

UNCLASSIFIED

AD NUMBER

ADB019171

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to U.S. Gov't. agencies only; Test and Evaluation; 20 JUN 1977. Other requests shall be referred to Night Vision Laboratory, Attn: DRDEL-NV-IO, Fort Belvoir, VA 22060.

AUTHORITY

DARPA ltr, 15 Feb 1978

THIS PAGE IS UNCLASSIFIED

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

**BEST
AVAILABLE COPY**

STUDY OF THE ELECTRONIC SURFACE STATE
OF III-V COMPOUNDS

SEMI-ANNUAL TECHNICAL PROGRESS REPORT

W. E. Spicer, Principal Investigator
Telephone: (415) 497-4643

15 March, 1977

NIGHT VISION LABORATORY
U. S. Army Electronics Command
Fort Belvoir, Virginia 22060

Sponsored by

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
DARPA ORDER NO. 2182
PROGRAM CODE NO. 4D10

CONTRACT NO. DAAK02-74-C-0069

Effective: 1973 September 01
Expiration: 1977 September 30 (\$564,360)

The views and conclusions contained in
this document are those of the authors
and should not be interpreted as neces-
sarily representing the official poli-
cies, either expressed or implied, of
the Defense Advanced Research Projects
Agency of the U. S. Government.

Each transmittal of this document outside
the agencies of the US Gov must have
prior approval of the Night Vision Lab,
Ft Belvoir, VA. 22060, ATTN: DRSEL-NV-10



Test
20 JUN 1977

STANFORD ELECTRONICS LABORATORIES
STANFORD UNIVERSITY • STANFORD, CALIFORNIA



AD INJ.
BDC FILE COPY

AD B019171

(6) STUDY OF THE ELECTRONIC SURFACE STATE OF III-V COMPOUNDS.

SEMI-ANNUAL TECHNICAL PROGRESS REPORT.

(10) W. E. Spicer, Principal Investigator

Telephone: (415) 497-4643

(11) 15 March 1977

(12) 74 p.

NIGHT VISION LABORATORY
U. S. Army Electronics Command
Fort Belvoir, Virginia 22060

Sponsored by

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
DARPA ORDER NO. 2182
PROGRAM CODE NO. 4D10

(15) CONTRACT NO. DAAK02-74-C-0069, DARPA Order-2182

Effective: 1973 September 01 Expiration: 1977 September 30 (\$564,360)

STANFORD ELECTRONICS LABORATORIES
STANFORD UNIVERSITY
STANFORD, CALIFORNIA 94305

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency of the U. S. Government.

332 400

Imc

CONTENTS

	<u>Page</u>
I. LIST OF WORKERS	1
II. OVERVIEW	2
III. ANALYZED WORK	3
IV. SUMMARY OF APPENDED PAPERS	4
V. SUMMARY OF MOST RECENT RESULTS	6
VI. FUTURE PLANS	7
Appendix A. THE USE OF SYNCHROTRON RADIATION (32 eV $\leq$ h ν $\leq$ 350 eV) TO STUDY THE ADSORPTION OF OXYGEN ON GaAs (110)	8
Appendix B. SURFACE AND INTERFACE STATES ON GaAs (110): EFFECTS OF ATOMIC AND ELECTRONIC REARRANGEMENTS	34
Appendix C. OXYGEN SORPTION AND EXCITONIC EFFECTS OF GaAs SURFACES	61

EXPL. CONTROL

DATE

BY

IDENTIFICATION/AVAILABILITY CODES

DATE

AVAIL. AND/OR SPECIAL

B

FIGURES

Appendix A

	<u>Page</u>
1. Electron energy distribution curve for cleaved GaAs (110) taken at a photon energy of 240 eV showing the core levels and many-electron lines that are accessible in these studies	9
2. Spectral distribution of the synchrotron radiation from SPEAR for several beam energies	12
3. Schematic of the 4° line monochromator system showing the main mirror (M_0), the monochromator, and the double focusing mirror at the exit slit	13
4. Diagram of the photoemission spectrometer showing the electron energy analyzer, sample carousel, Au evaporator, light port, and sample cleaver	14
5. EDC's of clean and oxygen exposed n-type GaAs (110) at $h\nu = 100$ eV	17
6. The relative oxygen uptake of the GaAs (110) surface as a function of exposure determined from the area under the shifted As-3d levels	18
7. EDC's of clean and oxygen exposed n-type GaSb (110) at $h\nu = 100$ eV	20
8. EDC's of GaSb exposed to 5×10^8 L O_2 for three photon energies showing the variation in the cross-section of the Sb-4d levels <u>versus</u> photon energy	22
9. The relative oxygen uptake of the GaSb (110) surface as a function of exposure, determined from the area under the O-2p level	23
10. Schematic of the GaAs lattice terminated on the ideal (110), (111), and ($\bar{1}\bar{1}\bar{1}$) surfaces	25
11. The reconstructed (110) surface with an energy level diagram showing the location of the filled (As-derived) and empty (Ga-derived) surface states	26
12. Plot of the ratio of the unshifted to shifted As-3d levels as a function of electron kinetic energy for the GaAs (110) surface + 10^{12} L O_2 (right-most scale)	29

FIGURES (Cont)

<u>Appendix B</u>	<u>Page</u>
1. The (110) GaAs surface	37
2. Theoretical results from Chelikowsky et al ²⁷ showing the change in surface electronic structure between an "ideal," i.e., unrear- ranged surface, and a surface rearranged (relaxed) as indicated in Fig. 1	41
3. Energy distribution curves (EDC's) showing typical differences in the valence electronic structure at the surface for different cleaves and different GaAs crystals	42
4. The effect of low exposures (given in Langmuir, L) of oxygen on the valence electronic struc- ture at the surface	46
5. The change in the valence electronic structure for exposures up to 10^9 L	48
6. The coverage of chemisorbed oxygen versus exposure measured by two different methods	50
7. Spectra showing the EDC's for four different surface conditions	53
8. A schematic diagram suggesting the morphology of a "very heavily oxidized" GaAs surface of Fig. 7	56
9. This diagram indicates how a passivating layer might be bonded to a (110) GaAs surface in order to minimize the density of interface states due to broken "back" bonds	56
10. These diagrams contrast the effect of oxygen on the Fermi level pinning of cleavage surfaces of n-type Si and GaAs	58
<u>Appendix C</u>	
1. Effects of "unexcited" and "excited" oxygen on the 3d core levels of GaAs	62
2. Low energy electron loss spectrum taken from Ref. 3	65
3. Effects of oxygen on the "excitonic" transition and on the surface valence bands	67

Chapter I

LIST OF WORKERS

P. W. Chye

C. M. Garner

E. I. Lindau

P. Pianetta

W. Saperstein

P. Skeath

Chapter II

OVERVIEW

In the last semi-annual report, we presented results for chemisorption of oxygen and oxidation on the (110) surfaces of GaAs, GaSb, and InP as well as our work on heat cleaning the (111B) noncleavage surface of GaAs. Our work in the past six months has concentrated on (1) carefully analyzing our oxidation data in terms of ligand shift analysis; (2) repeating some measurements at SSRP using the 8° line ($9 \leq h\nu \leq 30$ eV) where we wanted to obtain additional data on the effects of oxygen on the valence bands of GaAs, GaSb, and InP (this data is now in the process of being analyzed); (3) continuing our work on heat cleaning of the noncleavage faces of GaAs, especially the (111A), (110), and (100) where we are systematically studying the effects that the various etchants have on the cleanability of these surfaces as well as the nature and extent of the damage induced by Argon ion bombardment; (4) planning and initiating experiments at SSRP on the study of metal overlayers on the (110) cleavage faces of GaAs, GaSb, and InP (this will be discussed below in the summary of the most recent results); (5) preparing our new vacuum system which will incorporate all the surface preparation and analysis techniques that we have found suitable for the study of III-V surfaces (see section on future plans); and (7) developing capability for computer control of synchrotron radiation experiments in order to maximize data obtained in the very restricted periods when we can use this facility.

Chapter III

ANALYZED WORK

As mentioned in the previous section, [↓] much ~~of our~~ time and effort has gone into carefully analyzing ~~our~~ data from the last experimental runs. As a result, ~~we have~~ several papers ^{being} which ~~we~~ have either ^{been} submitted or are in the process of submitting for publication.

Highlights include:

- (1) An analysis of our chemical shift data for the oxidation of GaAs (including GaSb and InP) in terms of a ligand shift analysis. This paper, which is in the final pre-publication stage, also includes the determination of the escape depth of GaAs around the region of the escape depth minimum and a model for the oxidation of GaAs (110). This was discussed in our previous report.
- (2) A correlation of ~~our~~ valence band results showing the effects of strain and relating this to possible rearrangements of the surface lattice. [↑]

Chapter IV

SUMMARY OF APPENDED PAPERS

In Appendix A, we discuss the use of synchrotron radiation in the photon energy range between 32 and 300 eV for performing very surface sensitive x-ray photoemission spectroscopy. The usefulness of this technique is illustrated with results for the chemisorption of oxygen on the (110) surface of both GaAs and GaSb. Binding energy shifts in the 3d levels of Ga, As, and Sb due to chemisorbed oxygen can be seen for oxygen coverages below 5% of a monolayer combining the surface sensitivity of Auger electron spectroscopy with the precise chemical information of x-ray photoemission spectroscopy. When oxygen is adsorbed on GaAs, charge is transferred from the surface arsenic atoms to the chemisorbed oxygen with no breaking of back bonds, and, consequently, no oxidation of the surface. In GaSb, on the other hand, there is simultaneous charge transfer from both the surface gallium and antimony atoms, indicating that back bonds are broken and oxide formation is taking place. The escape depth for GaAs (110) was also measured for electron kinetic energies between 20 and 200 eV.

Research during the last year has led to a better understanding of the electronic and atomic structure of the (110) surfaces of 3-5 semiconductors. In Appendix B, we will briefly review these new developments as well as point out areas where agreement has been found between various experimental results presented in the literature. It is now generally agreed that there are no intrinsic surface states in the band gap on GaAs and the smaller band gap materials (e.g., GaSb, InAs, and GaSb) and that Schottky barrier pinning must be due to states produced when the metal adlayer is applied. Particular attention is focused on the large surface rearrangement which takes place on the (110) GaAs surface and effects of the strain which may be produced in joining this rearranged surface layer to the rest of GaAs crystal.

It is pointed out that this may lead to variations in the surface rearrangement which can produce variations in the valence electronic structure at the surface. Such variations are shown in experimental energy distribution curves obtained by the photoemission technique which

Chapter V

SUMMARY OF MOST RECENT RESULTS

Due to scheduling at SSRP, we were not given any time to do our metal overlayer experiments until the beginning of March. Since then, we have performed one series of experiments on the 8° line, studying the valence band electronic structure upon the adsorption of gold on GaAs, GaSb, and InP; In on InP; and preliminary attempts to evaporate aluminum on GaAs. We performed partial yield concurrently with the UPS (in order to probe the empty states) as well as Auger on selected samples. We were careful to avoid the use of Auger in most cases since we wanted to eliminate the possibilities of electron beam induced effects.

We are presently (April 15, 1977) in the middle of our 4° line run ($32 \lesssim h\nu \lesssim 600$ eV). Here, we are carefully studying the core levels of both the substrate and metal overlayer in order to detect any chemical shifts due to bonding as well as compositional changes at the substrate surface induced by the metal overlayer. This data has proven to be quite exciting in that we see very interesting differences in the composition of the interface for gold on the different III-V's. This correlated with sputter-Auger depth profiles obtained from complex photocathode structures fabricated by Varian. We should also note at this point that the energy range of the 4° line at SSRP has been extended to about 600 eV by replacement of the first focusing mirror. We have done preliminary scans in this region and found that we were able to operate quite easily (at reduced resolution) up to 500 eV. The upper range between 500 and 600 eV gives a lower counting rate but is still workable. We will be using this expanded energy scale to look for the oxygen 1s core level when we perform oxygen exposures. This will allow us to avoid Auger for this purpose.

samples principally the last two molecular layers. It is further shown that surprisingly small amounts of chemisorbed oxygen can produce first order effects in the valence band electronic structure. On all GaAs (110) surfaces studied, a phase-like transformation was observed with a few hundredths of a monolayer coverage of chemisorbed oxygen. Near this coverage, the Ga 3d exciton structure disappears and the oxygen uptake increases significantly. It is now clear that these excitations from the Ga-3d core level into the empty surface states are highly excitonic in nature (see Appendix C). These transitions can be studied by partial yield or low energy electron loss spectroscopy, and in the past their disappearance with oxygen exposure has been attributed to oxygen bonding on surface Ga atoms and destroying the empty surface states. By combining partial yield, ultraviolet photoemission and soft x-ray photoemission data, it is shown that this disappearance is not due to oxygen bonding on Ga atoms but due to exciton extinction from oxygen induced changes in the surface electronic structure at very low coverages.

On certain samples, first order changes in the valence band electronic structure were observed at a coverage of a hundredth of a monolayer or lower (Appendix B). These transformations are believed to be due to changes in atomic configurations at the surface.

Experimental data showing As and Ga 3d chemical shifts for oxidation as well as chemisorption are also presented and used to point out difficulties to be expected in passivating practical surfaces. In particular, the effect of mixed As and Ga oxides, the desirability of bonding passivating layers to the GaAs through As bonds, and the effect of strain induced interface states are discussed.

Chapter VI

FUTURE PLANS

The next six months should be both a very busy and rewarding period even though we will have no time at SSRP until next November since SIAC is down. We will be concentrating on analyzing data, improving our existing apparatus, and extending our experimental capabilities. We will start an intensive program to bring our LEED capability on line. Our major effort will be put into analyzing the data from our present SSRP run. It has proven so exciting that we feel that these results could have a very important impact on our future experiments as well as in Schottky barrier device fabrication in general. We will also be readying our new vacuum system for work on III-V's. This system consists of a specially modified Varian all metal bell jar. We will have the capabilities of performing UPS, XPS, Auger, LEED, and flash desorption on both cleavable samples and wafers. In addition, we will be able to cool one sample. Additional capabilities that are under development for this system are:

- (1) Cooled effusion cells and an e-gun evaporator so that we may cleanly evaporate almost any material onto our surfaces.
- (2) A dosing system so that we may selectively expose our surfaces to volatile materials without contaminating the whole system.

We are presently awaiting delivery on our computer system. We have almost all the interface equipment so that we will soon be able to bring this added capability on line.

Our experimental efforts in the next few months (after the SSRP run is finished) will be to concentrate on Auger and LEED to study the effect of oxygen and metals on GaAs. We will also be trying to correlate the problem of Fermi level pinning to cleave quality on GaAs by studying the effects of different crystal orientations.

Appendix A

THE USE OF SYNCHROTRON RADIATION ($32 \text{ eV} \leq h\nu \leq 350 \text{ eV}$) TO STUDY THE ADSORPTION OF OXYGEN ON $\text{GaAs}(110)$

1. Introduction

The use of synchrotron radiation to do photoemission spectroscopy has resulted in a very powerful technique for studying the surface physics and chemistry of a wide variety of chemisorption phenomena. We will illustrate the utility of this technique with our results for the chemisorption of oxygen on the (110) surfaces of GaAs and GaSb.¹

All the results presented here were obtained with soft x-ray photoemission spectroscopy (SXPS) using synchrotron radiation from the "4° line" at the Stanford Synchrotron Radiation Project (SSRP) in the photon energy range $32 \text{ eV} \leq h\nu \leq 350 \text{ eV}$.² This photon energy range is interesting because, first of all, it allows us to observe both the valence band and several core levels from both the Ga and As at high resolution (0.25 eV). In Fig. 1, we show a typical electron energy distribution curve (EDC) for the clean, cleaved GaAs (110) surface for $h\nu = 240 \text{ eV}$. The spectral features of interest for this work are the As and Ga core levels located 19.0 and 40.8 eV below the valence band maximum as well as the valence band (s-p derived levels) which occupy the top 12 eV of the spectrum. Besides these one-electron lines, we are also able to see Auger transitions and plasmon losses.

Secondly, by tuning through the available photon energies, we are able to adjust the kinetic energies of the various levels to be roughly between 20 and 200 eV. This is possibly the most significant aspect of our experiments because the escape length of electrons in a material is strongly dependent on the electron kinetic energy, and this escape depth goes through a minimum of $\sim 10 \text{ \AA}$ for kinetic energies between 50 and 150 eV for most materials.³ Therefore, by choosing the appropriate photon energy, we are easily able to concentrate on what is happening at the surface of our sample.

Experimental methods, such as LEED, AES, and UPS, all have high surface sensitivity. However, they lack the chemical information which can be obtained from x-ray photoemission (XPS) studies of core level

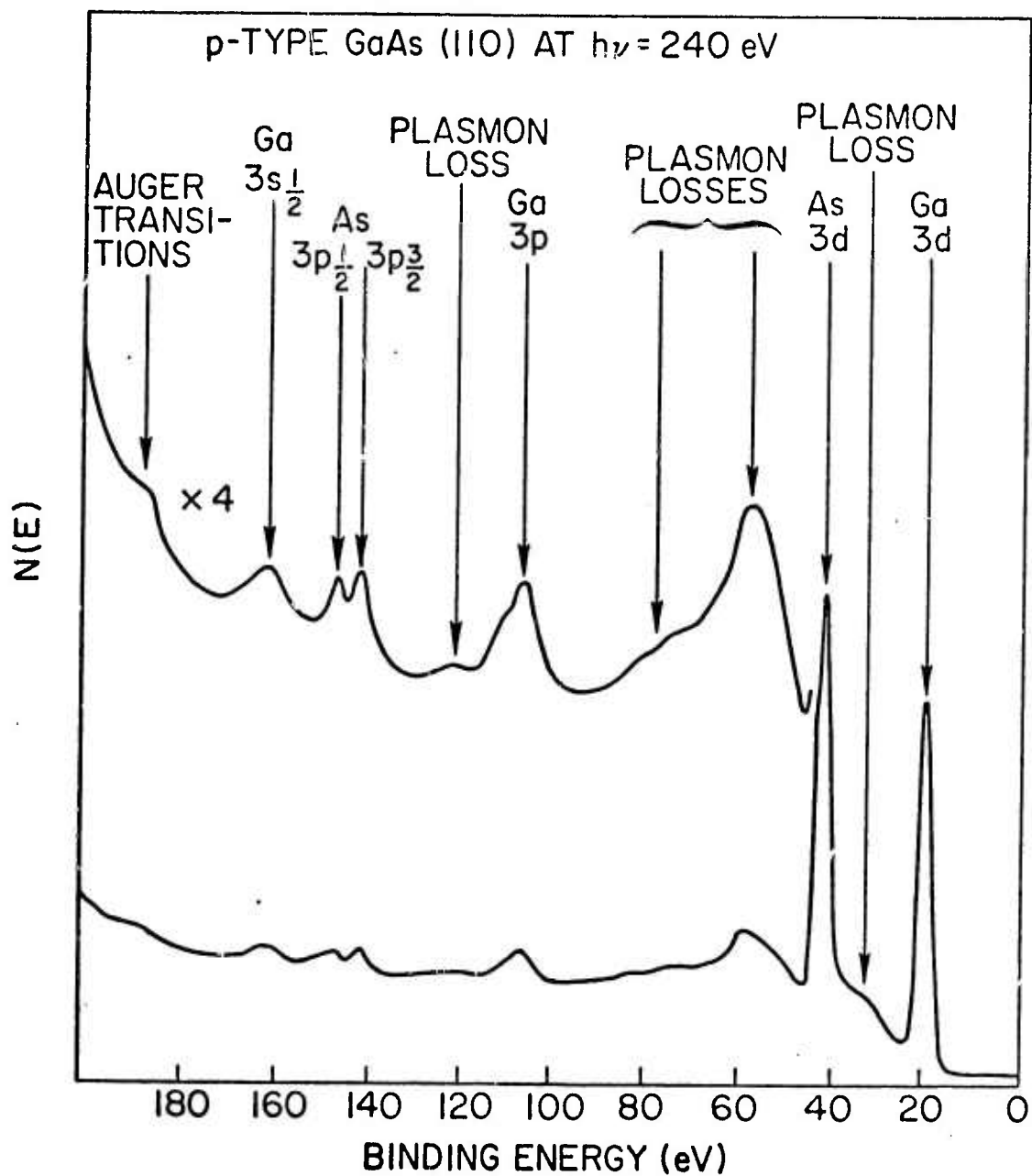


Fig. 1. ELECTRON ENERGY DISTRIBUTION CURVE FOR CLEAVED GaAs (110) TAKEN AT A PHOTON ENERGY OF 240 eV SHOWING THE CORE LEVELS AND MANY-ELECTRON LINES THAT ARE ACCESSIBLE IN THESE STUDIES.

shifts.⁴ AES can be used to look at chemical shifts in some materials, but the use of an e-beam as the excitation source can desorb the oxygen or destroy the integrity of the surface.^{1,5,6} This damage is minimized when using UV light or x-rays. However, conventional XPS ($h\nu = 1486.7$ or 1253.6 eV) lacks the necessary surface sensitivity.³ With SXPS, not only can we study the chemical shift of core levels upon forming a chemical bond, but we can also perform these studies at submonolayer coverages due to the inherent surface sensitivity of our technique.^{1,7} In our experiment, we adsorb oxygen on GaAs or GaSb and observe any core level shifts that take place upon adsorption. We then measure the magnitude of the core level shifts and correlate these shifts with chemical shift measurements made on bulk oxides using conventional XPS. This correlation allows us to determine the type of oxides forming at the surface in a relatively straightforward way, obviating the need to perform complicated calculations.⁴ The ratio of the area of the shifted to unshifted peaks can be used to determine coverages versus exposure as well as escape depth information.

