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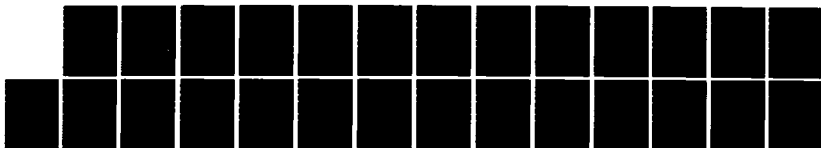   11 MAR 85 TR-0084A(5945-06)-2 SD-TR-85-09
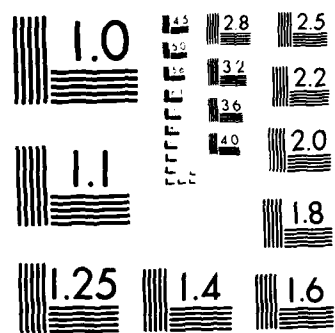UNCLASSIFIED   F04701-83-C-0084   F/G 7/5   NL

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The Photochemical Oxidation of GaAs

AD-A153 689

P. A. BERTRAND
Chemistry and Physics Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, CA 90245

11 March 1985

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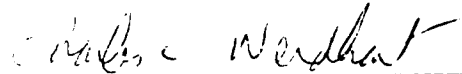
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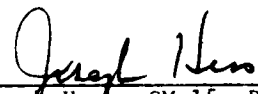
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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Charles Neidhart, Lt, USAF
Project Officer

Joseph Hess, GM-15, Director, West Coast
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The vacuum ultraviolet photochemical oxidation of GaAs by N_2O (wavelengths of 2537 Å and 1849 Å) was studied by X-ray photoelectron spectroscopy. We believe the model most consistent with our data involves (1) adsorption of molecular N_2O, (2) dissociation of the N_2O on the surface, and (3) oxidation of the surface by the adsorbed O atoms. The temperature dependence of the overall reaction on the stoichiometric surface is dominated by the temperature dependence of adsorption of N_2O. An As-rich surface oxidizes more

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slowly, and the reaction saturates; in this case the rate-limiting step and the cause of saturation is the oxidation of the surface by adsorbed O atoms. The As-covered surface does not present the proper sites (As atoms surrounded by Ga atoms) for fast, continued oxidation of GaAs.

PREFACE

The author thanks Mr. J. L. Childs for performing the XPS analyses.

1

CONTENTS

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FIGURES

TABLE

I. INTRODUCTION

Thermal, plasma, and anodic oxides of gallium arsenide (GaAs) have been heavily explored as insulating and passivating layers for this important semiconductor, with relatively little success. High trap density at the interface leads to poor electrical characteristics.[1,2,3] Certain nonnative insulators, such as silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) deposited by various methods, also have high interface-state densities. In this case the interface states seem to be related to the presence of an interfacial layer of oxidized GaAs, either native oxides present before deposition, or oxides created during the deposition process.[4-7]

For example, in the vacuum ultraviolet irradiation-(VUV) assisted chemical vapor deposition of SiO_2 on GaAs, the "Photox" process developed by Hughes Aircraft Company, a GaAs photochemical oxide is found at the GaAs-SiO_2 interface even when no initial GaAs native oxide is present before deposition.[8] Knowledge of the mechanism of photochemical oxidation of GaAs is important for reducing or eliminating this layer, and for enhancing the usefulness of the "Photox" process in GaAs passivation. In the experiments reported here, the kinetics of the VUV photochemical oxidation of GaAs by nitrous oxide (N_2O) have been observed by X-ray photoelectron spectroscopy (XPS). A probable mechanism for the reaction is suggested in which molecular N_2O adsorbs on clean, stoichiometric GaAs prior to its dissociation. This model is suggested by the temperature dependence of the reaction: The reaction is less complete as the substrate temperature is raised.

II. EXPERIMENTAL PROCEDURE

The GaAs coupons were polished <100> faces of p-type material, zinc (Zn)-doped to a carrier concentration of 5×10^{18} cm^{-3}. To produce the native oxides, coupons were cleaned with 2% bromine (Br) in methanol for 10 sec, rinsed in methanol, then placed in air at room temperature for several months.

