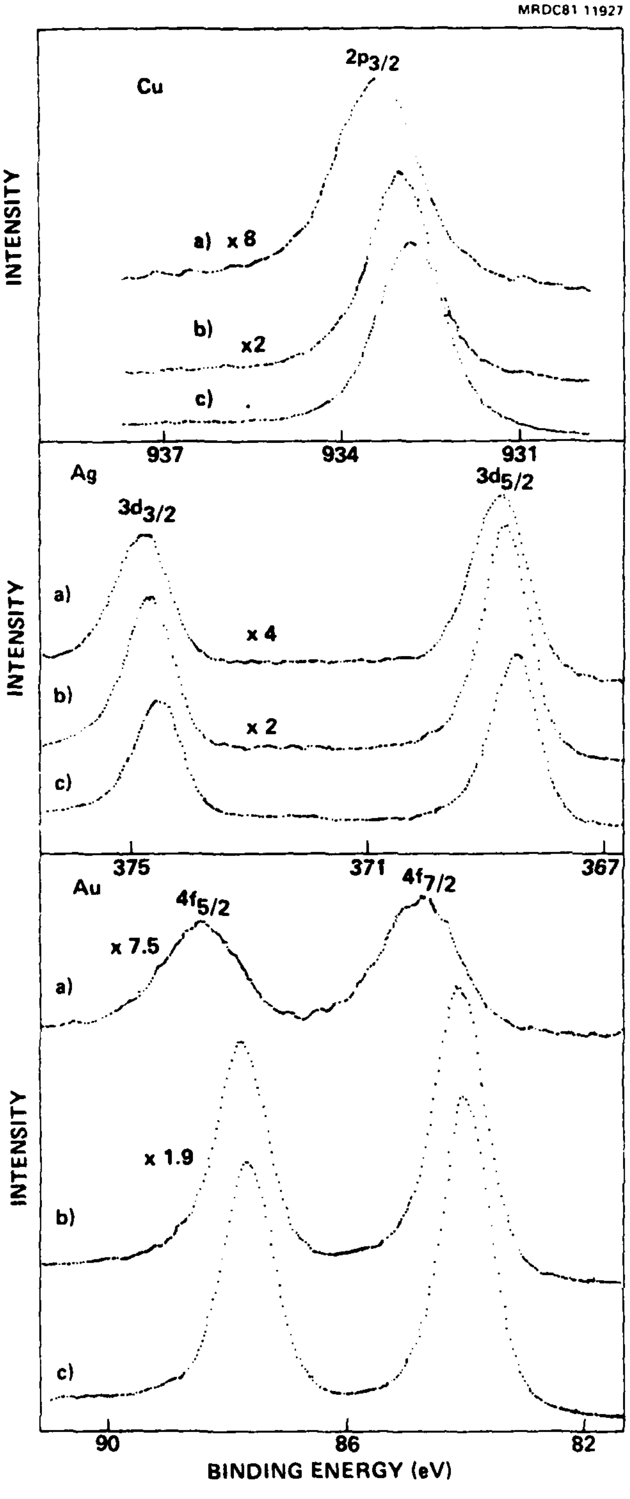

Fig. 6 XPS spectra of the Cu $2p_{3/2}$ (upper panel), Ag $3d_{3/2}$, $3d_{5/2}$ (middle panel), and Au $4f_{5/2}$, $4f_{7/2}$ (lower panel) core levels for increasing metal thickness (a-c). The film thickness determined by assuming uniform coverages for Cu are ~2, ~16, and >100Å; for Ag, ~7, ~19, and >100Å; and for Au, ~2, ~12, and >100Å.