In Section 2, we will discuss the experimental apparatus, procedure, and results. Section 3 will contain the discussion. In this section, we will correlate the chemical shifts obtained from the surface oxidation of GaAs (110) to the shifts obtained from ESCA measurements of bulk oxides.

2. Experimental

A. Apparatus

The experimental apparatus consists of the SPEAR storage ring, a grazing incidence monochromator, and the sample chamber.

⁸ SPEAR is the electron-positron storage ring located at the Stanford Linear Accelerator Center. In the present operating mode, SPEAR is run for high energy physics experiments in which stored, counter-rotating electron and positron beams are collided with each other at energies ranging from 1.5 to 4.0 GeV. SSRP operates in a parasitic mode in which the synchrotron radiation emitted from the rotating electron beam is channeled into a wide variety of experimental stations.² The radiation emitted from SPEAR forms a continuous spectrum from below the

visible to the hard x-ray region. The upper limit of the spectrum is a function of the electron beam energies, and in Fig. 2 we show typical spectra for several beam energies.

The second part of our apparatus is the monochromator system and is shown in Fig. 3. This consists of a main mirror,⁹ M_0 , which deflects the portion of the spectrum below 1 keV out of the main, high energy x-ray beam and focuses it onto the entrance slit of the monochromator.^{10,11} The monochromator is of the glancing incidence type and provides useable radiation for photoemission experiments between 32 and 300 eV.¹¹ There is a double focusing mirror after the exit slit of the monochromator to focus the light onto the sample.

The sample chamber consists of a stainless steel UHV bell jar, base pressure $< 1 \times 10^{-10}$ torr, and is shown schematically in Fig. 4. The pumping system is a 240 L/sec ion pump plus titanium cryopump with a poppet valve for sealing the pump off from the main chamber. The chamber contains a double pass cylindrical mirror analyzer (Physical Electronics), a cleaver, and a sample manipulator capable of holding 4 samples for cleaving, one sample for heat cleaning ($T_{\max} \approx 2000^\circ\text{C}$) and a substrate upon which Au or Cu may be evaporated for Fermi level (and thus binding energy) determinations.¹² An evaporator which contains copper and gold beads is also housed in the chamber.

Research grade oxygen was admitted into the vacuum system through a bakeable leak valve. For large exposures (pressures up to 750 mm O_2), an auxiliary pumping system was used to return the main chamber to pressures below $\sim 10^{-8}$ torr. This system consisted of vac-sorb pumps, an ion pump, and all the necessary gauging to measure pressures for the gas exposures.

The radiation enters the chamber through a bakeable straight through valve and strikes the sample as indicated in Fig. 4. The energy of the photoemitted electrons is then determined by the double pass cylindrical mirror analyzer operated in the retarding mode. This mode insures a constant resolution which is equal to 0.6% of the electron pass energy through the analyzer. In these experiments, we used a pass energy of 25 eV, giving a resolution of 0.15 eV. At $h\nu = 100$ eV, typical counting rates on the Ga 3d levels are about 5×10^3 counts per second for a circulating electron current in SPEAR of 20 ma.

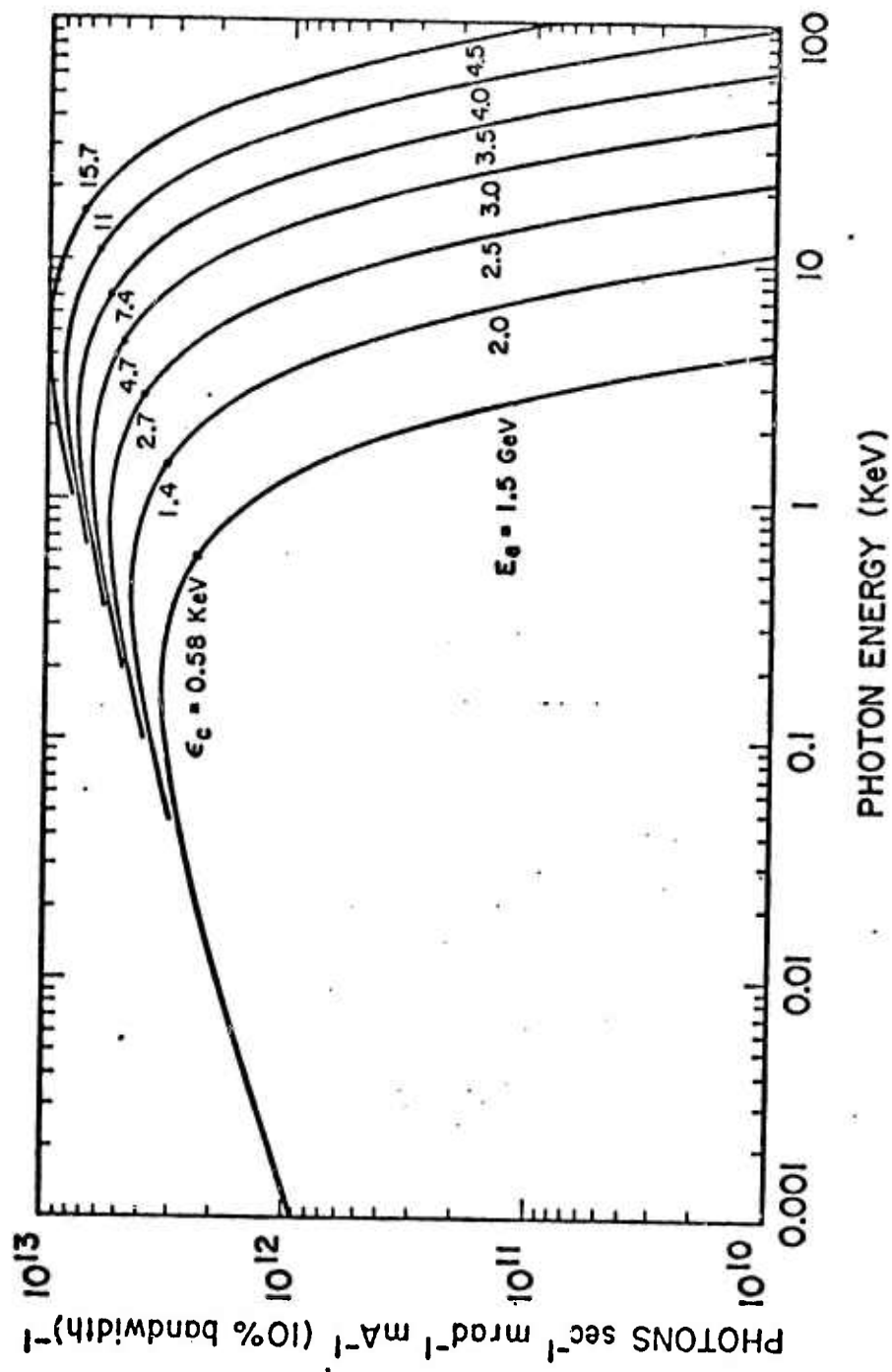


Fig. 2. SPECTRAL DISTRIBUTION OF THE SYNCHROTRON RADIATION FROM SPEAR FOR SEVERAL BEAM ENERGIES.

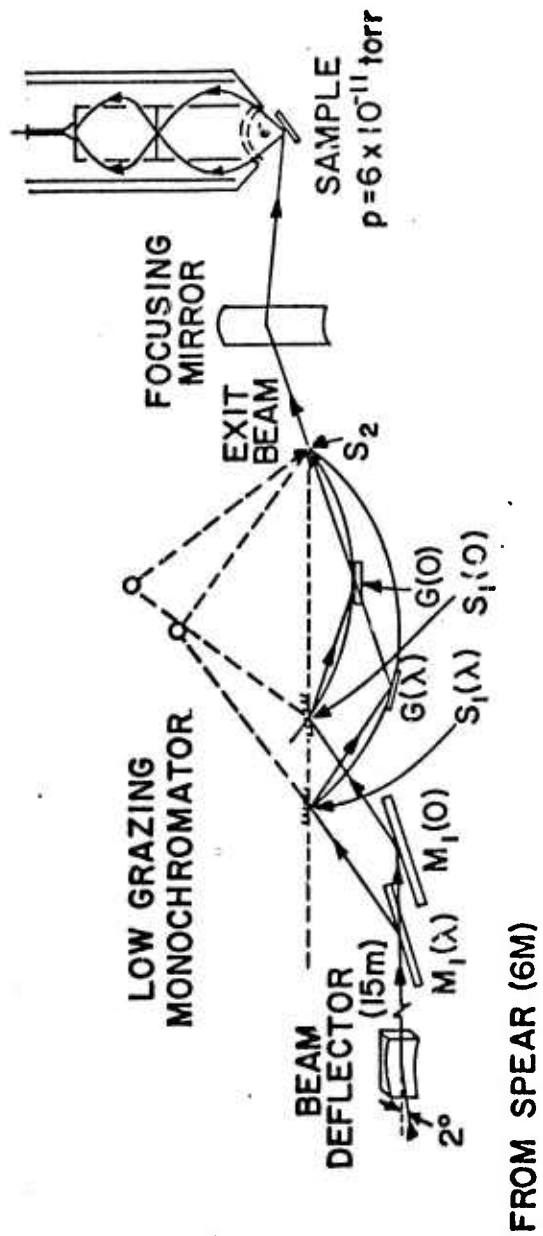


Fig. 3. SCHEMATIC OF THE 4° LINE MONOCHROMATOR SYSTEM SHOWING THE MAIN MIRROR (M_0), THE MONOCHROMATOR, AND THE DOUBLE FOCUSING MIRROR AT THE EXIT SLIT.

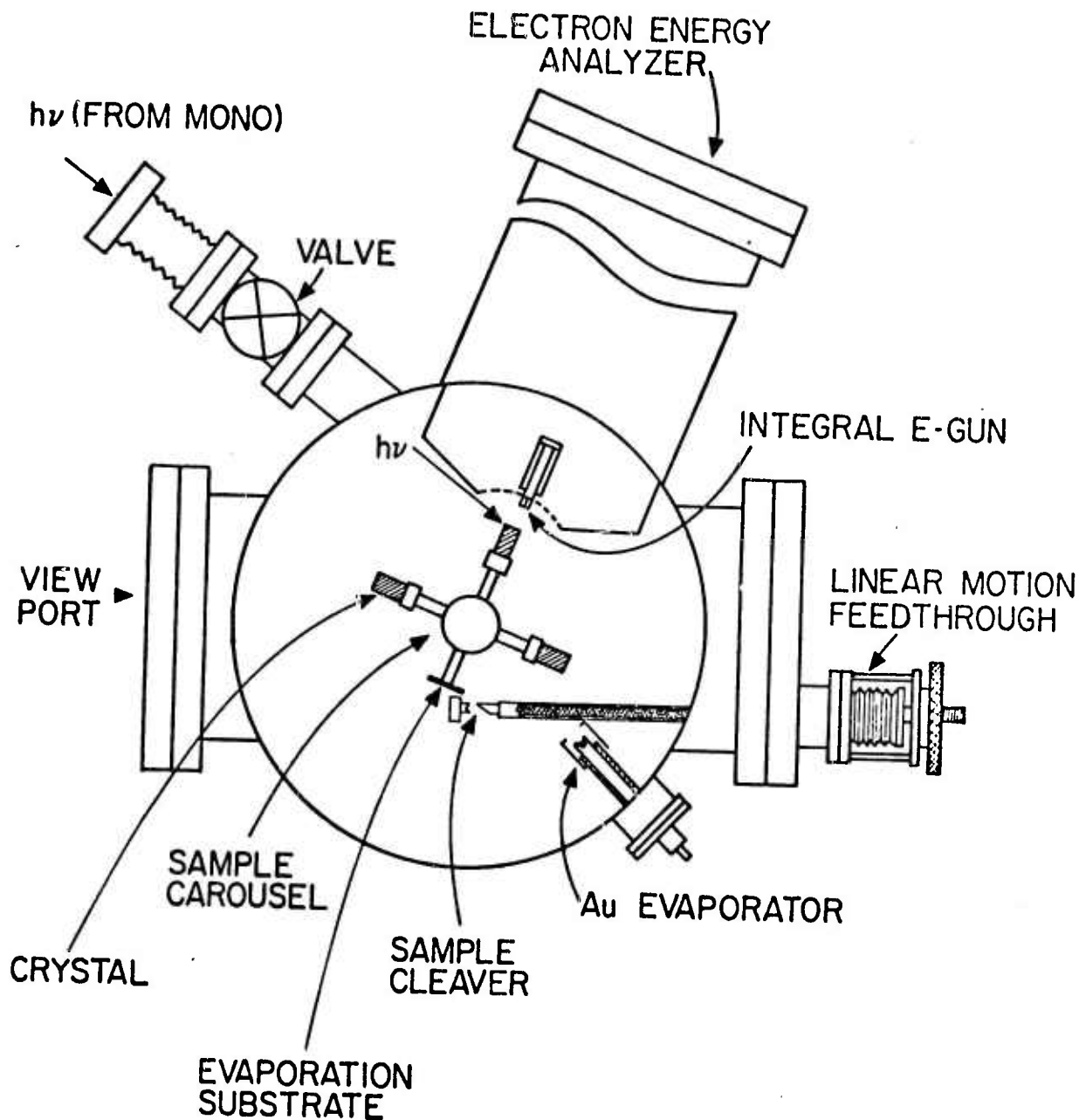


Fig. 4. DIAGRAM OF THE PHOTOEMISSION SPECTROMETER SHOWING THE ELECTRON ENERGY ANALYZER, SAMPLE CAROUSEL, Au EVAPORATOR, LIGHT PORT, AND SAMPLE CLEAVER. The anvil support bars on the cleaver, which are fastened to the stationary part of the linear motion feedthrough, have been cut away to show the wedge-shaped, tungsten-carbide blade.

The signals from the electron energy analyzer are amplified and fed into a 2048 channel signal averager (Tracor Northern) used as a multichannel scaler. The energy of the detected electrons was controlled by the signal averager through a voltage ramp synchronized with the memory sweep.

The samples that were studied in these experiments are Te doped n-type GaAs ($n = 3.5 \times 10^{17} \text{ cm}^{-3}$ and $n = 0.5 \times 10^{18} \text{ cm}^{-3}$) and Zn doped p-type GaAs ($p = 6 \times 10^{18} \text{ cm}^{-3}$) from Laser Diode (LD) Corporation; Te doped n-type GaSb ($n = 1.1 \times 10^{18} \text{ cm}^{-3}$) from Asarco; and Zn doped p-type InP ($p = 2 \times 10^{18} \text{ cm}^{-3}$) from Varian Associates. The GaAs and GaSb samples were rectangular prisms $5 \times 5 \times 10 \text{ mm}^3$, and the InP was $2 \times 5 \times 10 \text{ mm}^3$. In all the samples, the (110) axis was along the long dimension.

B. Procedure

First, the samples were cleaved along the (110) planes by slowly squeezing the sample between the annealed copper anvil and tungsten-carbide knife of the cleaver. The cleaved sample is inspected visually to insure the cleave has a mirror-like finish. A set of spectra is taken for $32 \leq h\nu \leq 300$. The sample is then subjected to a series of controlled oxygen exposures ranging from 1 to 10^{12} Langmuirs, L, ($1 \text{ L} = 10^{-6} \text{ torr-sec}$) with a set of spectra taken after each exposure.

The binding energies in these studies are measured relative to the valence band maximum of the clean surface. Binding energies with respect to the Fermi level can be determined by referring the unknown binding energies to either the 4f levels of Au (binding energy = 84.7 eV) or the Fermi level of a gold film evaporated in situ on a substrate in electrical contact with the sample.¹²

C. Results

In this section, we will present our photoemission results for oxygen adsorption on the (110) surface of GaAs and GaSb. These results include measurements of the chemical shifts of the substrate core levels upon oxygen adsorption and the determination of the oxygen coverage as a function of exposure. We also present results for the exposure of GaAs (110) to excited oxygen and measure the resulting substrate core level shifts.

In Fig. 5, we show spectra for the clean and oxidized GaAs (110) surface at $h\nu = 100$ eV. As we expose the surface to oxygen, we see a peak ($E_B = 43.7$ eV) growing 2.9 eV below the As-3d peak ($E_B = 40.8$ eV) with a proportionate decrease in the As-3d intensity. This is a chemically shifted peak indicating a transfer of charge from the surface As atoms to the adsorbed oxygen. Concurrent with the appearance of the shifted arsenic peak, we see the O-2p resonance level at a binding energy of about 5 eV.

As we go to higher exposures, the shifted As-3d peak and O-2p level grow simultaneously until saturation is reached between 10^9 and 10^{12} L O₂. An estimate of the relative amount of oxidized As atoms on the surface can be obtained by comparing the areas under the shifted and unshifted peaks. This is done in Fig. 6, where we plot the area in relative units under the shifted and unshifted peaks as a function of exposure. Here, the sum of the areas under the shifted and unshifted peaks were normalized to unity. As expected, the amount of oxidized arsenic increases while the unoxidized decreases for increasing exposure. At 10^6 L O₂, where we first start to see the effect of oxygen in the valence band as well as seeing a chemically shifted As-3d level, the coverage is only about 2% of saturation.

If we consider only the points up to an exposure of 5×10^9 L O₂ in Fig. 6, saturation seems to have been reached at about 10^9 L O₂. If, however, we include the point at 10^{12} L O₂, which gives a 1.7 times increase in coverage over that at 10^9 L O₂, the apparent saturation exposure is increased by three orders of magnitude. At present, we will not place too much emphasis on the coverage indicated by this one point because the spectrum for 10^{12} L O₂ was obtained from a different sample than the other spectra in Fig. 5.

It is also possible that cleave quality could affect oxygen uptakes by as much as a factor of two. On the other hand, we could be seeing a real effect indicating a change in adsorption kinetics between 10^{10} and 10^{12} L O₂. In any case, the question of oxygen uptake versus exposure merits further experimental investigation before we can make quantitative statements on the adsorption kinetics.

OXIDATION OF n-TYPE GaAs(110) AT $\hbar\omega=100$ eV

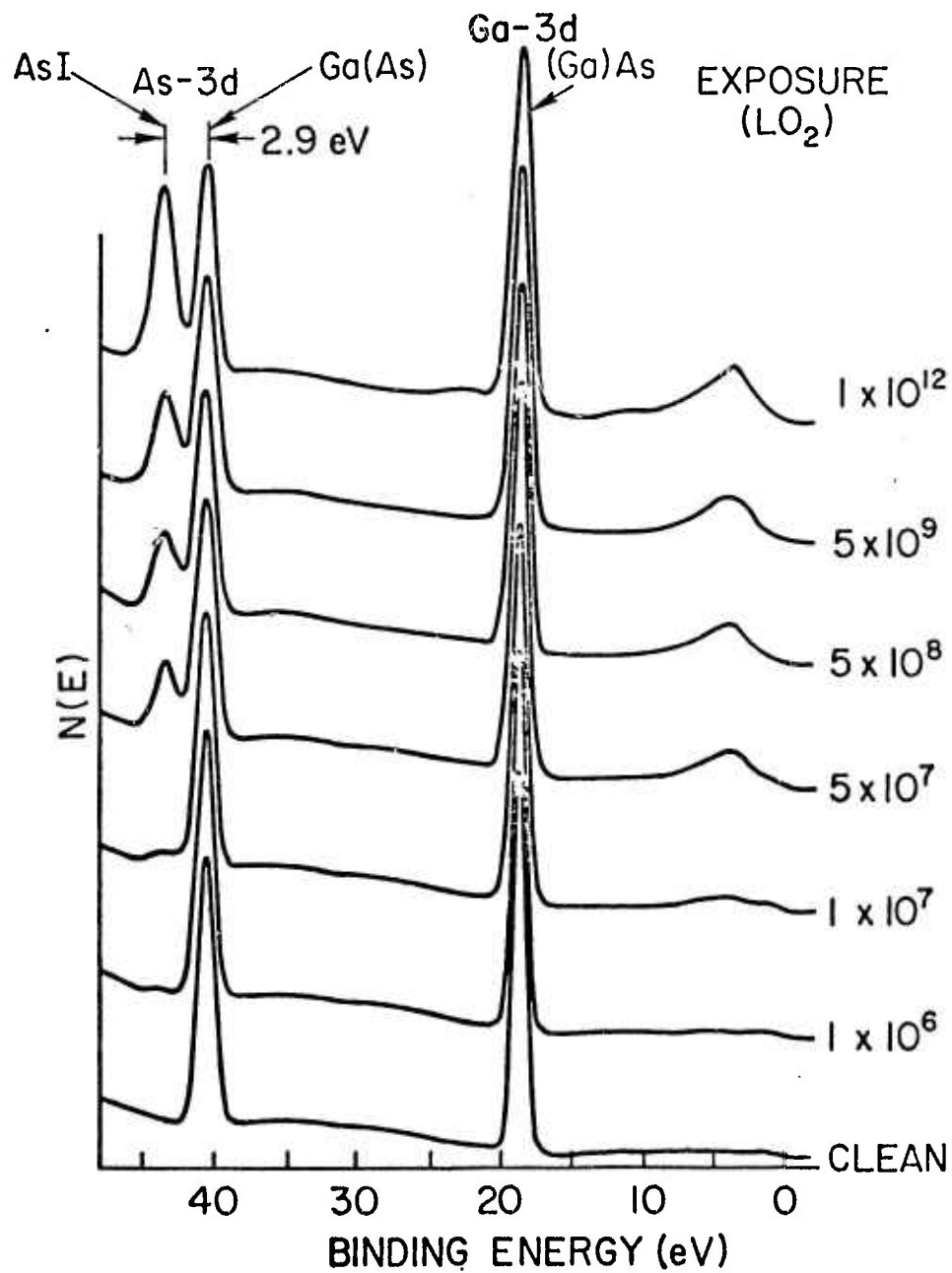


Fig. 5. EDC's OF CLEAN AND OXYGEN EXPOSED n-TYPE GaAs (110) AT $h\nu = 100$ eV.