For the photochemical oxidation experiments, the photochemical reactor was enclosed in a glove bag filled with flowing N_2. The GaAs coupons were etched in the glove bag in either 2% Br_2 in methanol for 10 sec (to produce a stoichiometric surface), or in concentrated HCl for 15 min (to produce an As-rich surface),[9] rinsed in ethanol, and loaded into the reactor chamber. Since this procedure was carried out in the glove bag, the cleaned samples were never exposed to air. To the sensitivity of our XPS measurements, no oxidized Ga or As is present on the surface. In the reactor the substrate was placed on a heated copper block where it would be illuminated from above by a low-pressure mercury (Hg) lamp. The photon flux of the lamp is about 1×10^{15} photons/cm^2 sec, equally split between the 2537-Å and 1849-Å lines. Both lines have sufficient energy for e^-h^+ pair production in GaAs, and the 1849-Å line can dissociate N_2O to produce $N_2(^1\Sigma)$ and $O(^3P, ^1D)$. N_2O was introduced into the evacuated chamber at a flow rate of 60 standard cubic centimeters per min (SCCM), and the pumping speed was adjusted to establish a pressure of 6 Torr in the chamber. These conditions are similar to those used in the photochemical deposition of SiO_2 on GaAs. The chamber has been used with a Hg sensitizer, but Hg was not intentionally added to the N_2O in these experiments. After the flow of N_2O was established, the lamp was turned on for an arbitrarily chosen period of time. As a result of the geometry of the reactor, the Hg lamp illuminates both the gas and the substrate surface.

The coupons were removed from the reactor chamber, again in an N_2 environment, and placed in a desiccator. The desiccator was transferred to an N_2-filled glove bag attached to a modified GCA-McPherson ESCA-36 XPS spectrometer that had a spherical-sector analyzer and a position-sensitive detector.[10] The

coupons were loaded into the spectrometer, also in an N_2 atmosphere, and the spectrometer was evacuated to 1×10^{-7} Torr. The entire procedure, from the unloading of the reactor chamber to the XPS analysis, generally took less than 30 min.

III. RESULTS

A. GaAs NATIVE OXIDES

The compositions of GaAs native oxides have been measured many times.[9,11] The results of this study are in agreement with the literature: the oxide is 80% gallium trioxide (Ga_2O_3), with 20% arsenic trioxide (As_2O_3) and occasionally a small amount of arsenic pentoxide (As_2O_5), depending on preparation conditions (Fig. 1). The oxidized As peak, separated by 3.8 to 4.2 eV from the more prominent peak as a result of GaAs in this study, is assigned to As_2O_3 by comparison to binding energy values for bulk As_2O_3.[12] Some workers have found smaller values for this separation for lightly oxidized GaAs,[11] values that could be due to either oxygen deficiency of the oxides or band-bending effects. There is elemental As present in the native oxide. The elemental As signal is unresolvable from the GaAs As signal in these experiments because of the signals' ~ 0.5-eV separation. However, the full width at half maximum (FWHM) of the As XPS peak in a native-oxide-covered surface is 1.9 eV, compared to 1.4 eV for a clean surface; this clearly indicates the presence of unresolved structure.

An additional form of oxidized As is present in the native oxide after exposure to VUV radiation (Fig. 2). It is not as highly oxidized as As_2O_3, as shown by its XPS peak position intermediate between those of GaAs and As_2O_3. The As(metal)-As_2O_3 separation of approximately 3.6 eV for a change of 3 in As oxidation state[12] implies that the 2.8-eV separation between GaAs and partially oxidized As corresponds to a formal As oxidation state of about 2. This should not be taken as an indication of the presence of an actual compound "AsO." The +2 oxidation state of As is not stable. Instead, this separation means that one of the As-O bonds has been broken during VUV irradiation, and the oxide is oxygen deficient. There is also a pronounced shoulder on the most intense As peak; we attribute this to elemental As.
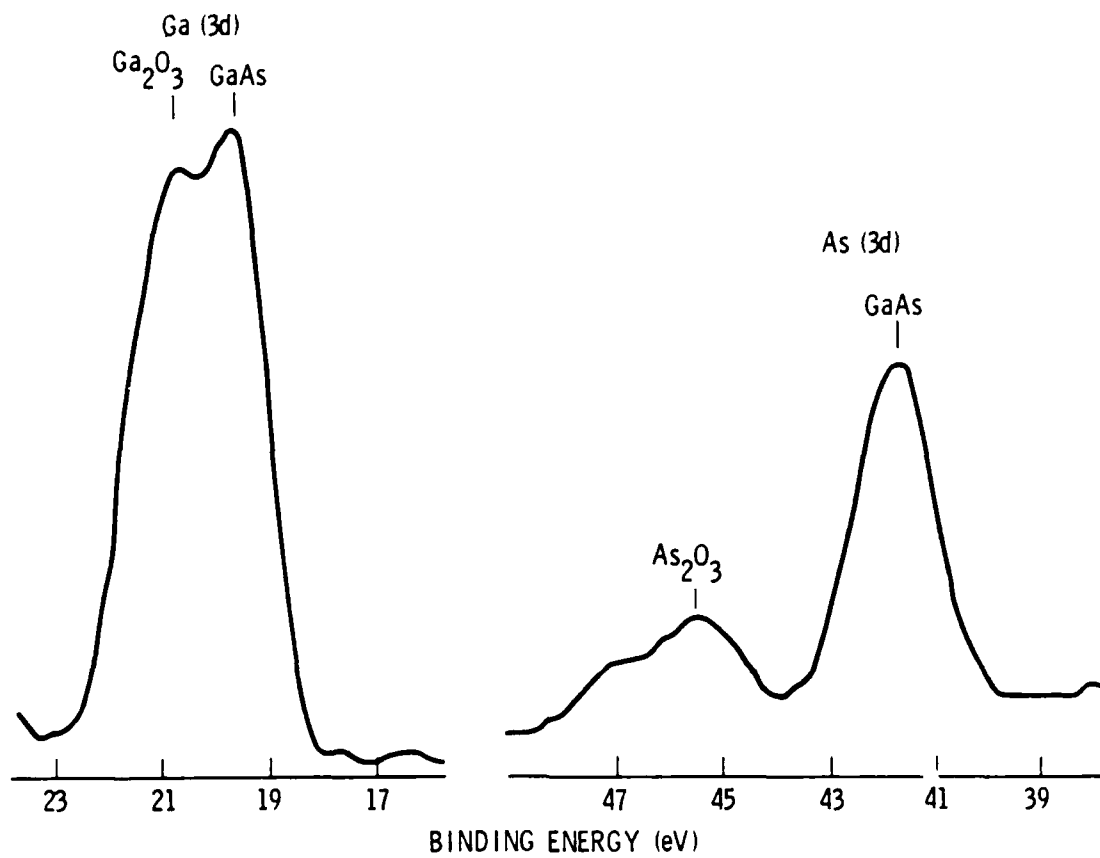
Fig. 1. XPS Spectrum of Native-Oxide-Covered GaAs

LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, environmental hazards, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, laser photoelectronics, solar cell physics, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and environmental chemistry.

Electronics Research Laboratory: Microelectronics, GaAs low noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics, communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging, millimeter wave, microwave technology, and RF systems research.

Information Sciences Research Office: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence and microelectronics applications.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves; atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation; solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems; space instrumentation.

REFERENCES

1. J. Lagowski, T. E. Kazior, W. Wolukiewicz, H. C. Gatos, and J. Siejka, J. Vac. Sci. Technol. 19, 519 (1981).

2. H. Hasegawa, T. Sawada, and T. Sakai, Surface Sci. 86, 819 (1979).

3. R. P. H. Chang, J. J. Coleman, A. J. Polak, L. C. Feldman, and C. C. Chang, Appl. Phys. Lett. 34, 237 (1979).

4. J. F. Wager and C. W. Wilmsen, J. Appl. Phys. 53, 5789 (1982).

5. J. D. Langan and C. R. Viswanathan, J. Vac. Sci. Technol. 16, 1474 (1979).

6. R. P. Vasquez and F. J. Grunthaner, J. Vac. Sci. Technol. 19, 431 (1981).

7. M. D. Clark and C. L. Anderson, J. Vac. Sci. Technol. 21, 453 (1982).

8. P. A. Bertrand, to be published.

9. P. A. Bertrand, J. Vac. Sci. Technol. 18, 28 (1981).

10. P. A. Bertrand, L. E. Tribble, W. J. Kalinowski, and L. U. Tolentino, Rev. Sci. Instrum. 54, 387 (1983).

11. H. Iwasaki, Y. Mizokawa, R. Nishitani, and S. Nakamura, Jpn. J. Appl. Phys. 17, 315 (1978); 17, 1925 (1978); 18, 1525 (1979).

12. C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, Eden Prairie, Minn. 1979; Y. Mizokawa, H. Iwasaki, R. Nishitani, and S. Nakamura, J. Electron Spectrosc. Relat. Phenom. 14, 129 (1978); L. D. Hulett and T. A. Carlson, App. Spec. 25, 33 (1971); and W. J. Stec, W. E. Morgan, R. G. Albridge, and J. R. Van Wazer, Inorg. Chem. 11, 219 (1972).

13. W. Ranke and K. Jacobi, Surface Sci. 81, 504 (1979).

14. P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. B, 18, 2792 (1978).

15. V. I. Nefedov, Surf. Interf. Anal. 3, 72 (1981).

16. S. P. Kowlaczyk, D. L. Miller, J. R. Waldrop, P. G. Newman, and R. W. Grant, J. Vac. Sci. Technol. 19, 255 (1981).

17. J. M. Woodall, P. Oelhafen, T. N. Jackson, J. L. Freeouf, and G. D. Pettit, J. Vac. Sci. Technol. B 1, 795 (1983).

V. CONCLUSIONS

The photochemical oxidation of clean, stoichiometric GaAs probably proceeds by (1) adsorption of N_2O, (2) dissociation of the N_2O on the VUV-excited surface, and (3) oxidation of the surface by the adsorbed O atoms. The temperature dependence of the overall reaction is dominated by the temperature dependence of adsorption of N_2O. An As-rich surface oxidizes more slowly and the oxidation process saturates at 30 min. In this case, either gas-phase or surface dissociation of N_2O may occur; the rate-limiting step and cause of saturation is the oxidation of the surface by adsorbed O atoms. The As-covered surface does not present the proper sites (As atoms surrounded by Ga atoms) for fast, continued oxidation of GaAs.

and their transport to the surface is less probable than the adsorption and decomposition of N_2O for the previously considered case of a clean surface, which would account for the overall slowing of the reaction. However, it would not account for the saturation of oxidation after 30 min.