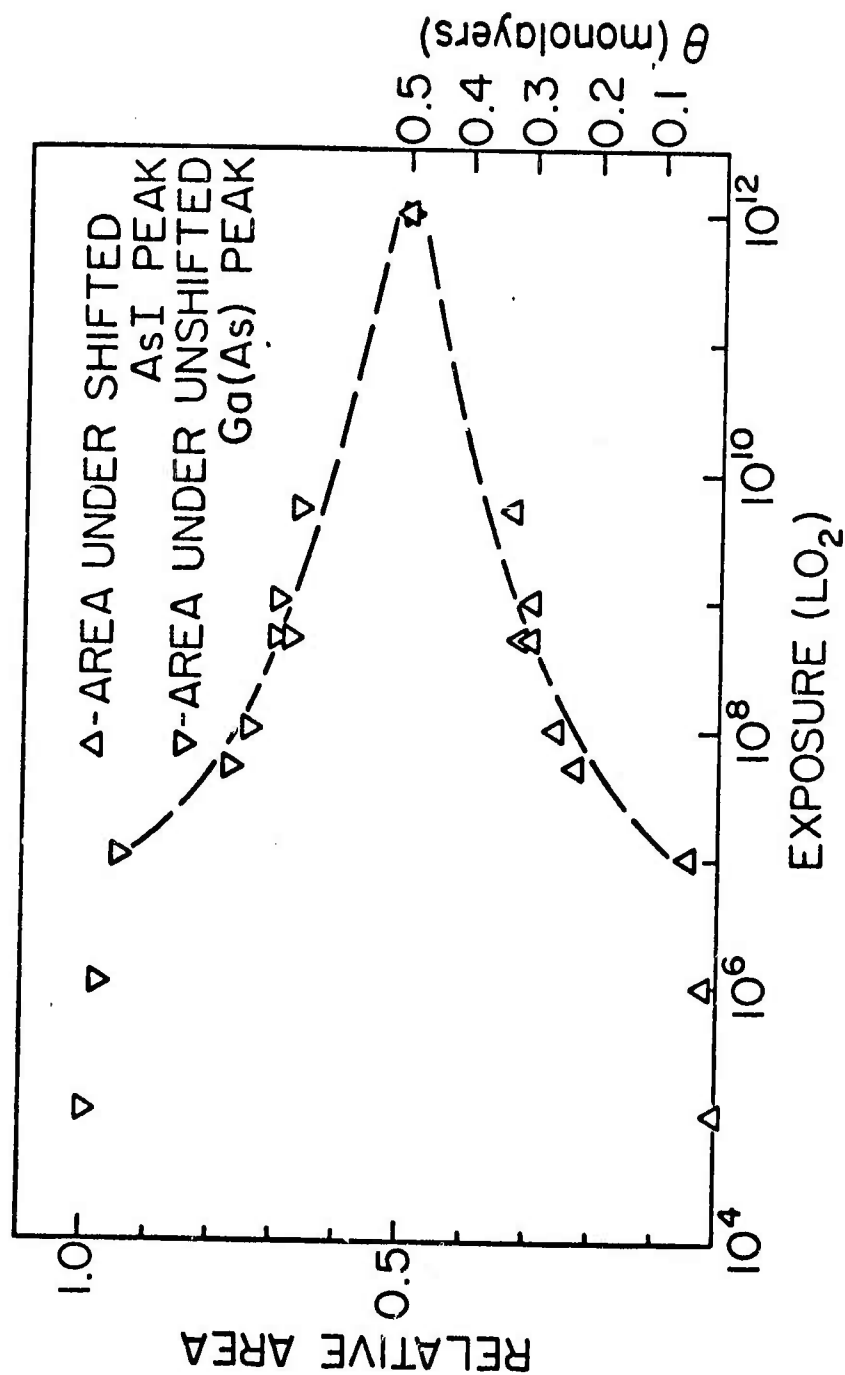


Fig. 6. THE RELATIVE OXYGEN UPTAKE OF THE GaAs (110) SURFACE AS A FUNCTION OF EXPOSURE DETERMINED FROM THE AREA UNDER THE SHIFTED As-3d LEVELS (Δ). The area of the unshifted As-3d levels (∇) is also plotted. The scale on the right assumes saturation is reached at 10^{12} L O_2 .

Information on relative oxygen coverages can also be obtained by measuring the area under the O2p resonance in the valence band. The major drawback to this technique is that the valence band and the O2p signal overlap so that it is difficult to get reliable coverage information below exposures of about 5×10^7 L O₂. Even above this exposure, the GaAs valence band is still a significant fraction of the total emission, so care must be used in separating out the oxygen contribution from that of the GaAs.

We should also note at this point that the coverage, as determined from the shifted arsenic level, gives a measure of the relative amount of oxygen that has chemically combined with the surface arsenic atoms. The coverage obtained from the O2p signal gives a measure of the total amount of oxygen sticking to the surface. Thus, comparison of the oxygen uptake determined in these two ways can be used to give additional information on the kinetics of the adsorption as well as the nature of the adsorbate. Our initial studies indicate that the two methods give similar results. However, as mentioned above, more experimental work needs to be done on exposures between 10^{10} and 10^{12} L O₂ before definitive conclusions may be drawn.

The significance of the curve for 10^{12} L O₂ is that, even for this very large exposure (this corresponds to an exposure of one atmosphere of O₂ for 20 minutes!), no shift in the gallium 3-d level is observed. The only effect on the gallium peak is a 0.4 eV broadening. Part of this broadening may be due to a nonuniformity in work function across the face of the sample since the unshifted arsenic peak is broadened by 0.1 eV. Also, notice that no broadening is seen in the Ga 3d level for the exposures below 10^{10} L O₂.

The oxidation of the GaSb (110) surface is shown in Fig. 7 for $h\nu = 100$ eV. As in the case of GaAs, all the spectral features of interest can be obtained at the same photon energy and in one spectrum, thus facilitating comparisons. The valence band extends approximately 12 eV below the valence band maximum. The Ga-3d level is at a binding energy of 19.4 eV, the Sb-4d doublet is at 32.1 eV ($4d_{5/2}$) and 33.2 eV ($4d_{3/2}$). The main differences between the clean spectra of GaSb and GaAs are: Firstly, we are able to clearly see the spin orbit splitting

OXIDATION OF n-TYPE GaSb(110) at $\hbar\omega = 100$ eV

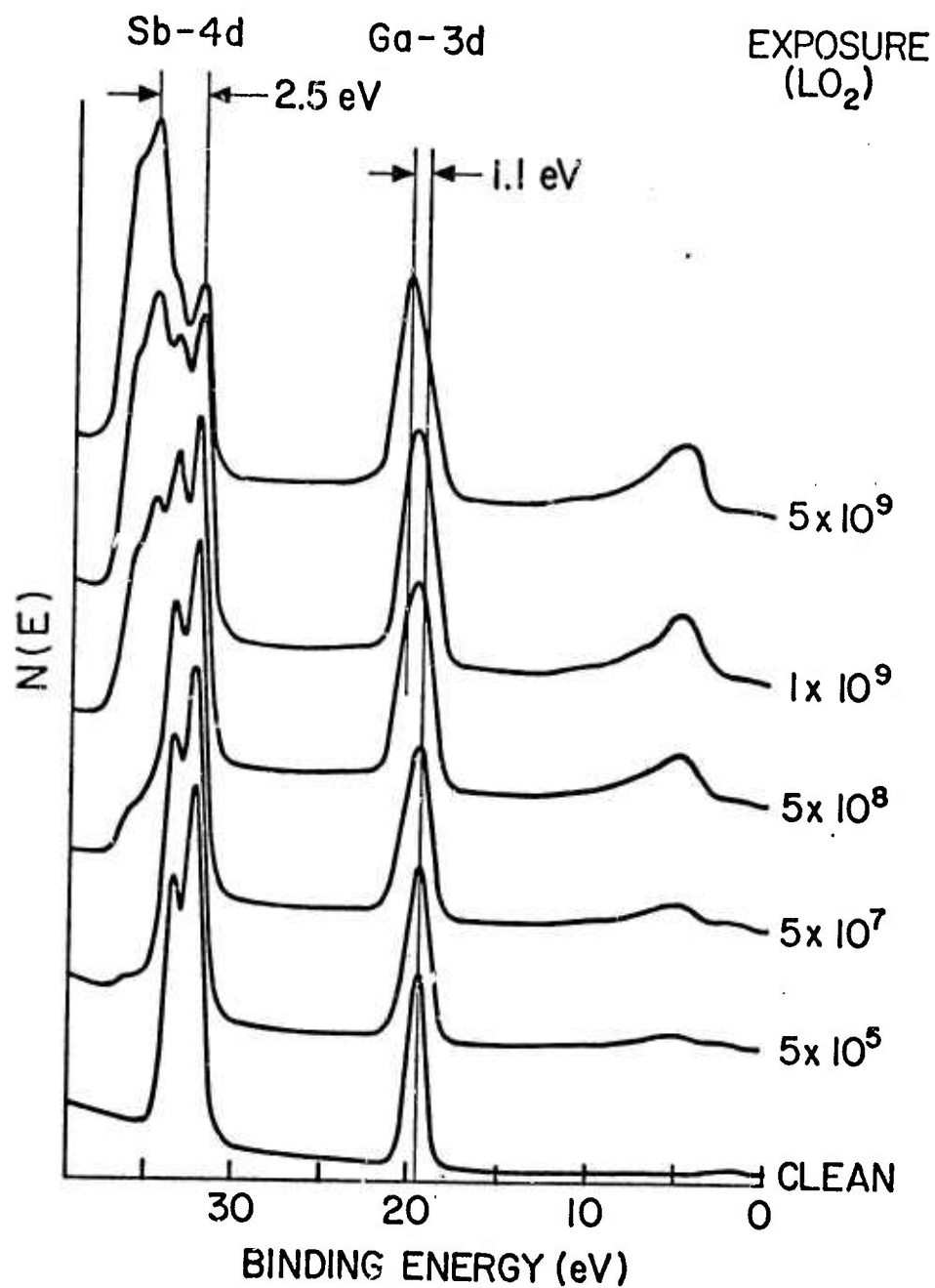


Fig. 7. EDC's OF CLEAN AND OXYGEN EXPOSED n-TYPE GaSb (110) AT $h\nu = 100$ eV. Notice that both the Ga and Sb shift simultaneously with increasing oxygen exposure.

in the Sb-4d levels, whereas we were not able to see it at these energies for the Ga and As levels, primarily because the splitting of the Sb-4d levels is much larger than that of the 3d levels of As or Ga; and, secondly, the As and Ga levels are 3d's while that of Sb is a 4d. The last point is important for the choice of photon energy since the variation of cross-section for the 4d levels versus photon energy is rather dramatic, as indicated in Fig. 8. Here, we show spectra of oxidized GaSb for several different photon energies. Notice that almost all the intensity is lost from the 4d levels over a very small photon energy range. The variation in cross-section of the 3d's is not as dramatic, but is nevertheless also large.¹³ Consequently, we are forced to use photon energies below about 120 eV.

As we oxidize the GaSb surface, we start to see changes in the spectra at about $5 \times 10^5 \text{ L O}_2$. This is about a factor of two sooner than with the GaAs. But, more importantly, as we increase the exposure to $5 \times 10^7 \text{ L O}_2$, we start to see a definite broadening of the Ga-3d level toward higher binding energy. In fact, even by $5 \times 10^8 \text{ L O}_2$, a definite shifted Ga-3d peak is seen ($\Delta E_B = 1.1 \text{ eV}$). Of course, the shifted Sb-4d ($\Delta E_B = 2.5 \text{ eV}$) level has also been growing at the expense of the unshifted level. The shifted peaks for both Sb and Ga completely dominate the unshifted peaks for exposures above $5 \times 10^9 \text{ L O}_2$.

In GaAs, only the As peak is shifted while the Ga peak is broadened. In GaSb, both the Sb and Ga are definitely shifted, indicating that charge transfer from both surface Sb and Ga atoms to the oxygen has taken place. This implies that bonds are broken between neighboring surface Ga and Sb atoms.

Another striking difference is seen if the coverage (area under shifted Sb peak or O-2p level) is plotted with respect to exposure (Fig. 9). The rate of oxygen adsorption from Fig. 9 does not show the saturation behavior which is characteristic of the GaAs surface as seen in Fig. 6.

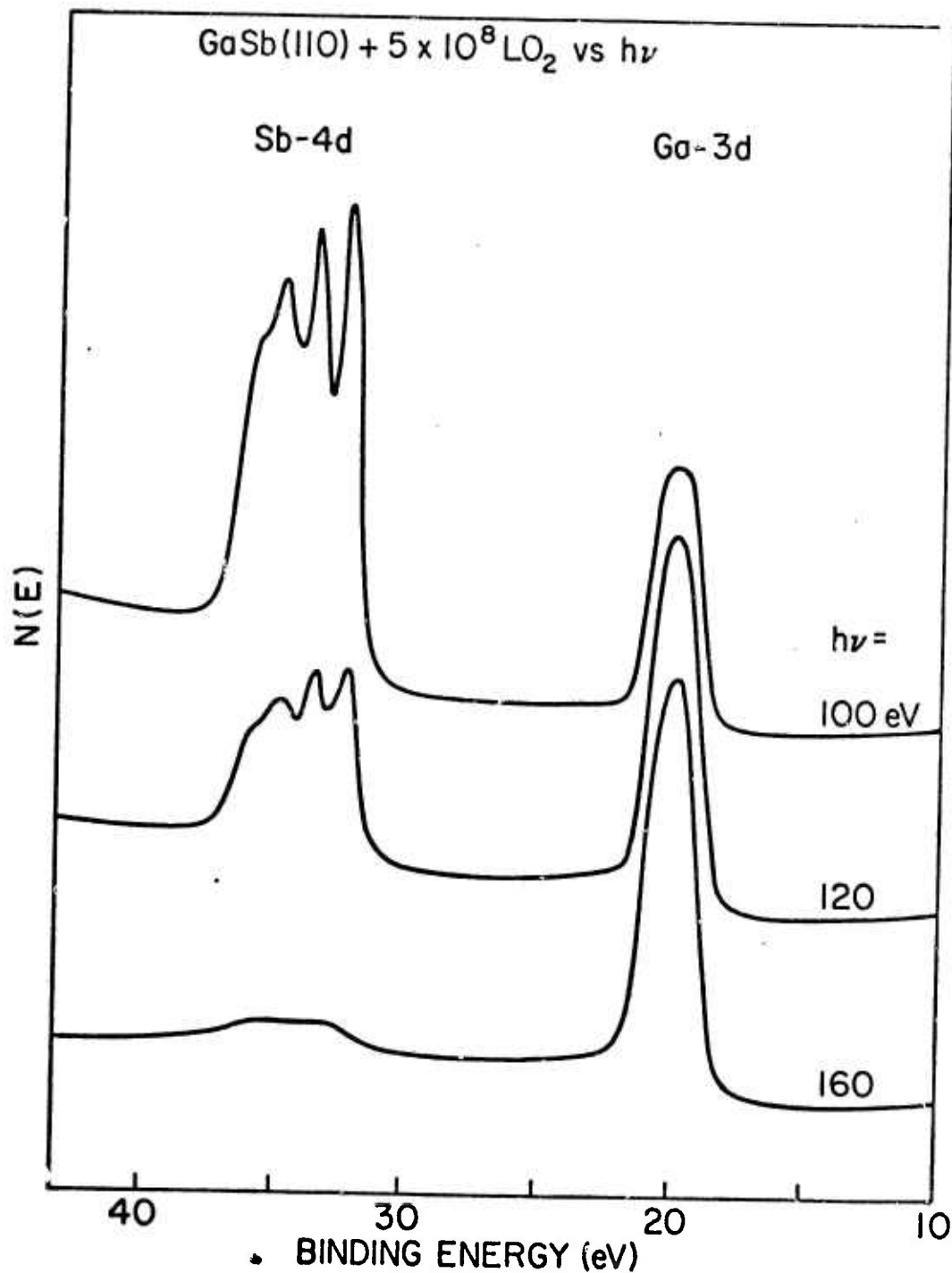


Fig. 8. EDC's OF GaSb EXPOSED TO $5 \times 10^8 \text{ L O}_2$ FOR THREE PHOTON ENERGIES SHOWING THE VARIATION IN THE CROSS-SECTION OF THE Sb-4d LEVELS VERSUS PHOTON ENERGY.

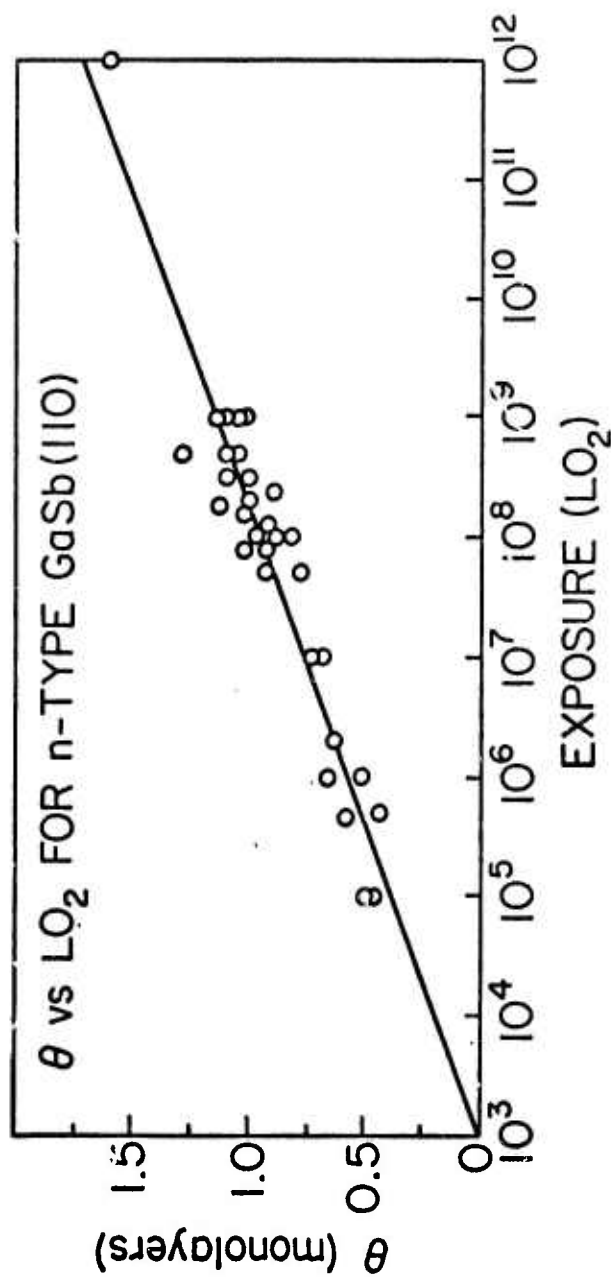


Fig. 9. THE RELATIVE OXYGEN UPTAKE OF THE GaSb (110) SURFACE AS A FUNCTION OF EXPOSURE, DETERMINED FROM THE AREA UNDER THE O-2p LEVEL. The vertical scale is obtained by comparing the areas under the O-2p in the spectra of Fig. 8 to the areas under the O-2p in Fig. 5 for GaAs.