The final step of the photochemical oxidation reaction, the oxidation of GaAs by adsorbed O atoms, must be rate-limiting in this case. This step should be very geometry- and composition-dependent. For example, room-temperature adsorption of O_2 has been found to produce two adsorbed oxygen-containing species on GaAs surfaces of various geometries and ccmpositions: an adsorbed molecular form, bound predominantly to As, and an oxidic form, bound predominantly to Ga.[13] Electron irradiation of the adsorbed molecular form converted it to the oxidic form. The mechanism of this reaction requires molecular adsorption sites in which the As atoms are surrounded by Ga atoms to enable subsequent reaction. An As-rich surface will have fewer such sites and should show reduced reaction with adsorbed O atoms. That is, the surface concentration of O in appropriate sites for reaction is rate-limiting.

The limited oxidation of an As-rich surface has been used in the protection of GaAs from atmospheric effects, by creation of an As-rich layer on the surface by molecular beam epitaxy (MBE)[16] or electrochemical methods.[17] Layers of As 50 to 1000 Å thick were found to oxidize only at their surfaces in air at room temperature and to prevent oxidation of the substrate GaAs. In the present experiments the thickness of the As layer created by the HCl etch could not be measured, since its XPS signal was unresolvable from that of the substrate. It is probably much thinner than the MBE and electrochemical films, and may not be continuous. However, even in this case the oxidation rate is decreased when the surface layers are As-rich.

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$$N_2O + GaAs \; \overset{\leftarrow}{\rightarrow} \; N_2O \cdot GaAs \qquad\qquad (1)$$

$$N_2O \cdot GaAs + h\nu \rightarrow (N_2O \cdot GaAs)^* \qquad\qquad (2)$$

$$(N_2O \cdot GaAs)^* \rightarrow O \cdot GaAs + N_2(g) \qquad\qquad (3)$$

$$O \cdot GaAs \rightarrow oxides \qquad\qquad (4)$$
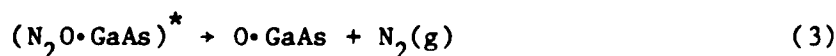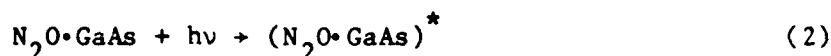
where $N_2O \cdot GaAs$ and $O \cdot GaAs$ represent adsorbed N_2O and O atoms, respectively.

Another possible explanation of the decreases in F with increasing temperature is that unoxidized Ga and/or As diffuses into the oxide layer, thus increasing the denominator of the fraction F. However, solid-state diffusion processes usually have activation energies of tens of kcal, many times greater than that observed here.

The thickness of the oxide layers can be calculated approximately[15] with two assumptions. First, the escape depth λ of the photoelectrons was taken to be 15 Å for both Ga and As. Second, the oxide layer is assumed to be a homogeneous film with an abrupt interface on top of the GaAs substrate. The thickness of the native oxide is calculated to be 5 Å, while the thickest photochemical oxide on a Br_2-etched surface in these experiments is ~ 8 Å thick.

The surface stoichiometry has a profound effect on the reaction. The As-covered surface does not oxidize as readily as the stoichiometric surface: the fraction of oxidation is less and saturates at ~ 30 min. The approximate thickness of the oxide layer at this point is only 6 Å. The reaction has no discernible temperature dependence, of reaction, as a temperature-dependence plot shows (Fig. 6b). The change in surface stoichiometry may eliminate or reduce the physisorption sites for N_2O, requiring gas-phase dissociation of N_2O and transport of O to the surface. The gas-phase production of O atoms
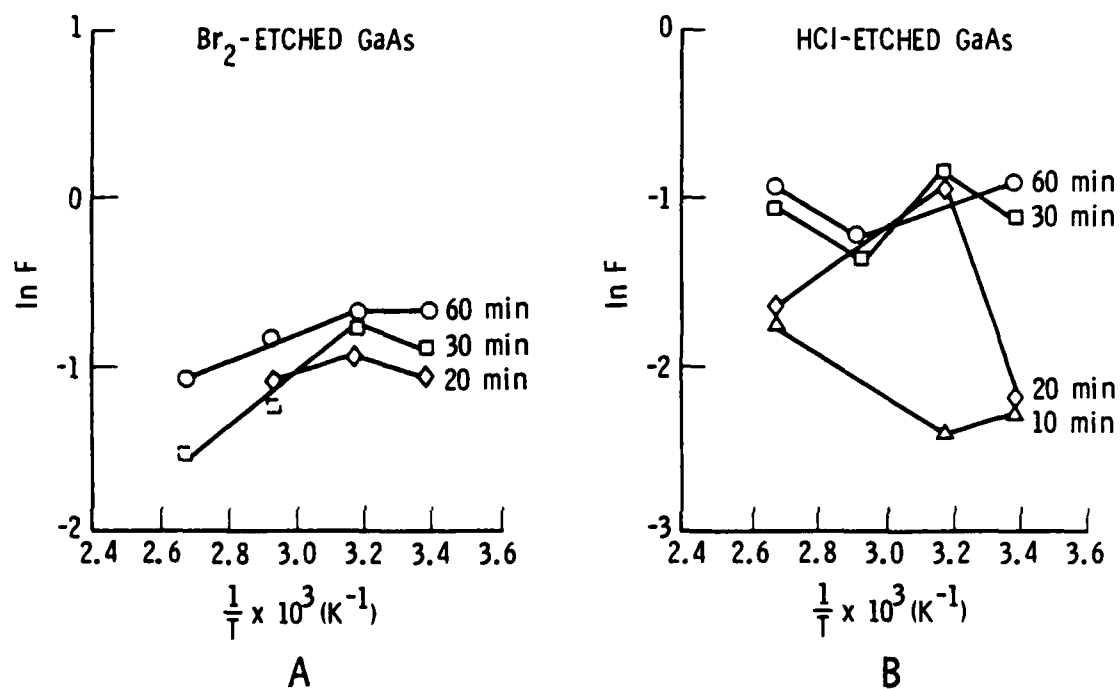
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Fig. 6. Temperature Dependence of Photochemical Oxidation of GaAs.
(a) Br_2-etched surface. (b) HCl-etched surface.

IV. DISCUSSION

The observed temperature dependence of the photochemical oxidation (a decrease in the fraction of oxidation as temperature increases) of clean, stoichiometric GaAs by N_2O and VUV irradiation indicates that a gas adsorption step could be present in the reaction mechanism. The photodissociation of N_2O, whether in the gas phase or on the surface, is temperature independent, and the rate of oxidation of GaAs by adsorbed oxygen (O) atoms produced by the dissociation of N_2O should increase slightly with increasing temperature. An adsorption step will have its equilibrium shifted towards reactants (unadsorbed gas and the clean surface) by increased temperature. Then, since there is less gas adsorbed at higher temperature, the overall reaction will be slower. Another possibility would be diffusion of Ga or As into the oxide layer (this will be discussed later).

Given the assumption that a gas adsorption step is responsible for the temperature dependence, the adsorption energy Q can be calculated from the temperature dependence of adsorption through the equation $F \propto e^{Q/RT}$ (Fig. 6a), and is 2 ± 1 kcal/mole, a value typical of physical adsorption. Oxygen atoms created on the surface by electron irradiation are known to adsorb strongly to GaAs,[13] and the "excited oxygen" used in many oxidation studies to produce fast, heavy oxidation may also be atomic oxygen.[14] The adsorbing species in the experiments described here is only physisorbed, and thus is probably N_2O. The O atoms produced in the gas phase may be quenched too quickly in our experimental conditions to live long enough to react with the surface, although this seems unlikely. Another possibility is that the oxygen atoms produced in these experiments are not as reactive as those produced by electron irradiation or by interaction with an ion-gauge filament; indeed, the states of these latter two forms of "excited oxygen" have not been characterized. Therefore, the photodissociation of N_2O occurs while it is adsorbed on the surface, either directly or through mediation by the excited surface. The adsorbed O atoms produced by this step then react with the GaAs surface to produce Ga and As oxides. The overall reaction can be pictured as