3. Discussion

A. Introduction

Crystals of the III-V compounds have the zincblende structure, illustrated in Fig. 10, where we give a view of the lattice along the $(\bar{1}\bar{1}0)$ axis and terminate it on the ideal (110) , (111) , and $(\bar{1}\bar{1}\bar{1})$ faces. We should note that, in terminating the lattice to create the ideal surfaces, one covalent bond per surface site has been broken, leaving three intact.¹⁴

On the (110) surface, which is the cleavage face of the III-V semiconductors, a rearrangement of charge takes place, and it becomes energetically favorable for the surface atoms to seek a bonding configuration more characteristic of their covalent bonding in small molecules. To be more precise, the currently accepted model is that the surface Ga now has only three electrons (in an sp^2 configuration), all involved in back bonding, while the As has five electrons (in a $p^3 s^2$ configuration), three of these electrons take part in the back bonds (p^3) and the remaining two (s^2) are the "dangling bond orbitals,"¹⁴⁻¹⁸ This charge rearrangement has two important consequences. First, the change in the bonding configuration of the surface atoms results in a distortion of the lattice at the surface consistent with the planar sp^2 Ga back bonds and the prismatic p^3 As back bonds (see Fig. 11).^{15,17,18} Secondly, since all of the electrons on the surface Ga are used in forming the back bonds, the Ga has no filled surface state orbitals. The surface As atoms, on the other hand, have two available electrons to contribute to the filled surface state band which lies well below the valence band maximum.^{14,19} The position of the filled and empty surface states on an energy level diagram is also shown in Fig. 11 after Gregory et al.^{7,14,15,20-22}

One of the major predictions of the model of Fig. 11 is that, for the (110) surface, oxygen is adsorbed preferentially on the arsenic atoms by interacting with the filled surface states. Furthermore, since all the bonding electrons associated with the surface gallium atoms are involved in the back bonds, the oxygen will bond to the gallium only after one or more of the back bonds are broken.^{1,7,14}

IDEAL GaAs LATTICE

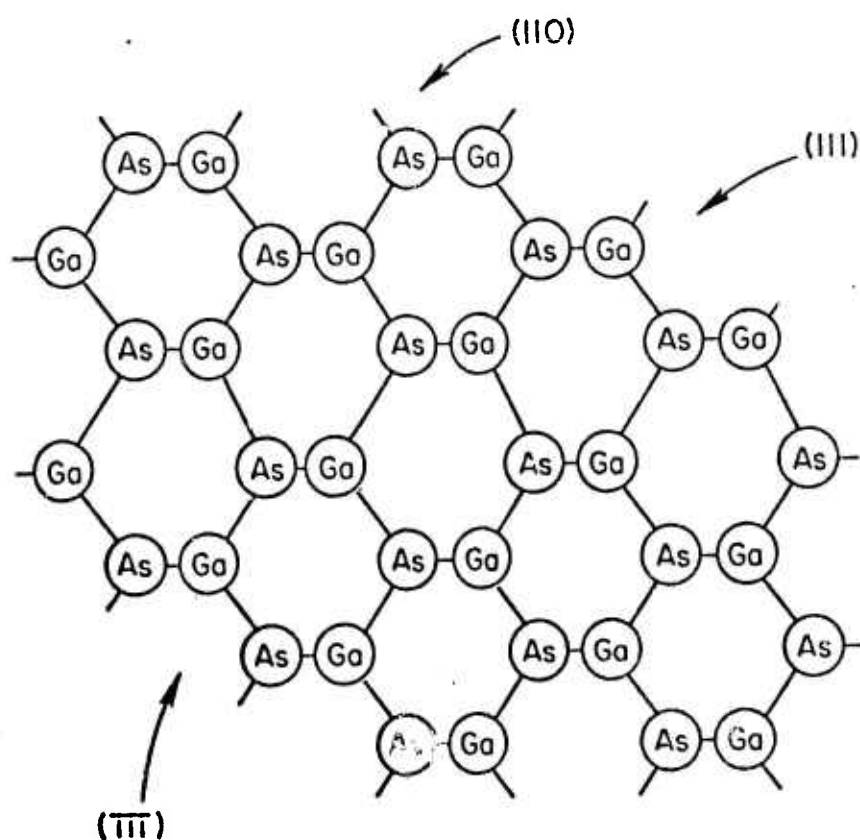
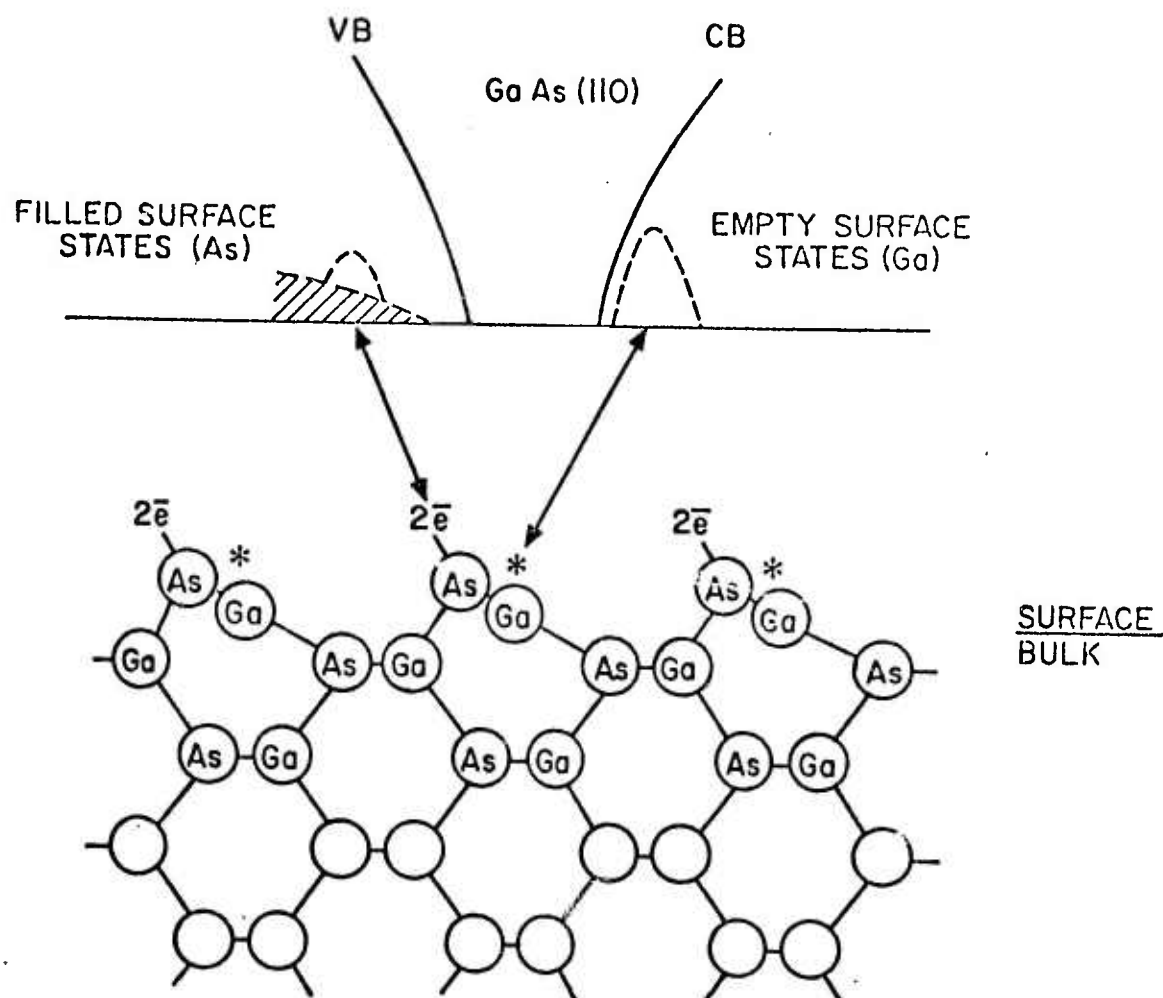


Fig. 10. SCHEMATIC OF THE GaAs LATTICE TERMINATED ON THE IDEAL (110) , (111) , AND $(\bar{1}\bar{1}\bar{1})$ SURFACES. The view is along the (110) direction.



* LOCATION OF EMPTY SURFACE STATE

Fig. 11. THE RECONSTRUCTED (110) SURFACE WITH AN ENERGY LEVEL DIAGRAM SHOWING THE LOCATION OF THE FILLED (As-DERIVED) AND EMPTY (Ga-DERIVED) SURFACE STATES.

In the following part of this section, we will use the above model to interpret our chemical shift results, and we will also compare the measured shifts to shifts obtained from standard compounds using conventional XPS.

In the third part of this section, we will use the photon energy dependence of the spectra to determine the relative escape depth of GaAs for $20 \text{ eV} \leq h\nu \leq 240 \text{ eV}$. We will then be able to determine the absolute escape depth by estimating the thickness of the chemisorbed oxygen layer.

B. Interpretation of Chemical Shifts

The spectra of Fig. 5 for the chemisorption of oxygen on GaAs (110) clearly show that charge is transferred preferentially from the surface arsenic atoms to the adsorbed oxygen. The gallium core level shows no shift, indicating that the experimental situation fits in very well with the model presented above. However, the 2.9 eV shift of the As-3d level is much larger than what one would expect for a single or even a double arsenic-oxygen bond as found in bulk oxides such as As_2O_3 or As_2O_5 .^{1,23,24} These shifts are 0.87 and 1.9 eV for each single or double bond, respectively.²³ In the case of the oxides, each oxygen ligand competes for the charge on the arsenic since oxygen is more electronegative than arsenic. If we replaced one or two of the oxygens with less electronegative ligands, there would be less competition for the charge on the arsenic, but the charge transfer due to each ligand would still be away from the arsenic, and the situation for the remaining oxygen ligand would not be that different from As_2O_3 . If, however, we replaced two of the oxygens by three gallium atoms which are actually transferring charge to the arsenic, the oxygen has the only ligand in which there is charge transfer away from the arsenic. That is, the single oxygen ligand no longer has any competition for the charge on the arsenic from the other (gallium) ligands. Consequently, the oxygen ligand in this case could give a much larger shift than would be predicted by a simple analysis where the different electronegativities of the various ligands had not been taken into account. This is, of course, precisely the situation for oxygen chemisorbed on an arsenic atom on the

GaAs (110) surface. Therefore, the 2.9 eV shift we observe for the As-3d level could reasonably be explained by a single oxygen arsenic bond.

Since no peak characteristic of Ga_2O_3 (a 1 eV shift of the Ga-3d level) is seen in Fig. 5, we can conclude that definitely no back bonds have been broken in the chemisorption process.

The situation presented in Fig. 7 for GaSb is clearly quite different from that of GaAs. In this case, we see a simultaneous shift in both the Ga and Sb core levels. This indicates that back bonds have been broken in order to allow charge transfer from both the surface gallium and antimony atoms, resulting in the simultaneous formation of both gallium and antimony oxides. The difference between GaSb and GaAs can be understood by considering the ionicities of Ga, As, and Sb. There is a larger electronegativity difference between Ga and As than between Ga and Sb. This would imply that the GaAs bond is stronger than that of GaSb, giving a surface that is more resistant to chemisorption of oxygen. The dependence of oxygen uptake with electronegativity difference that we see here agrees with the work of Mark and Creighton²⁵ in which they observe a decrease in oxygen uptake with increasing bonding ionicity.

Combining these results together in the light of the model presented above gives us a fairly consistent picture of what can happen on the surface of a III-V compound during exposure to oxygen: the oxygen will adsorb preferentially to the column V element (As, etc.), while adsorption to the column III element will occur only if back bonds have been broken.

C. Determination of the Escape Depth

The relative escape depth for electrons with kinetic energies between 20 and 200 eV may be determined from our experimental results quite simply and elegantly by merely plotting the ratio of the areas under the shifted and unshifted arsenic peaks, As/AsI, as a function of photon energy. This curve is given in Fig. 12. The horizontal scale gives the kinetic energies of the electrons in the crystal. The photon energies that were used for each point are obtained by adding 40 eV (the approximate As-3d binding energy) to the given kinetic energies. The

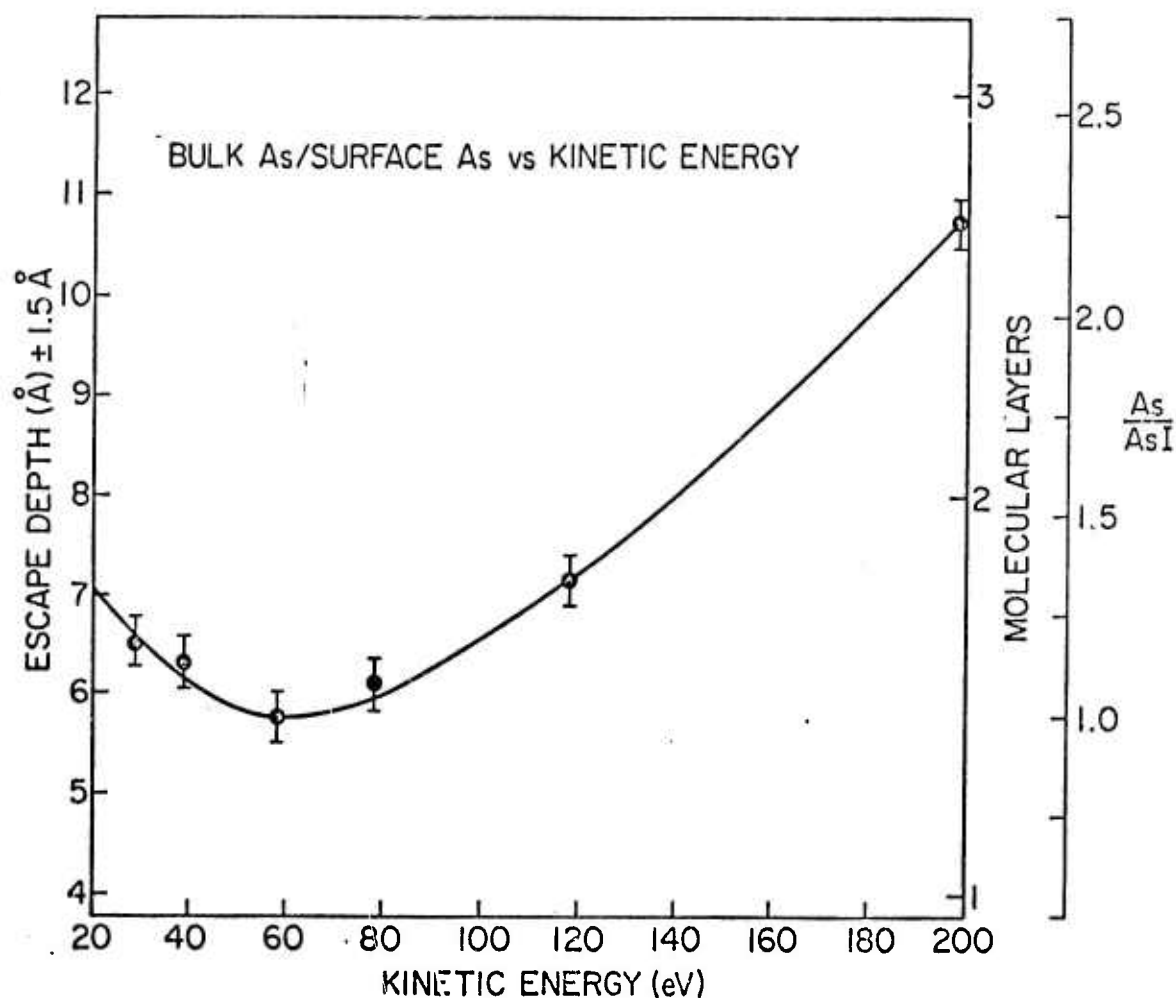


Fig. 12. PLOT OF THE RATIO OF THE UNSHIFTED TO SHIFTED As-3d LEVELS AS A FUNCTION OF ELECTRON KINETIC ENERGY FOR THE GaAs (110) SURFACE + 10^{12} L O_2 (RIGHT-MOST SCALE). The other two scales give the escape depth in Angstroms and molecular layers (see text).

right-most vertical scale gives the actual ratio of the areas of the unshifted to shifted As-3d peaks as measured from the spectra of GaAs (110) + 10^{12} for various photon energies. The minimum in the escape depth curve occurs around 60 eV kinetic energy (100 eV photon energy) and was taken from the top spectrum of Fig. 5. The error bars associated with the points are due to the uncertainties in measuring the areas under the peaks.

One assumption that allows us to calculate the escape depth is that there is one oxygen per surface arsenic atom by an exposure of 10^{12} L O₂. It seems adequately clear that saturation is reached at 10^{12} L O₂, but we have not yet done any measurements to determine the actual oxygen coverage at this exposure. However, from the results of Fig. 5, it does seem to be a reasonable assumption. The major source of error is introduced into the calculation when we try to fix the absolute value of the escape depth. This entails estimating the thickness of the topmost GaAs plus chemisorbed oxygen layer. This one thickness will then allow us to give an absolute value to the escape depth.

Assuming that the GaAs (110) surface plus a saturation coverage of oxygen can be treated as a system composed of two uniform layers, i.e., the surface plus oxygen and the rest of the crystal, the escape depth, $L(E)$, can be written as

$$L(E) = \frac{x_1}{1/\ln (A_s/A_{sI}) + 1} \quad (1)$$

where x_1 is the thickness of the top layer (GaAs plus oxygen).²⁴ Using tabulated values for the radii of arsenic and oxygen, we let x_1 equal 4 ± 1.5 Å.²⁵ This with Eq. (1) gives the $L(E)$ scale on the left-hand side of Fig. 12. The second scale on the right of Fig. 12 giving the molecular layers is obtained by dividing the nominal escape depth by the distance between the (110) planes which is approximately 4 Å. At the minimum, the escape depth is 5.8 ± 1.5 Å or approximately 1.5 molecular layers, substantiating our claims of a very high surface sensitivity.

4. Summary

In the preceding discussions, we have shown that, when the cleaved (110) surface of GaAs is exposed to oxygen, only chemisorption takes place, and this is on the surface arsenics, not on the gallium. No back bonds are broken even for very large exposures. We have also studied the oxidation of GaSb (110). In GaSb, oxidation takes place immediately, without the intermediate chemisorption step characteristic of GaAs. The oxygen uptakes for GaAs and GaSb were found to be quite different.

The escape depth of GaAs was measured for electron kinetic energies between 20 and 200 eV. At the minimum, which is at 60 eV electron kinetic energy, the escape depth was found to be $5.8 \pm 1.5 \text{ \AA}$.

Therefore, using this very surface sensitive photoemission technique, we have been able to successfully study the chemistry at the surface of GaAs and GaSb for submonolayer coverages of oxygen.

Acknowledgment

We would like to thank the staff of the Stanford Synchrotron Radiation Project for their cooperation and assistance in this study.

References

1. P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. Lett. 35, 1356 (1975) and 37, 1166 (1976).
2. S. Doniach, I. Lindau, W. E. Spicer, and H. Winick, J. Vac. Sci. Technol. 12, 1123 (1975).
3. I. Lindau and W. E. Spicer, J. Electron Spectrosc. 3, 409 (1974); M. Klasson, J. Hedman, A. Berndtsson, R. Nilsson, and C. Nordling, Physica Scripta 5, 93 (1972).
4. K. Siegbahn, J. Electron Spectrosc. 5, 3 (1975); U. Gelius, Physica Scripta 9, 133 (1974); T. D. Thomas, J. Am. Chem. Soc. 92, 4184 (1970); J. M. Hollander and D. A. Shirley, Ann. Rev. Nucl. Sci. 20, 435 (1970).

5. W. Ranke and K. Jacobi, *Surf. Sci.* 47, 525 (1975).
6. H. Ibach, *Surf. Sci.* 53, 444 (1975).
7. W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, *J. Vac. Sci. Technol.* 13, 780 (1976).
8. J. M. Paterson, *IEEE Trans. Nucl. Sci.* NS-22, 1366 (1975).
9. J. L. Stanford, V. Rehn, D. S. ~~ser~~, V. O. Jones, and A. Klugman, *Vacuum Ultraviolet Physics*, ~~ser~~, E. Koch, R. Haensel, and C. Kunz (Pergamon, New York, 1975), p. 783.
10. F. C. Brown, R. Z. Bachrach, S. B. M. Hagstrom, and C. Pruett, *ibid*, p. 785.
11. R. Z. Bachrach, S. A. Flodstrom, R. S. Bauer, V. Rehn, and V. O. Jones, Stanford Synchrotron Radiation Project Report No. 75/13 (1976).
12. G. F. Derbenwick, D. T. Pierce, and W. E. Spicer, *Methods of Experimental Physics* (Academic Press, New York, 1974), Vol. 11, pp. 89-92.
13. I. Lindau, P. Pianetta, and W. E. Spicer, *Phys. Lett.* 57A, 225 (1976), and *Proceedings of the International Conference on the Physics of X-ray Spectra*, 30 Aug-2 Sep 1976, National Bureau of Standards, Gaithersburg, Maryland.
14. P. E. Gregory, W. E. Spicer, S. Ciraci, and W. A. Harrison, *Appl. Phys. Lett.* 25, 511 (1974); P. E. Gregory and W. E. Spicer, *Phys. Rev. B* 13, 725 (1976) and *Surf. Sci.* 54, 229 (1976); W. E. Spicer and P. E. Gregory, *Crit. Rev. Solid State Sci.* 5, 231 (1975).
15. W. A. Harrison, *Surf. Sci.* 55, 1 (1976).
16. H. C. Gatos and M. C. Lavine, *J. Electrochem. Soc.* 107, 427 (1960); H. C. Gatos, *J. Appl. Phys.* 32, 1232 (1961); H. C. Gatos, *J. Electrochem. Soc.* 122, 287C (1975).
17. A. U. Mac Rae and G. W. Gobeli, in *Semiconductors and Semimetals*, Vol. 2, *Physics of III-V Compounds*, eds., R. K. Willardson and A. C. Beer (Academic Press, New York, 1966), pp. 115-137; A. U. Mac Rae, *Surf. Sci.* 4, 247 (1966).
18. A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, *Phys. Rev. Lett.* 36, 1058 (1976); C. B. Duke, A. R. Lubinsky, B. W. Lee, and P. Mark, *J. Vac. Sci. Technol.* 13, 761 (1976).
19. *Proceedings of the 3rd Annual Conference on the Physics of Compound Semiconductor Interfaces* in *J. Vac. Sci. Technol.* 13, No. 4 (1976).
20. J. D. Levine and S. Freeman, *Phys. Rev. B* 2, 3255 (1970).