have F ≈ 0.4. On the Br_2-etched surface for reaction temperatures of 70 and 100°C, the reaction does not appear to be nearing completion; F is still increasing at 60 min. Reactions were not run for longer periods of time, so the value of F at completion is not known. For lower temperatures the reaction appears to slow after 30 min. Except for the 23°C case, the fraction of oxidation decreases with increasing temperature. On the HCl-etched surface the reaction is clearly slowing after 30 min; it is probably complete at 60 min for all temperatures studied, and has no obvious temperature dependence.
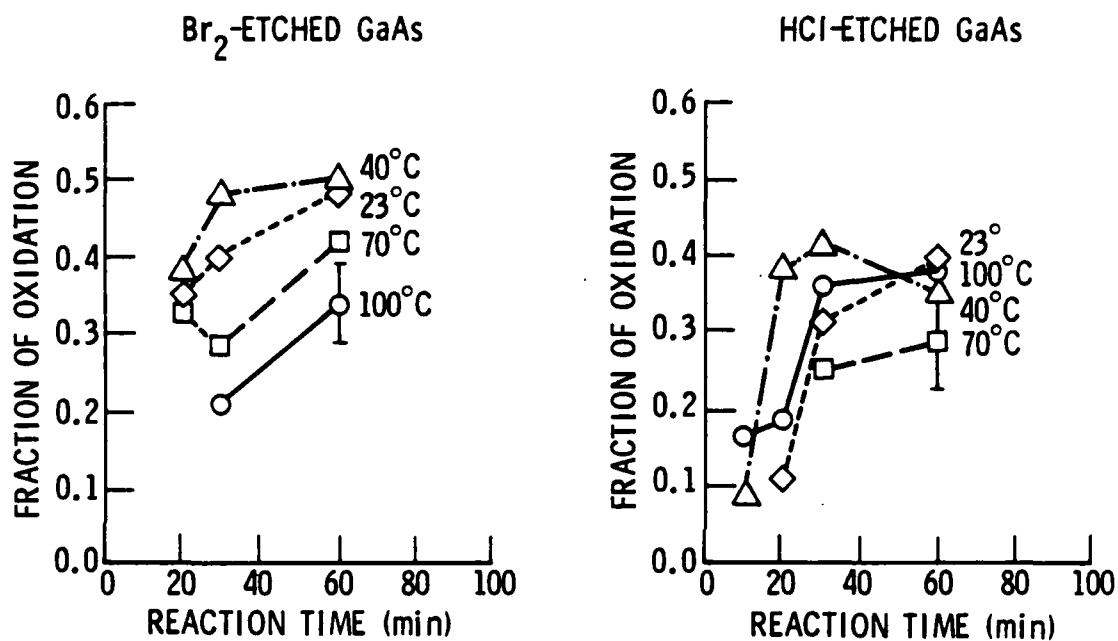
Br$_2$-ETCHED GaAs

HCl-ETCHED GaAs

Fig. 5. Progress of Photochemical Oxidation of GaAs, Illustrated
by the Fraction of Oxidation as a Function of Time.
Error bars represent the reproducibility expected in F as
a result of the 15% reproducibility of XPS intensity measure-
ments. (a) Br$_2$-etched surface. (b) HCl-etched surface.

Ga (3d)   As (3d)

GaAs   GaAs

                                          "AsO"

                                    As₂O₃

23   21   19   17   47   45   43   41   39

                    BINDING ENERGY (eV)
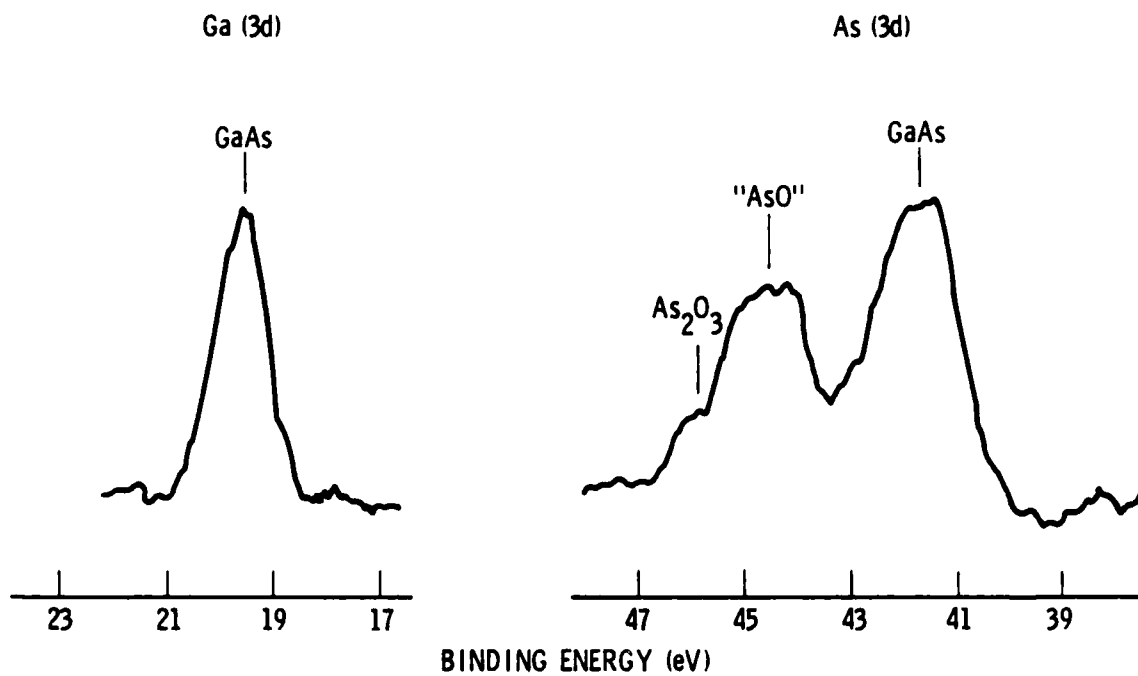
Fig. 4.   XPS Spectrum of HCl-Etched GaAs after Exposure to N₂O and VUV
          Radiation for 30 min at 40°C