21. D. J. Miller and D. Haneman, Phys. Rev. B 3, 2918 (1971).
22. R. Ludeke and L. Esaki, Phys. Rev. Lett. 33, 653 (1974), and R. Ludeke and A. Koma, Phys. Rev. Lett. 34, 817 (1975).
23. M. K. Bahl, R. O. Woodall, R. L. Watson, and K. J. Irgolic, J. Chem. Phys. 64, 1210 (1976).
24. P. Pianetta, Ph.D. Thesis, Stanford University, 1976 (unpublished).
25. P. Mark and W. F. Creighton, Appl. Phys. Lett. 27, 400 (1975).
26. Handbook of Chemistry and Physics, R. C. Weast, ed. (the Chemical Rubber Company, Cleveland, Ohio, 1972), p. E-55.

Appendix B

SURFACE AND INTERFACE STATES ON GaAs (110): EFFECTS OF ATOMIC AND ELECTRONIC REARRANGEMENTS

1. Introduction

In the last few years, there has been a rapid development in research on the surfaces (particularly the (110) cleavage surface) of GaAs and other 3-5 semiconductors. This period has been characterized by the introduction of new or refined experimental tools (e.g., those associated with synchrotron radiation) as well as new theoretical calculations of the surface electronic structure and a combination of theory and LEED experiments which has given insight into the surface atomic arrangements. The first part of this period was characterized by considerable conflict and confusion both with regard to the results of these theoretical and experimental programs and their interpretation. In the last 18 months, this situation has been clarified. In the next part of this appendix, we shall attempt to review this situation and outline the critical points on which there is now some general agreement. We shall also point out areas in which discussions are now going on and present our own considered opinions.

In the final section of this appendix, we shall concentrate on the question of oxidation of the (110) GaAs surface and try to make contact with the question of passivation by native oxides. In particular, we will address the question as to why it is so much more difficult to passivate GaAs than Si. In doing so, we will draw on the fundamental understanding outlined in Sections 2, 3, and 4.A,B.

2. The Present State of Knowledge of (110) and Other Surfaces of 3-5 Compounds

A. Intrinsic Surface Electronic Structure

a. States in the Band Gap

There is now general agreement that the clean (110) cleavage faces of most of the 3-5 materials have no intrinsic filled or empty surface states located in the band gap.¹⁻⁴ Of the materials studied to

date, GaAs, InAs, GaSb, and InSb appear to fall within this class. GaP appears to have no filled surface states in the gap, but there is evidence for empty surface states about 0.5 eV below the conduction band minimum (CBM).² Photoemission studies have detected no strong structure due to filled surface states within about 1 eV of the valence band maximum (VBM),⁵ but a surface sensitive structure 1 eV below VBM has been assigned to filled surface states by Knapp and Lapeyre⁶ in angle-resolved photoemission. Thus, we would suggest that the band gap between empty and filled surface states on the (110) cleavage GaAs face may be of the order 2.5 eV and probably of comparable size on the other 3-5 (110) surfaces.

There is much less data available for other crystal faces of the 3-5 compounds. However, recent studies using photoemission and oxidation of the (111) face of GaAs have convinced the present authors that there are no filled surface states in the band gap.^{7,8}

b. Excitonic Transitions from Ga 3d Core States

In both energy loss⁹ and partial yield¹⁰ experiments, a transition is observed involving 3d or 4d core levels of the column 3 element (e.g., Ga) and states near the CBM. Since the excitation energy was less than that necessary for a one electron excitation into the CBM, it was first assumed that this was a single particle excitation into the empty surface states and that the excitation energy determined the position of the empty surface states.^{9,10} The agreement discussed above, that the intrinsic empty surface states do not lie in the band gap, invalidates this interpretation and verifies earlier suggestions of the excitonic nature of this transition.¹¹ Thus, the strong structure at the threshold of excitation from the column 3 element must be assigned to a surface exciton with binding energy of order 0.5 eV. Once it is recognized that the empty surface states do not lie in the band gap, there is no a priori reason to associate this transition with empty surface states. The exciton may only involve states near the CBM. If this is the case, the lack of such transitions from 3d or 4d states on the column 5 element may be due to atomic selection rules rather than the localization of the empty surface states on the column 3 surface atom.

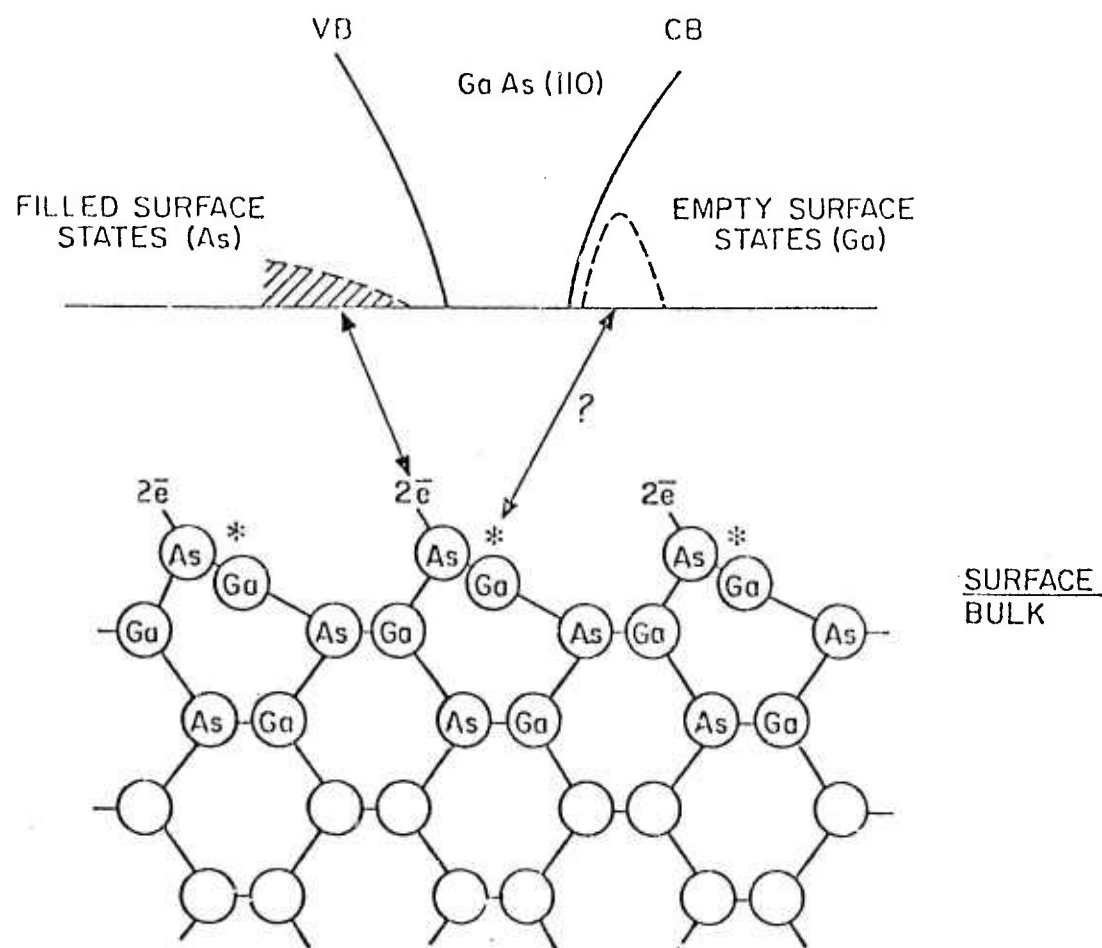
c. Electronic Rearrangement at 3-5 Surfaces

In 1960, Gatos¹² and coworkers have provided evidence that the polar faces of 3-5 compounds rearrange electronically so that the "dangling" bond electrons are localized on the column 5 element. Independently, Gregory et al¹³ concluded (in the GSCH model) that the dangling bond electrons pair up on the As surface atoms on the nonpolar (110) face, as shown in Fig. 1. These electronic rearrangements have been supported by much independent work and are now generally accepted.¹⁴⁻¹⁶

B. Atomic Rearrangement at the Surface

The available LEED data and its interpretation indicates that on the (110) surface the As atoms move outward and the Ga atoms inward.^{16,17} It is very important to recognize that such a rearrangement will move atoms by sizeable fraction of the cell dimensions and lead to large strains between the surface and the rest of the crystal. It is also important to note the arguments of Harrison¹⁸ and others that this surface rearrangement is driven by the need to minimize the covalent bond energies. In particular, Harrison¹⁸ argues that the covalent bond energies will be minimized if the surface As is joined to its three neighbors by p^3 bonds (with the two remaining electrons in a s^2 configuration); whereas, the bond energy of the surface Ga atom would be minimized by bonding it to its three nearest neighbors by sp^2 bonds. Such a scheme would move the As outward and the Ga inward as indicated by the LEED.¹⁶ However, in the opinion of the present authors, there may be a delicate balance between strain and bond energies which will determine the exact surface rearrangement.

Further studies of the surface electron structure (which will be reviewed in more detail in Section 3) suggest to us that surprisingly small perturbations of the surface by, for example, imperfections or small amounts of chemi-adsorbed oxygen may cause significant changes in the surface rearrangement.



* LOCATION OF EMPTY SURFACE STATE

Fig. 1. THE (110) GaAs SURFACE. Both the electronic and atomic surface rearrangements are indicated.

The suggestion that the surface rearrangement is driven by minimizing the bond energy for the surface atoms seems to us to be very important. Surface defects or adatoms may, for example, interact with the surface atoms and change the minimum bond energies. This may, in turn, lead to new rearrangements. When one also takes into account the large strains in the clean surface, the possible sensitivity of the surface atomic rearrangement becomes particularly striking. We will return to this theme a number of times in this paper.

C. Schottky Barrier Formation

Since it is clear that there are no intrinsic surface states in the band gaps of most of the 3-5 compounds for the (110) cleavage faces, it follows at once that the Schottky barrier pinning found and studied so profitably by Mead, McGill, McCaldin, and their coworkers¹⁹ is not due to intrinsic surface states, but due to states induced by the metal. We will not attempt to review the various mechanisms suggested for this pinning since Heine²⁰ made his original suggestions in this regard. However, we will make the observation that no explanation of pinning can be considered complete until atomic rearrangements at the metal-semiconductor interface are properly taken into account. It is even conceivable that the systematic changes noted by Mead et al.¹⁹ due to electronegativity differences are closely related to such rearrangement. Much fundamental work must be done in this area.

D. Extrinsic Surface States in the Band Gap

One of the results that led to confusion in determining the surface state configuration was the pinning near mid-gap found originally in all studies on (110) cleaved surfaces of n-type GaAs,^{13,21} except for those of Van Laar et al.¹ Several groups, including our own, erroneously inferred that this pinning was due to intrinsic empty surface states. Recognizing that this is not the case, it is now apparent that the states responsible for the pinning are extrinsic in nature, i.e., are due to defects or surface impurities. It is thus apparent that extrinsic as well as intrinsic surface states must be taken into account in general.

We have developed a fairly extensive data base involving a total of 16 cleaves on 4 different crystals in the same equipment without breaking vacuum.^{4,22} Some of this data will be presented and discussed here, and a complete report will be made elsewhere.²³ It appears from our work that the extrinsic states are most likely due to surface defects associated with the cleaving. However, cleavage effects can be more subtle than those associated with the visibly roughened cleaves displayed by Van Laar and Huijser.² Both Eastman and Gudat³ and our group have found that pinning can occur even when the cleaved surface has a "mirror-like" finish. On the other hand, if, as Van Laar and Huijser² showed, the cleavage surface is strongly roughened, pinning has always been found.

When pinning does not occur on n-type samples, it can be induced by a small fraction of a monolayer of adsorbed oxygen.^{3,4, 2,23} Studies of the Ga 3d excitonic transition via partial yield measurements (see also Section 2.A.b and Ref. 24) suggest that this effect of oxygen cannot be associated with any movement of the intrinsic surface states. Rather, it must be assigned to extrinsic states induced by the oxygen. It also raises the question as to whether the Schottky barrier pinning may be due to extrinsic rather than intrinsic states. In this regard, it is interesting to note that in the few cases reported to date^{4,25,26} the Schottky barrier pinning position is surprisingly close to that in which the Fermi level is stabilized by oxygen adsorption.

It is important to note that Van Laar and Huijser² report an inability to prepare (110) GaAs surfaces by sputtering and annealing in which the Fermi level was not pinned. This suggests that, on an atomic level, these surfaces are less perfect than the best that can be produced by cleaving. Based on our present knowledge, one would infer that this pinning is due to extrinsic surface states. However, this has not been definitively established.

It is very important that we recognize the occurrence of extrinsic as well as intrinsic surface states on semiconductor surfaces. The fact that it only takes a surface state density of approximately $10^{12}/\text{cm}^2$, i.e., one surface state per thousand surface atoms, to pin the Fermi level, means that a relatively small number of extrinsic surface states can produce pinning.

3. Surface Valence Electronic Structure and Atomic Rearrangement

A. Introduction

In this section, we will present and discuss the valence electronic structure from a representative sampling of the large data base mentioned earlier. The most complete compilation of this data is to be found in the thesis of P. Pianetta.²² We have found striking variations from cleave to cleave in the surface valence electronic structure and find that interesting correlations may be made with the occurrence or absence of pinning on n-type GaAs (110).²³ This will be reported first. Secondly, we describe rather striking changes in this electronic structure induced by small quantities of oxygen. We also discuss the effect of the same oxygen coverage on the partial yield spectrum involving the 3d-excitonic transition. A correlation is also reported between the uptake of oxygen and changes in valence band structure. Suggestions are made concerning these changes in surface valence band structure and the rearrangement of atoms at the surface.

B. Variations in Surface Electronic Structure

In Fig. 2, we present the results of theoretical calculations of the local density of states near the surface by Chelikowsky, Louie, and Cohen.²⁷ Similar results have been obtained by Calandra, Manghi, and Bertoni.²⁸ The striking thing about these calculations is that they show a very strong variation in the density of states in the last few atomic levels due to changes in the lattice rearrangement at the surface. We have found similar variations in valence electronic structure as reflected in the EDC's for various cleaves even on the same crystal. This is illustrated by Fig. 3 where data from four different cleaves on two crystals are shown.

The spectral distribution of the emission was studied in detail and is reported elsewhere.^{22,23} A photon energy of 21 eV was chosen for the studies since the minimum escape depth is about two molecular layers and the matrix elements for the valence band are relatively strong (they decrease rapidly with increasing $h\nu$).

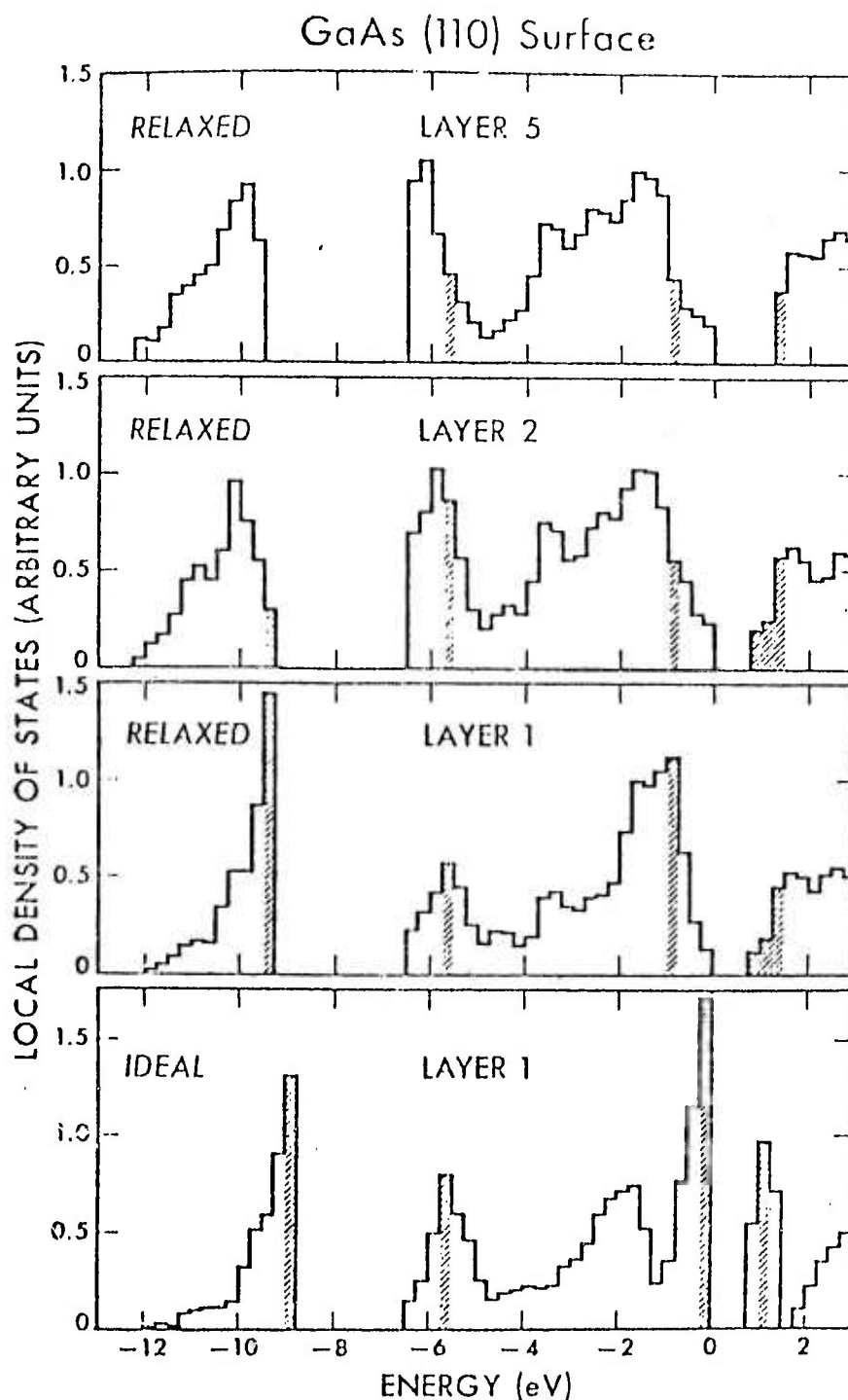


Fig. 2. THEORETICAL RESULTS FROM CHELIKOWSKY ET AL²⁷ SHOWING THE CHANGE IN SURFACE ELECTRONIC STRUCTURE BETWEEN AN "IDEAL," i.e., UNREARRANGED SURFACE, AND A SURFACE REARRANGED (RELAXED) AS INDICATED IN FIG. 1. NOTE THE LARGE CHANGES NEAR THE BAND GAP, i.e., ZERO OF ENERGY. Surface states are indicated by cross-hatched areas.