15

Ga (3d)

As (3d)

GaAs

Ga₂O₃ GaAs

"AsO"

As₂O₃

23   21   19   17   47   45   43   41   39

BINDING ENERGY (eV)
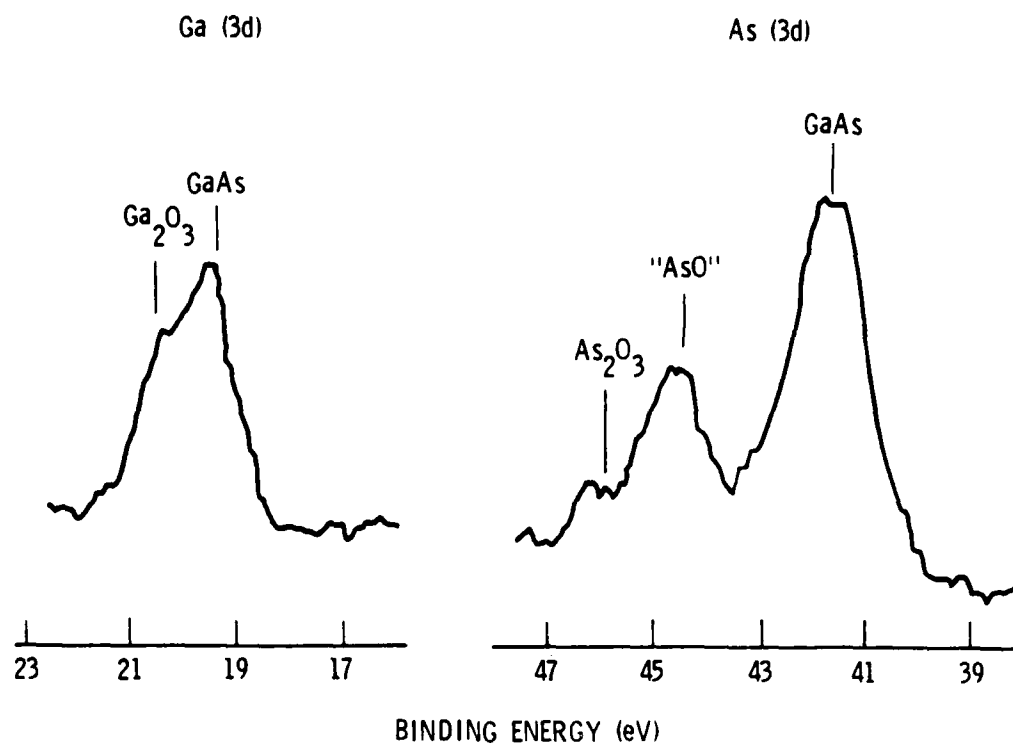
Fig. 3. XPS Spectrum of Br₂-Etched GaAs after Exposure to N₂O and VUV
Radiation for 60 min at 70°C

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Table 1. Photochemical Oxide Composition

Etch	Temperature, °C	Reaction Time, min	As (oxides)[a] Ga_2O_3	Oxidation Fraction
Br_2	100	60	0.98	0.34
		30	0.77	0.21
	70	60	0.82	0.42
		30	0.73	0.29
		20	1.2	0.34
	40	60	1.6	0.50
		30	0.92	0.49
		20	1.1	0.38
	23	60	1.6	0.49
		30	0.77	0.40
		20	1.0	0.35
HCl	100	60	1.5	0.38
		30	1.2	0.36
		20	b	0.19
		10	b	0.17
	70	60	1.6	0.29
		30	1.4	0.25
	40	60	1.2	0.35
		30	1.8	0.42
		20	b	0.39
		10	b	0.09
	23	60	2.4	0.39
		30	0.94	0.32
		20	b	0.11

[a]Ratio of the amount of oxidized As to the amount of oxidized Ga observed by XPS, using the corrected XPS peak intensities as the amounts.

[b]No Ga_2O_3 observed.