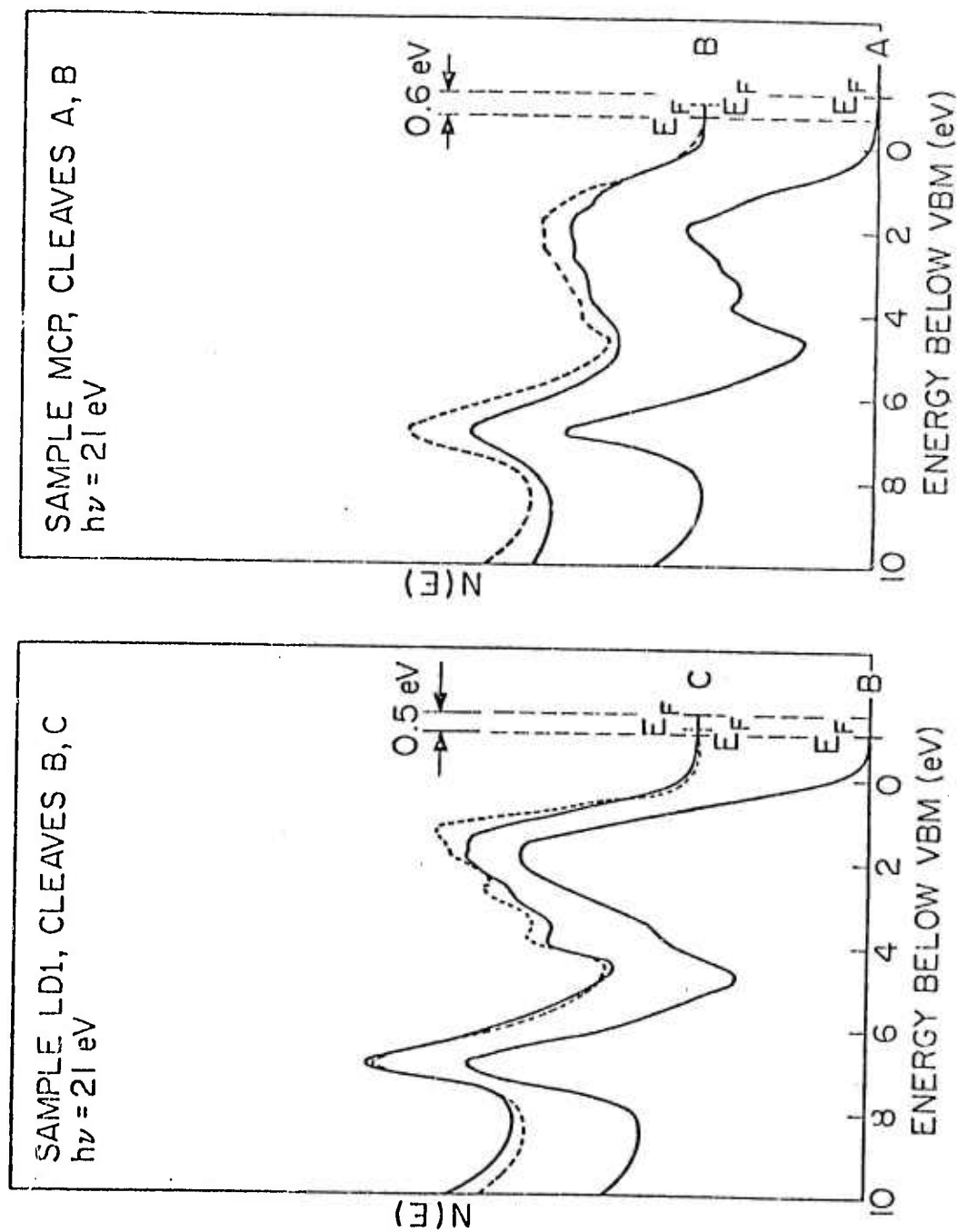


Fig. 3. ENERGY DISTRIBUTION CURVES (EDC's) SHOWING TYPICAL DIFFERENCES IN THE VALENCE ELECTRONIC STRUCTURE AT THE SURFACE FOR DIFFERENT CLEAVES AND DIFFERENT GaAs CRYSTALS. The solid curves for LDIC and MCPB were taken less than an hour after cleaving; whereas, the dashed curves were taken 12 and 20 hours, respectively, after cleaving (pressure about 10^{-11} torr).

Recognizing the importance of crystal orientation and angle of photoemission, care was taken that these parameters were carefully reproduced on each cleave of a given crystal; likewise, alignment from crystal to crystal was reproduced as closely as possible.²² Details of the experimental arrangement is given elsewhere.^{22,23} It is sufficient to mention here that a PHI cylindrical mirror analyzer was used with integration over a large range of angles.

The energy distribution curves (EDC's) of Fig. 3 clearly suggest a strong variation of electronic structure in the top 4 eV of the valence band from cleave to cleave. Up to four pieces of structure can be resolved on some cleaves. These are approximately equally spaced and 0.5-0.8 eV apart. To the first approximation, one might describe the variation from cleave to cleave in terms of a variation in relative intensity and sharpness of these peaks. Note also the variation in the surface position of the Fermi level (marked as E_F in the figure).

For two samples, the crystal was measured after it had been left in the dark for some hours. As can be seen from Fig. 3, sample LDI, cleave C sharpened noticeably and the relative strength of certain peaks changed after 12 hours in the dark; whereas, the structure of sample MCP cleave B changed very little after 20 hours in the dark (pressure in both cases was of the order 10^{-11} torr). For both crystals, a movement of the Fermi level occurred during the time in the dark as shown in Fig. 3. We believe it is most likely that the changes observed were a result of room temperature annealing; however, the effect of adsorption of residual gases (as discussed in the next section) cannot be ruled out.

We attribute the variations in the EDC's of Fig. 3 from cleave to cleave to changes in the surface electronic structure and, in turn, suggest that this is due to detailed variations in the atomic rearrangement at the surface. Note that, for two of the curves of Fig. 3, the surface Fermi level position corresponds to the CBM (i.e., the bulk Fermi level position for these n-type samples); whereas, in the other cases, the surface Fermi level is pinned in the band gap. We attribute this pinning to surface defects or impurities. As mentioned in an earlier publication,⁴ there is a correlation between the sharpness of the valence band structure and the occurrence of surface Fermi level pinning. Where

such pinning occurs, the valence structure, within 4 eV of the VBM, is usually (but not always) smeared out; where no pinning occurs, sharp structure is always found in the critical valence band structure within 4 eV of the VBM.

To summarize, strong variations are found in the surface electronic structure from cleave to cleave. These are attributed tentatively to variations in rearrangement of the surface atoms. It is of clear importance that detailed ELEED or other structural studies be made and correlated with the EDC's.

C. Effects of Oxygen Chemisorption

a. Oxygen Chemisorption and Atomic Surface Rearrangement

In Section 2, it was suggested that the atomic rearrangements on the GaAs (110) surface was driven by electronic reorganization among the surface atoms followed by new bonding schemes which will serve to minimize bond energies. If this is the case, the consequence is that chemisorption of, e.g., oxygen, may produce a second reordering of electrons between the surface atoms. This, in turn, could lead to a new rearrangement of the surface atoms and a corresponding change in surface electronic structure. Evidence for such changes in electronic structure will be given in this section. The surprising characteristic of this data is that very small oxygen coverage can produce first order changes in the valence electronic structure. In Section 2.B, we pointed out the strains which must be present in the surface because of the lattice mismatch between the rearranged surface and the rest of the crystal. We now suggest that oxygen chemisorption can produce long range effects by changing these strain fields as discussed below.

It is now well established through chemical shift data that there is a large transfer of charge from As surface atoms to the oxygen on chemisorption.^{4,29} This transfer, by changing the electron population associated with the As surface atoms, should change the bonding scheme locally. This local effect could then make itself felt over a long distance by virtue of interaction with the large strain field or by other means.

b. Effects of Low (Up to 10 L) Oxygen Exposures

In Figs. 4 and 5, we give typical data showing the effect of chemisorbed oxygen on the valence band structure. In Fig. 6, we present data showing oxygen coverage as a function of oxygen exposure. The data points of Fig. 6 were obtained either by measuring from an EDC taken at, for example, $h\nu = 100$ eV, the area under the oxygen 2p peak (Fig. 6a) or that under the shifted As 3d core level (see, e.g., Fig. 7 of this article, Fig. 1 of Ref. 4, or Fig. 1 of Ref. 29 (1976)). The saturation value for this chemisorption of oxygen is taken to be one-half a monolayer. Details are given elsewhere.^{22,23}

In Fig. 4, note that first order changes in the EDC's for sample MCPB occur for exposures between 1 and 10 L of oxygen; i.e., the sharp structure appears in the EDC where none existed prior to the oxygen exposure. The precautions described elsewhere^{4,29} were taken to make sure only unexcited molecular oxygen was present in all of the work reported in Section 3. The limit of detectability using the present techniques is about a percent of monolayer coverage. This occurred between 10^5 and 10^6 L exposure where the strong changes for MCPB take place. Thus, while the changes in Fig. 4 must be associated with variations in the electronic structure on the majority of the surface atoms (in order to explain their magnitude), there is oxygen chemisorption on less than one in a hundred surface atoms. The conclusion appears inescapable--the oxygen is producing long range effects which extend over many atomic sites.

One has to be sure that changes such as those in Fig. 4 are not due to Fermi level pinning which varies with position across the sample ("patch" effect) before oxygen exposure and is made uniform by oxygen addition. Evidence for such a patch effect has been presented and discussed in some detail by Gudat and Eastman.³ In the present work such a possibility can be eliminated since there is such pronounced sharpening of the structure in the first 4 eV of the valence band but no corresponding sharpening of strong peak at 7 eV or in the upper edge of the EDC defining the valence band maximum (VBM). (As Gudat and Eastman³ pointed out, a "patch" effect would produce extra structure at the VBM.) Also, note that there is little shift in the Fermi level with exposure

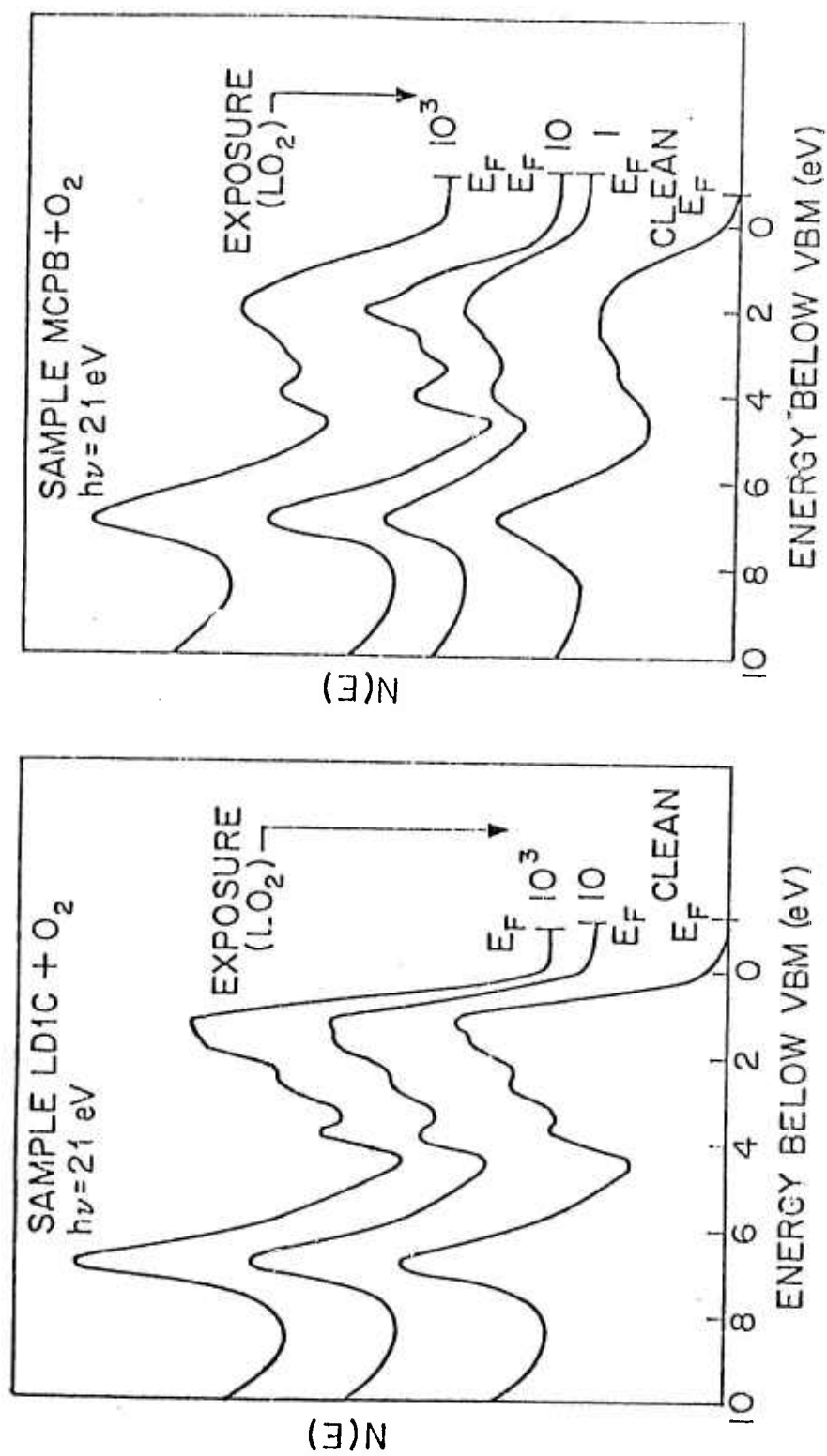


Fig. 4. THE EFFECT OF LOW EXPOSURES (GIVEN IN LANGMUIR, L) OF OXYGEN ON THE VALENCE ELECTRONIC STRUCTURE AT THE SURFACE. Note the first order change in MCPB between 1 and 10 L. The oxygen coverage at 10 L is estimated to be less than 1% of a monolayer.

and none at all between 1 and 10 L. Thus, there seems no way in which the sharpening in Fig. 4b can be fully accounted for by the removal of nonuniform Fermi level pinning upon oxygen exposures.

As can be seen from Fig. 4, there was much less sharpening at low exposures in a case where the valence band structure was sharp before oxygen exposure. This trend was systematically observed, i.e., where sharp structure appeared before cleaving, the effect of oxygen exposures in the 10 L range were only to produce relatively small changes in the valence band density of states. However, where the EDC's before oxygen exposure were smeared, without sharp structure, oxygen exposure in the 10 L range tended to produce strong sharpening.

It is premature to attempt a definitive explanation of the behavior shown in Fig. 4; however, as mentioned above, the behavior is suggestive of strain effects smearing the valence band structure (the strain could also produce the defects which pin the Fermi level) and this strain being relieved by small (< 0.01) oxygen coverages. It is intriguing to consider the possibility of dislocation pinning at the surface being removed by the small oxygen exposure. However, much more work must be done before more complete understanding is obtained.

c. Phase-like Change Near 10^6 L Exposure

In Fig. 5, we present EDC's of the surface valence electron structure for sample LDIC of Fig. 4 over a much wider range of oxygen exposure (up to 10^9 L). As can be seen, there is little change in the valence structure up to exposures of about 10^5 L. However, between 10^5 and 10^6 L, there is a very strong and abrupt change in the valence band structure; i.e., the sharp structure is lost and replaced by an almost featureless "ramp" extending down to the 7 eV peak. Such a transition occurs for all cleaves independent of whether or not the as cleaved surface was characterized by sharp structure or Fermi level pinning. There could be a variation of at least an order of magnitude in the oxygen exposure for which the transition took place for different cleaves.

Not only does the surface valence band structure undergo an abrupt phase-like change at an oxygen exposure of about 10^6 L, but the structure in the partial yield spectra disappears at approximately

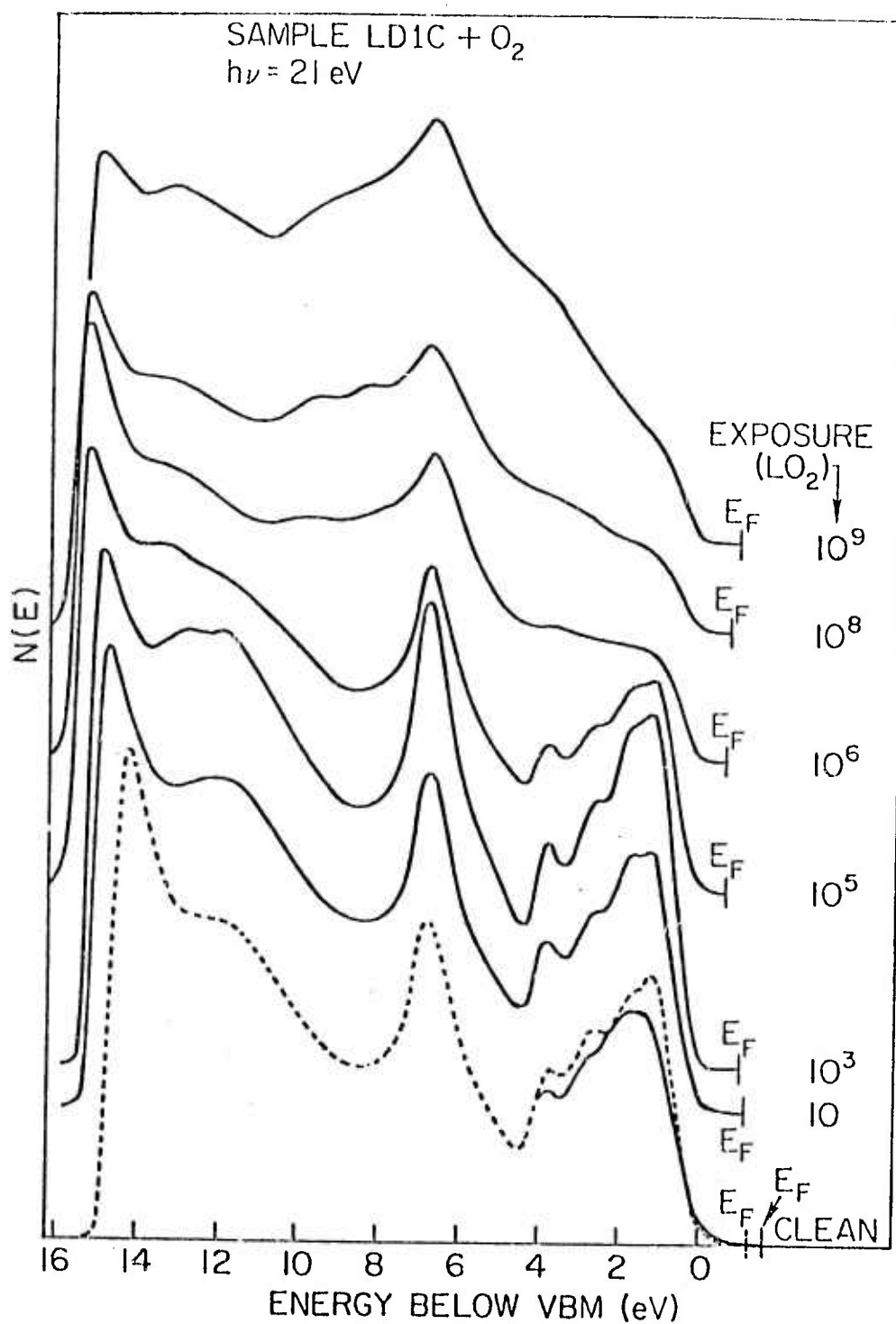


Fig. 5. THE CHANGE IN THE VALENCE ELECTRONIC STRUCTURE FOR EXPOSURES UP TO 10⁹ L. Note the sharp change in structure for exposures between 10⁵ and 10⁶ L. A similar transformation was observed in all samples studied.

the same oxygen exposure (see Fig. 6 of Ref. 4). This is discussed in detail in Appendix C of this report.²⁴ Suffice it to say here that the partial yield structure is due to an excitonic transition at the surface involving a Ga 3d core level and an empty conduction or surface final state. The fact that it disappears at approximately the same oxygen exposure as the surface valence band structure suggests that the oxygen induces a disordering phase-like transition which affects the empty, as well as the filled, surface electronic structure.

The oxygen coverage versus exposure (Fig. 6) also shows a strong change near or just after the phase transition. Only a few percent coverage was achieved up to 10^7 L exposure. Then, about 25% coverage was achieved between 10^7 and 10^8 L exposure. This exposure also coincides roughly with that at which the Fermi level becomes stabilized near mid-gap due to oxygen chemisorption (see Fig. 5 of Ref. 4).

Data discussed above leads us to the suggestion that a phase-like change is induced in the surface rearrangement at exposures near 10^6 L and that this rearrangement tends to disorder the surface in such a way as to remove structure from the top 4 eV of the valence band. It also appears likely that this transition enhances the probability of oxygen chemisorption; however, more precise data are necessary before we can be absolutely sure that the enhancement follows the transition.

d. Summary

A large variation is found in the EDC's from the surface valence band from cleave to cleave, and as a function of oxygen exposure. This variation is tentatively associated with variations in the details of rearrangement of the surface atoms. The need for detailed LEED studies and correlation with photoemission results to test these suggestions is emphasized.