B. GaAs PHOTOCHEMICAL OXIDE

The photochemical oxide grown under our reaction conditions on a stoichi-
ometric Br_2-etched GaAs surface has equal amounts of oxidized Ga and As and is
not Ga_2O_3-rich, as is the native oxide (Table 1). The Ga oxide present is
Ga_2O_3, and the As oxides are As_2O_3 and the less oxidized "AsO"-like form
mentioned above (Fig. 3). Elemental As is present, as indicated by the FWHM
of the GaAs As peak of 1.7 eV. The photochemical oxide grown on an As-rich,
HCl-etched surface is As-rich (Table 1 and Fig. 4). In fact, for short reac-
tion times only oxidized As (predominantly AsO) is observed, and no oxidized
Ga is present. Without VUV exposures, no oxide is formed on either type of
surface.

The progress of the reaction can be monitored by calculating the fraction
F of the total Ga and As in the analysis volume that is oxidized (Table 1,
column 5; Fig. 5). F is calculated by taking the sum of the peak intensities
for GaAs, Ga_2O_3, and As as As_2O_3 and "AsO" and dividing that quantity by the
sum of the peak intensities for Ga and As in these forms as well as in oxi-
dized GaAs. Peak heights rather than peak areas were used because of the
difficulty of uniquely resolving overlapping peaks. The O (1s) spectra were
not used in the analysis since they were very broad, indicating the presence
of more than one type of O environment, and could not be resolved. The peak
intensities have been corrected for the spectrometer sensitivity but not for
matrix effects (which are largely unknown), molar volumes (which are not well
defined, especially for the oxygen-deficient oxide "AsO"), or depth into the
sample of the emitting atom (since it is not known whether the layers are
smooth or island-like). If the oxides are present as islands, the signal for
the oxides will not rise as rapidly as it would if the oxides were smooth
layers, and the signal for the substrate will not fall as rapidly. Thus F
will depend less on reaction time for an island-growth mode than for a smooth-
layer growth mode, but will follow the same general trends.

For the native oxide, F ≈ 0.4, or 40% of the Ga and As in the region
sampled by XPS is oxidized (as discussed below, this can be thought of as an
oxide ~5 Å thick). For a 60-min reaction time, the photochemical oxides also

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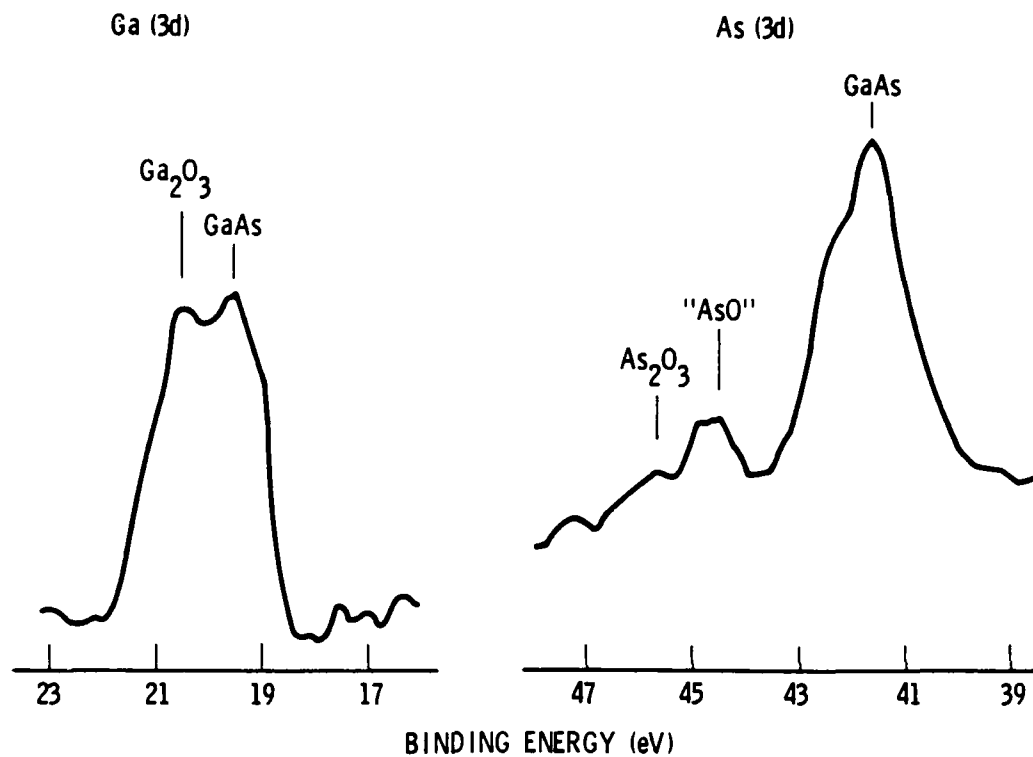Fig. 2.   XPS Spectrum of Native-Oxide-Covered GaAs after Exposure to VUV
Radiation for 30 min at 23°C

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