4. Chemisorption, Oxidation, and Passivation

A. Distinction between Chemisorption and Oxidation

In considering the oxygen sorption on 3-5 compounds, it is important to distinguish between chemisorption and oxidation.^{22,23,30} We

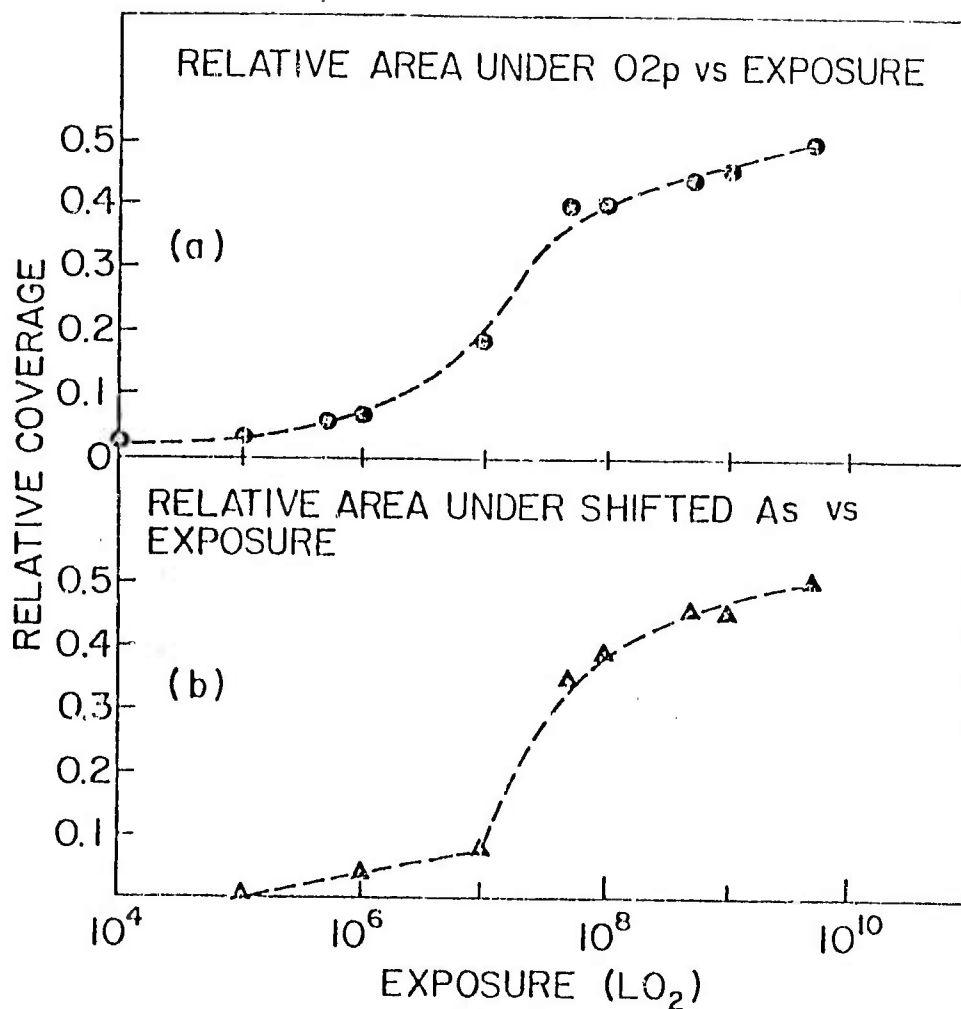


Fig. 6. THE COVERAGE OF CHEMISORBED OXYGEN VERSUS EXPOSURE MEASURED BY TWO DIFFERENT METHODS. Note the break near 10^6 or 10^7 L exposure. The saturation coverage is taken to be one-half of a monolayer.

define chemisorption as the chemical attachment of oxygen to the surface of the 3-5 compound without the direct chemical necessity of breaking any of the bonds of the surface atoms with the rest of the crystal. Oxidation is defined as sorption of oxygen in which s of the surface atoms with the rest of the crystal are broken. By observing chemical shifts of the core levels of the surface atoms, we then empirically determine what type of sorption has taken place. For GaAs (Fig. 7) and InP, a (single) chemically shifted peak is observed only on the surface As atoms (as long as unexcited molecular oxygen is used); we identify this with chemisorption. However, excited oxygen^{4,29} produces an increased shift on the As as well as a Ga shift; this is associated with oxidation. On the other hand, for GaSb, it has been found that even unexcited molecular oxygen will cause oxidation.⁴

Detailed knowledge of the manner in which an oxide or other layer is bonded to a semiconductor is essential if we are to understand the success or failure of a particular approach to passivation in order to form practical devices; e.g., MOS (metal-oxide-semiconductor) transistors. If the oxide or other added layer is connected to the semiconductor through bonds analogous to the "chemisorption" bonds defined above, no bonds need be broken at the semiconductor surface and the density of defect states at the interface will be minimized. On the other hand, if processes analogous to the oxidation described above occur at the interface, there will be an increase in broken bonds at the interface associated with partially oxidized As or Ga atoms which will contribute to the density of interface states.

To follow the GaAs (110) example in a straightforward but simplistic way, if the oxide or other passivation layer bonds through the two excess or "dangling" electrons on the As surface atom, there is no absolute necessity to break bonds associated with As and Ga atoms in the outermost GaAs layer (Fig. 9); however, in order for the oxidation to proceed a bit further by, for example, bonding a fraction of the Ga atoms to oxygen, electrons must be partially removed from GaAs bonds breaking those bonds and leaving some of the electrons previously associated with them chemically "unsaturated." Thus, the number of harmful interface states would increase. Only if the outermost GaAs layer was completely swept away and incorporated in the oxide and the oxide bonded

only to the "dangling" electrons of the As atoms in the next layer of GaAs, would the density of harmful interface states be minimized. Once again, it must be emphasized that this is, at best, a first approximation to a complex situation; however, it is hoped that it will provide a starting point for useful discussion and fruitful research.

3. Chemisorption and Oxidation of GaAs (110)

As mentioned in the last section, for the 3-5 materials, studies of the chemical shift of the core states at the surface have provided a convenient method of distinguishing between chemisorption and oxidation. When chemisorption occurs on the (110) face, a relatively large chemical shift is observed on the column 5 surface atom and no shift is seen on the Ga.²⁹ As Fig. 1 illustrates, the "two dangling bond" electrons are available on the As but all of the three valence electrons associated with the surface Ga are tied up in covalent bonds.

Figure 7 gives spectra taken at $h\nu = 100$ eV.^{22,23} The uppermost curve shows the position of the As and Ga 3d levels for the clean surface. The second curve shows the effect of exposure to 10^{12} L of unexcited O_2 . Such an exposure ensures saturation of chemisorption. As can be seen, a strong As peak (labeled AsI) is observed shifted by 2.9 eV and no shift is observed for the Ga 3d. In addition, a peak just below the VBM has appeared due to the oxygen 2p levels (the matrix elements for excitation from the GaAs valence band are very small for $h\nu = 100$ eV). The third curve (labeled "Heavily Oxidized I.G.") shows the spectra after exposure to an additional 5×10^5 L of oxygen excited by turning on an ion gauge (with 0.4 ma of ionization current) as described elsewhere^{22,29} and oxide formation is apparent. The strength of the unshifted As and Ga peaks are greatly reduced. A strong Ga 3d peak (labeled GaI) is seen shifted by 1.0 eV as would be expected for formations of Ga_2O_3 . An As 3d peak shifted by 4.5 eV (AsII) is present. This has been associated by Planetta et al.²³ with As coordinated by four oxygen atoms.

The lowest curve in Fig. 7 was obtained after exposing a clean surface to 5×10^5 L of oxygen with the ion gauge turned on with 4 ma of ionization current rather than the 0.4 ma used to produce the surface shown in the preceding curve. Almost all the Ga within the escape depth

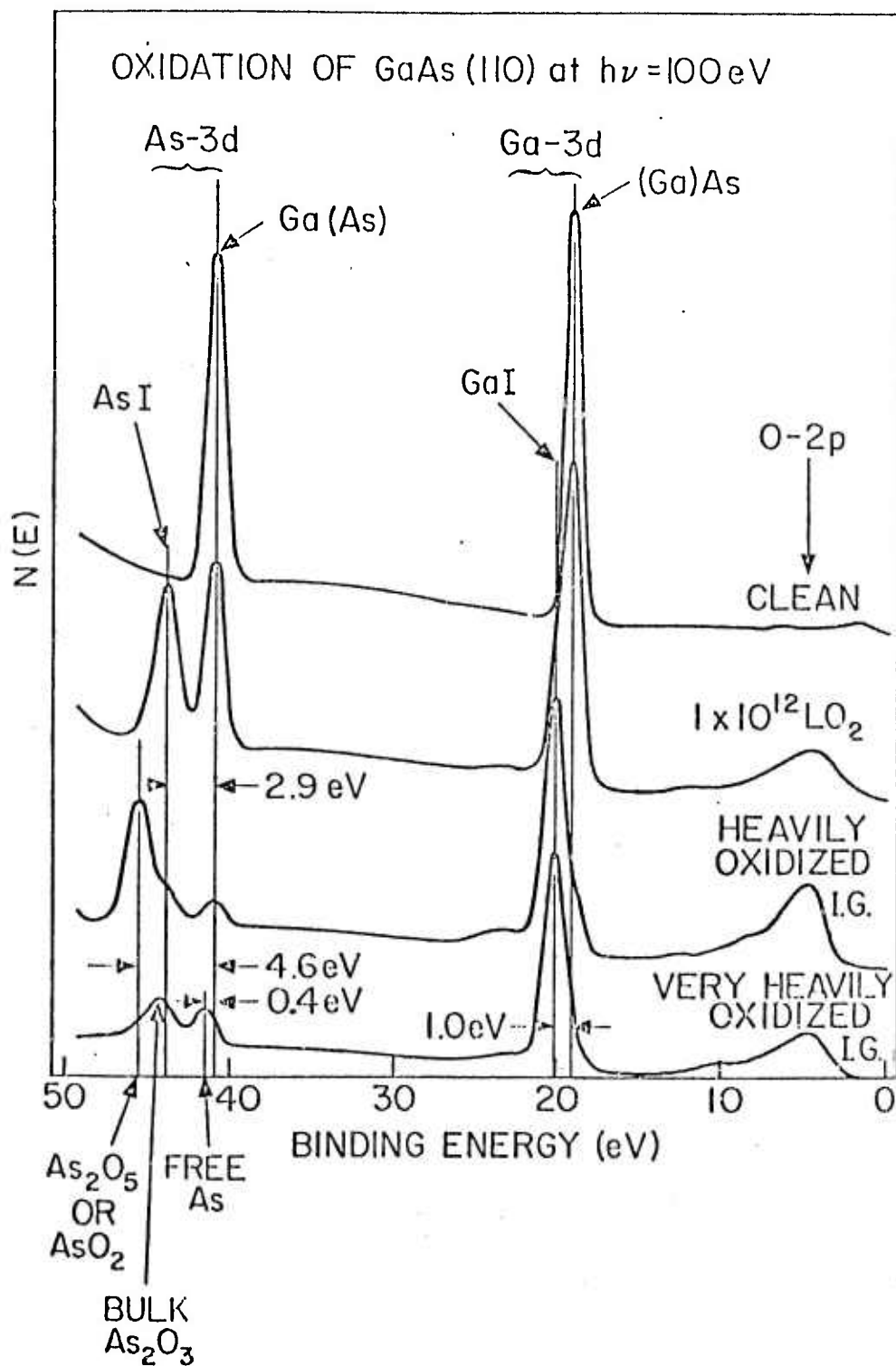


Fig. 7. SPECTRA SHOWING THE EDC's FOR FOUR DIFFERENT SURFACE CONDITIONS. The curve labeled $1 \times 10^{12} \text{ L O}_2$ has a saturation coverage of chemisorbed oxygen. The two lower curves show the result of oxide formation.

(about two molecular layers) is now oxidized (Ga_2O_3). One As peak (AsIV) is apparent at 3.2 eV corresponding to As_2O_3 and a second peak (AsIII) shifted by 0.4 eV associated with elemental As or As with reduced Ga coordination is observed.

Most strikingly, the integrated area under the As peaks is a small fraction of that observed on clean GaAs. Notice also that the unshifted Ga and As peaks are not seen indicating formation of an oxide layer thick compared to the escape depth.^{22,23} The loss in intensity of the As peak is probably due to the volatility of As_2O_3 .

C. Relationship of the Present Work to Passivation of GaAs

Knowing all the complexity of the "real" world in general and practical surfaces in particular, one must proceed with caution in extrapolating from basic results such as those reported here to passivation of practical surfaces. However, it is clear that this must be done if a true understanding of the physics and chemistry of the passivation is to be obtained. The probability of economically making maximum use of 3-5 semiconductors should be greatly enhanced by such knowledge. Further, we recognize that knowledge of the processes essential to passivation of 3-5 surface is much more likely to grow in an evolutionary way rather than to appear as the result of a rather limited body of work. Our object then is to help accelerate this process by pointing out aspects of our work which may help in developing the necessary understanding.

We would like to direct attention to three phenomena observed in our work. One rather obvious and the other two more surprising. The obvious result is the difficulty in passivating using the native oxide of a two component system in which the constituents are as different as As and Ga. In Fig. 7, the surface core level spectroscopy gives some insight to this complexity. Note in the most heavily oxidized surface the loss of As and the change in chemical state of As as the oxidation proceeds. For the sake of discussion, we show in Fig. 8 a schematic drawing showing the complexity which one may have in a "heavily" oxidized surface such as that of the bottom curve of Fig. 7. The surface in Fig. 8 is shown as irregular because evaporation of volatile As_2O_3 may leave

a pitted surface. The composition of the oxidized layer is shown to vary with depth because of the different chemistry of the As and Ga. For the same reason, a fairly complex interface between the GaAs and the oxide layer is expected. Figure 6 is not to be taken literally but is only intended to suggest the complexities which are implied by the data of Fig. 7.

After considering Figs. 7 and 8, one must ask if a native oxide is the optimum passivating layer for the 3-5 compounds. May it not be easier to bond a passivating layer of a different composition (e.g., Al_2O_3 , Si_3N_4 , Ga_2O_3 , etc.) onto the surface of the 3-5 compound? One must then ask how such a layer will chemically bond to the GaAs without creating an overwhelming density of interface states. Here we come to the second conclusion from our work. For most surfaces (e.g., the (111) and (110)), the bonding should be done through the surface As atoms since only they contain electrons not already tied up in GaAs covalent bonds (the (100) surface might be an exception). Bonding between a passivating adlayer and the GaAs is shown schematically in Fig. 9 for the (110) face.

Our studies suggest a third more subtle problem in GaAs which does not occur in similar studies of Si, if we use the change of Fermi level pinning with adsorption of fractional to monolayer quantities of oxygen (Fig. 10). We suggest that this is associated with strain in the GaAs interface. Figure 5 gives evidence of a strong phase-like transformation which takes place on all cleaved (110) surfaces studied. We have associated this with strain produced by oxygen adsorption. The effect of oxygen on the Fermi level has been reported at length previously.^{3,4} On both n- and p-type samples which are initially unpinned, oxygen adsorption moves the surface position of the Fermi level into mid-gap and finally pins it near mid-gap. For n-type where we have data taken under extremely well controlled conditions,^{4,22,23} the final pinning takes place at approximately the same exposure as the phase-like change in the valence band shown in Fig. 5. We have suggested in Section 3.C that, by chemically adsorbing on the As surface atoms (see Fig. 1), the oxygen removes electrons from the As (as established by the As chemical shift, Fig. 7) and thus changes the optimum As bonds from their p^3 surface configuration. Thus, whenever an oxygen has chemisorbed on an As, that As attempts to move into

SCHEMATIC OF VERY HEAVILY OXIDIZED GaAs

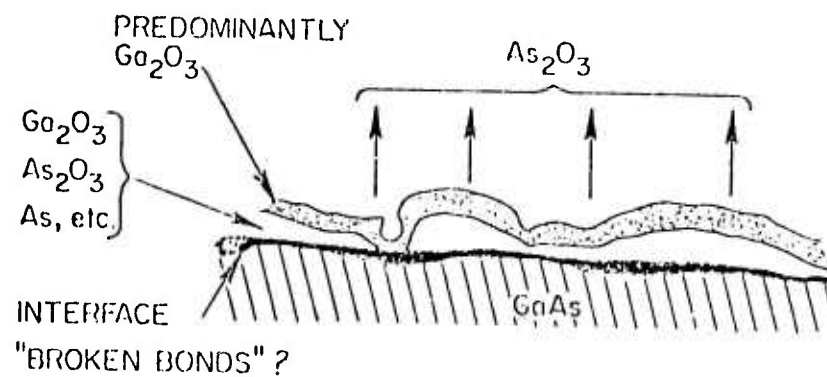


Fig. 8. A SCHEMATIC DIAGRAM SUGGESTING THE MORPHOLOGY OF A "VERY HEAVILY OXIDIZED" GaAs SURFACE OF FIG. 7.

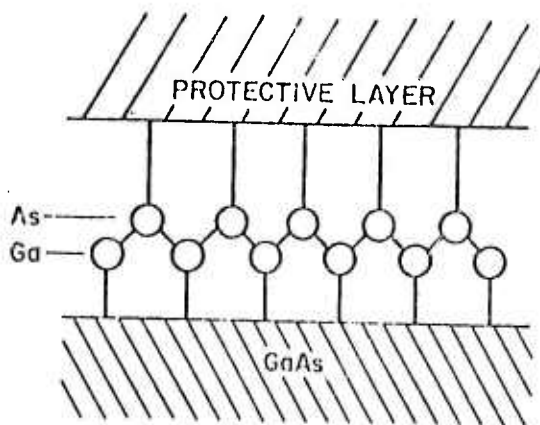


Fig. 9. THIS DIAGRAM INDICATES HOW A PASSIVATING LAYER MIGHT BE BONDED TO A (110) GaAs SURFACE IN ORDER TO MINIMIZE THE DENSITY OF INTERFACE STATES DUE TO BROKEN "BACK" BONDS.

the surface (due to increased Sp^3 or Sp^2 bonding) and causes local strains which produce defects and thus induce interface states. Near exposures of 10^6 L (Fig. 5) result in a disordered surface and thus loss of the surface valence band structure. At or before that point, a density of surface states near mid-gap ($\sim 10^{12}/\text{cm}^2$) is created.

In order to make more graphic the difference between GaAs and Si in this regard, we present, in Fig. 10, data showing the change in surface Fermi level position versus oxygen exposure (or coverage) for n-type material. As can be seen, Si starts by being pinned (presumably by intrinsic surface states); however, this pinning is removed by 10^3 L of oxygen.³⁰ In contrast, the GaAs starts by being unpinned and is pinned near mid-gap after an exposure of about 10^6 L of oxygen.^{4,22,23}

Clearly, even if the configuration of Fig. 9 could be achieved, one might expect, due to the strain effect discussed above, over $10^{12}/\text{cm}^2$ interface states. In order to provide a practical surface, these would have to be removed perhaps by addition of hydrogen, chlorine, or some other atoms to the interface and/or by an annealing procedure which would "heal" the strain-induced effects of the interface bonding.

Valuable discussions with Walter Harrison and our other colleagues at Stanford are gratefully acknowledged.

References

1. J. van Laar and J. J. Scheer, *Surf. Sci.* 8, 342 (1967).
2. J. van Laar and A. Huijser, *J. Vac. Sci. Technol.* 13, 769 (1976); A. Huijser and J. van Laar, *Surf. Sci.* 52, 202 (1975).
3. W. Gudat and D. E. Eastman, *J. Vac. Sci. Technol.* 13, 331 (1976).
4. W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, *J. Vac. Sci. Technol.* 13, 780 (1976).
5. P. E. Gregory and W. E. Spicer, *Phys. Rev.* 13, 725 (1976).
6. J. A. Knapp and G. J. Lapeyre, *J. Vac. Sci. Technol.* 13, 757 (1976).
7. K. Jacobi and W. Ranke, *J. Elect. Spect. and Related Phenomena* 8, 225 (1976).

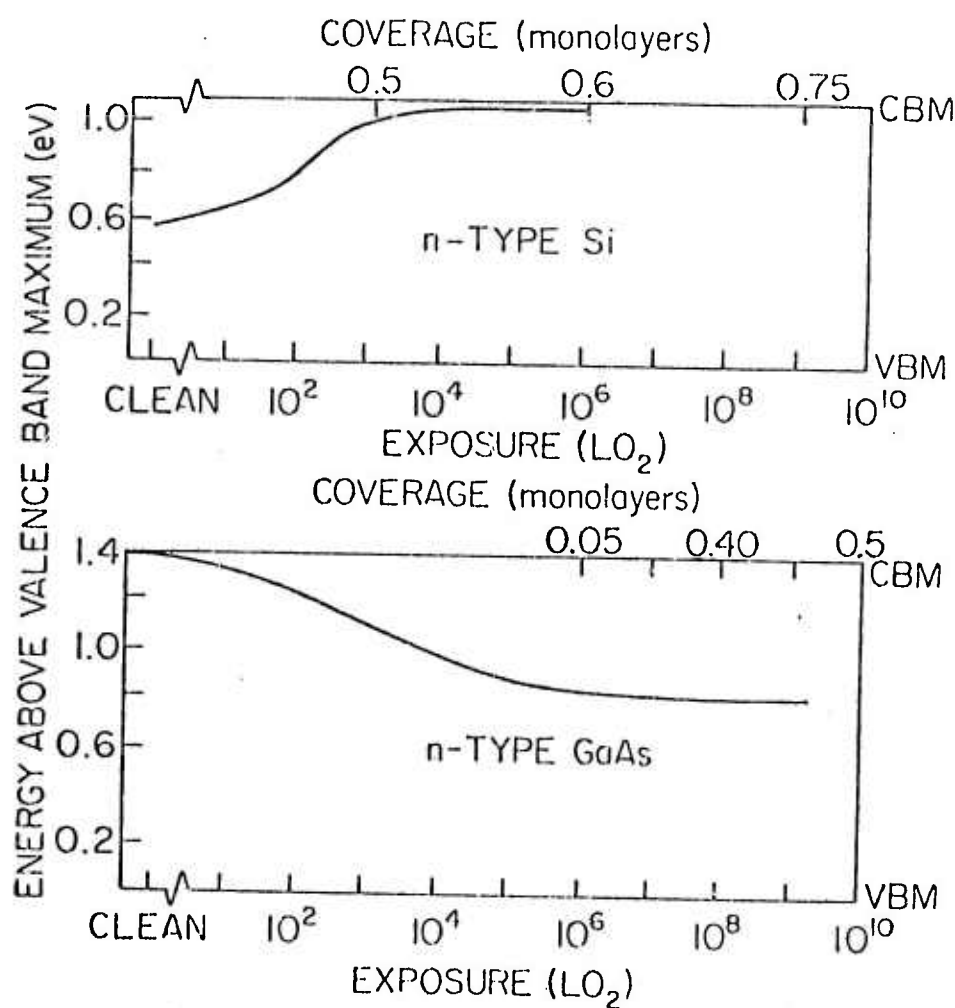


Fig. 10. THESE DIAGRAMS CONTRAST THE EFFECT OF OXYGEN ON THE FERMI LEVEL PINNING OF CLEAVAGE SURFACES OF n-TYPE Si AND GaAs. The fact that oxygen produces pinning on GaAs (whereas it removes it on Si) is associated with strain produced by the oxygen.

8. P. R. Skeath, P. E. Gregory, and W. E. Spicer, Bull. Amer. Phys. Soc. 21, 1313 (1976).
9. R. Ludeke and A. Koma, CRC Crit. Rev. Solid State Sci. 5, 259 (1975) and references therein.
10. J. L. Freeouf and D. E. Eastman, CRC Crit. Rev. Solid State Sci. 5, 245 (1975) and references therein.
11. G. J. Lapeyre and J. Anderson, Phys. Rev. Lett. 35, 117 (1975).
12. H. C. Gatos and M. C. Lavine, J. Electrochem. Soc. 107, 427 (1960); H. C. Gatos, J. Electrochem. Soc. 122, 287C (1975).
13. P. E. Gregory, W. E. Spicer, S. Ciraci, and W. A. Harrison, Appl. Phys. Lett. 25, 511 (1974).
14. J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B 10, 5075 (1974).
15. W. E. Spicer and P. E. Gregory, CRC Crit. Rev. Solid State Sci. 5, 231 (1975) and references therein.
16. C. B. Duke, A. R. Lublinsky, B. W. Lee, and P. Mark, J. Vac. Sci. Technol. 13, 761 (1976).
17. A. U. MacRae and G. W. Gobeli, J. Appl. Phys. 35, 1629 (1964).
18. W. A. Harrison, Surf. Sci. 55, 1 (1976); J. Vac. Sci. Technol., to be published; and private communication.
19. C. A. Mead, Solid State Electronics 9, 1023 (1966); J. O. McCaldin, T. C. McGill, and C. A. Mead, J. Vac. Sci. Technol. 13, 802 (1976); S. Kurtin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. 22, 1433 (1969).
20. V. Heine, Phys. Rev. 138, A1689 (1965).
21. J. H. Dinan, L. K. Galbraith, and T. E. Fischer, Surf. Sci. 26, 587 (1971); L. K. Galbraith and T. E. Fischer, Surf. Sci. 30, 185 (1972); D. E. Eastman and J. C. Freeouf, Phys. Rev. Lett. 33, 1601 (1974).
22. P. Pianetta, Ph.D. thesis, Stanford University (1976).
23. I. Lindau, P. Pianetta, W. E. Spicer, P. E. Gregory, C. M. Garner, and P. W. Chye, submitted for publication; P. Pianetta et al, to be published.
24. P. Chye et al, J. Vac. Sci. Technol., to be published.
25. P. E. Gregory and W. E. Spicer, Phys. Rev. 12, 2370 (1975).
26. P. W. Chye, I. A. Babalola, T. Sukegawa, and W. E. Spicer, Phys. Rev. 13, 4439 (1976).

27. J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 14, 4724 (1976).
28. C. Calandra, P. Manghi, and C. M. Bertoni, to be published.
29. P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. Lett. 35, 1356 (1975); 37, 1166 (1976).
30. L. F. Wagner and W. E. Spicer, Phys. Rev. B 9, 1512 (1974).

Appendix C

OXYGEN SORPTION AND EXCITONIC EFFECTS OF GaAs SURFACES

1. Introduction

Recently, there has been a great deal of interest in the behavior of GaAs surfaces upon exposure to oxygen. One controversial point is the oxygen chemisorption site. Pianetta et al^{1,2} examined the Ga and As-3d core level chemical shift using soft x-ray photoemission spectroscopy (SXPS) and concluded that "unexcited" molecular oxygen only chemisorbs to the As surface atoms, while oxygen "excited" by a hot filament from a Bayard-Alpert ionization gauge can break Ga = As bonds and form true Ga and As oxides. Ludeke and Koma,^{3,4} on the other hand, conclude from their low energy electron loss experiments (LEIS) that oxygen bonds onto the Ga as well, based on the sensitivity to oxygen of the transitions from Ga-3d to final states near the conduction band minimum (CBM) at the surface. These final states are assumed to be empty surface states strongly localized on the Ga atoms, as similar transitions from the As-3d's were not observed.

In this paper, we will examine in some detail the above experiments and the conclusions drawn from them. We will also draw on more recent ultraviolet photoemission spectroscopy (UPS) and photoemission partial yield spectroscopy data in order to better understand the details of the effects which occur at the GaAs surface when it is exposed to oxygen.

2. Results and Discussion

The experiments of Pianetta et al^{1,2,5,6,7} were done exclusively on the cleaved (110) surface. Figure 1 shows some of their results. The photoelectron energy distribution curves (EDC's) were taken using synchrotron radiation as the light source and the energy analyzer was a double pass cylindrical mirror analyzer. The photon energy was chosen to be 100 eV for maximum surface sensitivity. When the sample was exposed to molecular oxygen--using, depending on the amount of the exposure, a cold-cathode Redhead gauge, a millitorr gauge, a thermocouple gauge, and a mechanical gauge--a 2.9 eV chemical shift towards higher binding energy in the As-3d level starting at about 10^6 Langmuirs

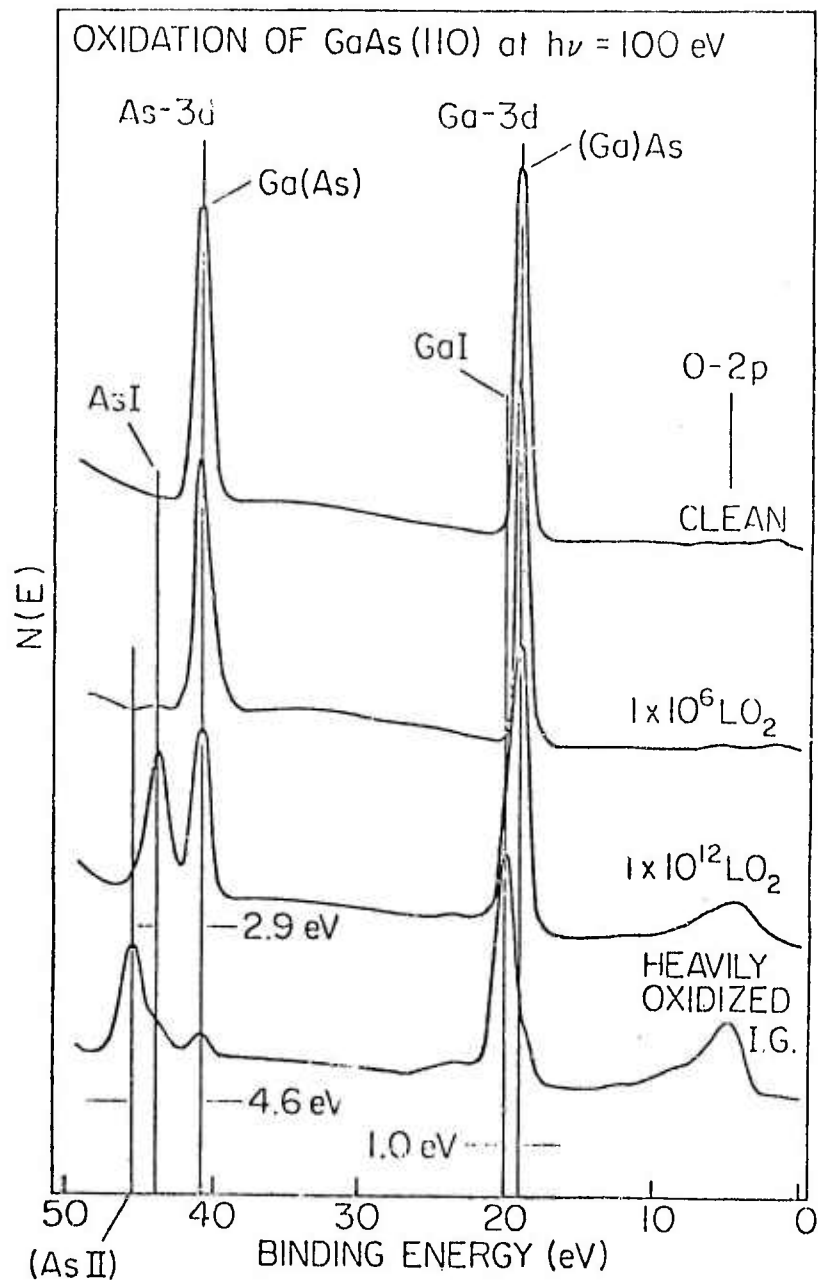


Fig. 1. EFFECTS OF "UNEXCITED" AND "EXCITED" OXYGEN ON THE 3d CORE LEVELS OF GaAs.

(1 L = 10^{-6} torr-sec) of oxygen exposure was observed, indicating a charge transfer from the As surface atoms. In contrast, even at the very high exposure of 10^{12} L, no chemical shift in the Ga-3d core level can be resolved as long as "excited" oxygen is not used. Then, when the sample is exposed to 5×10^5 L of oxygen with an ionization gauge turned on^{5,6,7} (emission current = 0.4 ma), a Ga-3d chemical shift of 1 eV towards higher binding energy is observed, together with a second 4.6 eV chemically shifted As-3d level. The appearance of the second As peak is simultaneous with the appearance of the Ga-3d shift.¹ Pianetta et al have given detailed analyses of chemical shifts in terms of various oxides.^{5,6}

From their data, the following was concluded: when cleaved GaAs (110) is exposed to "unexcited" molecular oxygen, the oxygen only chemisorbs onto the surface As atoms and saturation (half a monolayer coverage) is reached between 10^9 and 10^{12} L. "Unexcited" oxygen is unable to break Ga = As bonds to bond onto the surface Ga atoms. When oxygen is "excited" by a hot filament ionization gauge, however, it is able to break Ga = As bonds and bond to both As and Ga atoms, causing chemical shifts in both 3d core levels and disrupting the covalent bonding of the rest of the molecules with the surface. The significance of the various chemically shifted peaks will be discussed in a future publication.⁶

Ludeke and Koma^{3,4} studied the GaAs (100), (111), and (110) surfaces prepared by molecular beam epitaxial overgrowth or annealed in an As vapor background. Observation of the surface crystallography during growth was achieved with a RHEED system. By varying the surface treatment, the polar (100) surface may be made to be As rich (1×1) with the As coverage approximately one monolayer ($\theta_{\text{As}} \approx 1$), As-stabilized C(2×8) with $\theta_{\text{As}} \approx 0.5$ or As-depleted (4×6), $\theta_{\text{As}} = 0$. Oxygen coverage was estimated from the ratio of the O(510) and Ga(1070) Auger signals. On all three (100) surfaces, oxygen saturation occurred at around 10^{-3} torr-min (6×10^4 L) of oxygen exposure. The adsorption process proceeded fastest on the Ga-rich (4×6) face and slowest on the As-rich (1×1) surface. In the negative second derivative of the electron loss spectrum--the derivative being taken for increased sensitivity--a loss peak at around 20 eV which was not observed on the As-rich surface is attributed to the excitation of Ga-3d core electrons into empty surface states. Part of the

electron loss spectrum for (110) is shown in Fig. 2. This loss peak was observed to be split, at lower primary electron energy, by the spin orbit splitting of the Ga-3d core level. No similar transition was observed for As-3d, which was interpreted as strong localization of the empty surface states on the Ga surface atoms. Upon exposure to oxygen, this 20 eV loss peak rapidly decreased and disappeared at 0.3 saturation coverage. The Ga-rich (111)-2 surface shows saturation at 10^{-2} torr-min (6×10^5 L) of oxygen, with the 20 eV loss peak greatly diminished by 0.1 saturation coverage. On GaAs (110),⁴ 5×10^7 L of oxygen was required for complete disappearance of the 20 eV loss peak although clear weakening was observed at 5×10^4 L. These authors conclude from the above results that oxygen bonding to the surface Ga's occurs.

The experiments of Pianetta et al do definitively show a charge transfer to the surface As atoms. However, is it possible for bonding to the surface Ga atoms to occur without a resolvable chemical shift? Since the surface Ga atoms in GaAs are already partially "oxidized" before exposure to oxygen due to charge transfer to the more electro-negative As's, the chemical shift of the Ga-3d's is expected to be much smaller than that of the As-3d's, and there is some question as to whether it can be resolved with SXPS. Experimental evidence strongly suggests that it is resolvable when Ga oxide is formed. When Pianetta et al exposed their cleaved sample to "excited" oxygen so that bonding to the Ga atoms occur, the resulting 1 eV Ga-3d chemical shift is unambiguously observable. The "excited" oxygen changes the nature of the bonding and, by breaking of Ga = As bonds, permits the bonding of oxygen to the Ga atoms and thus goes past the chemisorption stage and forms true oxides.^{5,6}

If the oxygen bonds initially to the surface As atoms, then how can we explain Ludeke and Koma's observations? First, let us examine the disappearance of the 20 eV loss peak with oxidation and decide whether this tells us that oxygen is bonding to the Ga atoms.

The 20 eV loss peak comes from the excitation of Ga-3d electrons into final states which have been assumed to be empty states. This transition has been observed in photoemission partial yield spectroscopy^{5,8,9} and is strongly excitonic (exciton binding energy ~ 0.5 eV) in nature as first pointed out by Lapeyre and Anderson¹⁰ and also discussed by Gudat and Eastman.¹¹ There is now general agreement on its excitonic nature.⁷

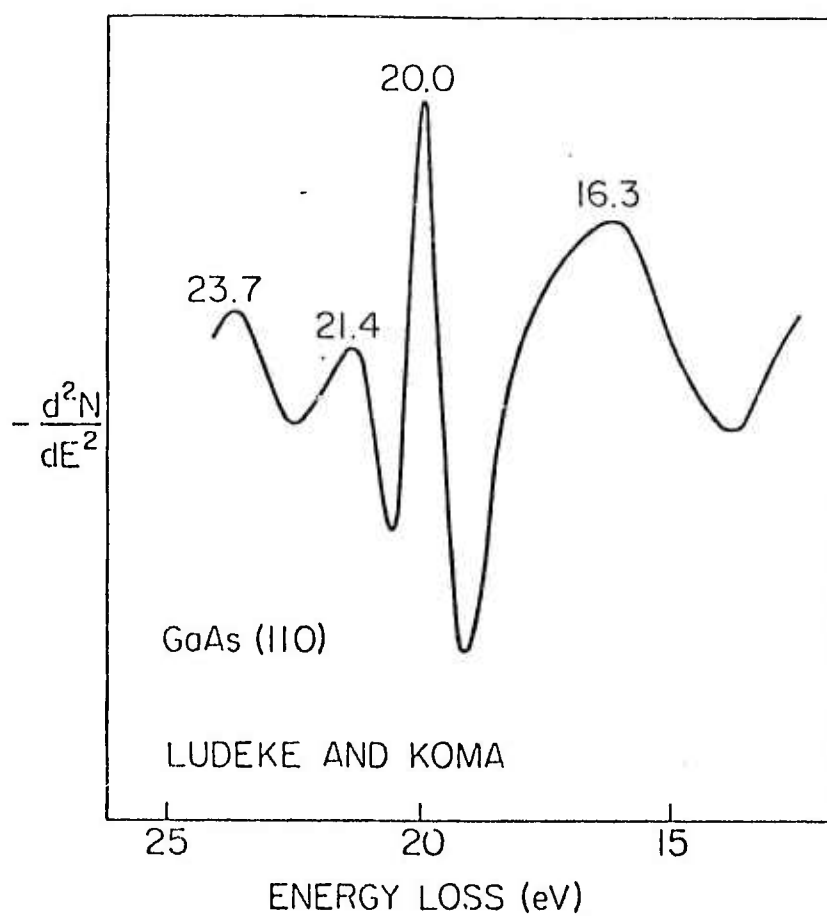


Fig. 2. LOW ENERGY ELECTRON LOSS SPECTRUM TAKEN FROM REF. 3. The 20 eV loss peak disappears with oxygen exposure.

In light of recent agreement that the empty surface states do not lie in the band gap^{7,9,11,12} and the recent data of Bauer¹³ which show excitation of As 3p--but not 3d--electrons into these final states, the assumption that the final state involves the empty surface state is no longer so certain.

Figure 3 shows the behavior under oxygen exposure of this transition, as observed by photoemission partial yield spectroscopy.⁹ This excitonic transition is strongly affected at 10^6 L of O_2 and has vanished by 10^7 L of O_2 . The coverage at 10^7 L is only a few percent of saturation coverage, as estimated from SXPS data⁵ at 100 eV. Both the area under the chemically shifted As-3d peak and the emission from the oxygen 2p resonance are used, and the two track quite well.^{5,6,7} Simultaneous with the disappearance of the excitonic transition, are changes in the surface valence bands, as seen from the EDC's^{5,6,7} in Fig. 3. It is apparent that oxygen has long range forces and a small fraction of a monolayer of coverage is sufficient to change the surface electronic structure drastically. Since the amount of oxygen on the surface is so small, it is not possible to explain the disappearance of the Ga-3d to surface state transition by oxygen adsorption on the Ga surface atoms. Rather, it appears that this excitonic transition has been extinguished by the large surface electronic structural changes which are discussed elsewhere^{6,7} and correlate well with the change in partial yield. It may be noted that SXPS, which studies 3d electron excitation into continuum states high above the vacuum level, is much less sensitive to oxygen induced final state changes, while changes in the empty surface state or conduction band states involved in the excitonic transition may smear the excitonic spectra. It is clear that theoretical examination of this transition is strongly needed. Therefore, it cannot be concluded that oxygen is bonding onto the surface Ga atoms from the disappearance of the 20 eV loss peak with oxygen exposure.

Oxygen can bond to the surface Ga, however, provided that (1) there is a source of excitation or (2) there are broken Ga bonds on the surface. Ion bombarded and annealed surfaces may have a large number of broken Ga bonds, and Ga terminated surfaces should have a large number of broken Ga bonds. Even MBE surfaces may not be free of broken bonds.

In the experiments of Ludeke and Koma, it is quite possible that oxygen bonding to Ga occurred, as their sticking coefficients are orders of magnitude higher than Pianetta et al with unexcited oxygen.² Use of AES during exposure, for example, would also lead to excitation of oxygen inside the chamber.

3. Conclusions

The disappearance of the excitonic transition seen in electron loss spectroscopy and photoemission partial yield spectroscopy with oxygen coverage is due to large changes in the final states caused by the long range forces of the oxygen, and not to oxygen adsorption on every surface Ga atom, it having been shown that there are too few oxygen molecules/atoms on the surface when extinction occurs. When there are no broken bonds on the surface, "unexcited" molecular oxygen cannot break back bonds and only chemisorption on the As surface atoms occurs, with no bonding to Ga atoms. "Excited" oxygen can break back bonds and form true oxides, giving rise to new chemical shifts in both the As as well as the Ga-3d core levels. Bonding to Ga surface may also occur when there are broken bonds on the surface, which may be present on noncleaved surfaces prepared by, for example, argon ion bombardment followed by annealing. It is therefore essential to exercise caution when comparing results obtained on differently prepared surfaces and when the nature of the oxygen used ("excited" or "unexcited") is unknown.

References

1. P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. Lett. 35, 1356 (1975).
2. P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, Phys. Rev. Lett. 37, 1166 (1976).
3. R. Ludeke and A. Koma, Crit. Rev. Solid State Sci. 5, 259 (1975), and J. Vac. Sci. Technol. 13, 241 (1976).
4. R. Ludeke, Bull. Am. Phys. Soc. 21, 937 (1976).
5. P. Pianetta, Ph.D. Thesis, Stanford University (1976).

6. P. Pianetta, I. Lindau, C. M. Garner, and W. E. Spicer, to be published.
7. W. E. Spicer, P. Pianetta, I. Lindau, and P. W. Chye, J. Vac. Sci. Technol., to be published.
8. D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 33, 1601 (1974).
9. W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta, and P. W. Chye, J. Vac. Sci. Technol. 13, 780 (1976).
10. G. J. Lapeyre and J. Anderson, Phys. Rev. Lett. 35, 117 (1975).
11. W. Gudat and D. E. Eastman, J. Vac. Sci. Technol. 13, 831 (1976).
12. J. van Laar and A. Huijser, J. Vac. Sci. Technol. 13, 769 (1976).
13. R. S. Bauer, J. Vac. Sci. Technol., to be published.