that C–H···O bonds, far from being passive bystanders, may actually discriminate between alternative O–H···O networks which, though geometrically reasonable, are structurally quite distinct. In the present context, it could be possible that the manifestation of C–H···O bonds would lead to the dimer motif and their absence to the catemer. Such a conclusion is in agreement with calculations that show that the isolated catemer is slightly more stable than the dimer.[9,11]

In spite of its greater stability, the catemer is far more sensitive than the dimer to steric factors. Therefore, a possible auxiliary reason for the adoption of the catemer by the title compound could be the lack of substituents adjacent to the carbonyl group or even an interaction of the acidic proton with the alkyne bond. However, the five other phenylpropiolic acids with known crystal structures[17] adopt the dimer motif, and the lack of more detailed structural information on this family of compounds makes further discussion speculative.

As in several other planar chloroaromatic compounds, the crystal structure of acid **2** is characterized by short Cl···Cl contacts (which lead incidentally to the adoption of a 4-Å short axis[22]), and a pertinent question is whether the catemer motif is forced on the structure because of the optimization of these Cl···Cl interactions. However, these short contacts are also found in 4-chlorobenzoic acid (3.44 Å)[14] and 4-chlorocinnamic acid (3.79 Å),[19] and yet both of these acids display the centrosymmetric dimer motif with the dimer units being linked by C–H···O bonds. It would appear then that Cl···Cl interactions are not incompatible with the dimer motif.

It could also be argued that the absence of significant C–H···O bonding ability in acid **2** is correlated with an awkward molecular shape; inspection of Figure 2 shows that there is a close packing of carboxylic and alkynic residues in neighboring molecules that seems to decide the hydrogen bond geometry. However, these are post facto rationalizations, and the manifestation of crystal structures such as those of compound **2** shows that the prediction of hydrogen-bonded structures is still a complex and tricky issue.[1,24]

In spite of these difficulties, it is suggested that materials chemists will find it worthwhile to consider *all* interactions, strong and weak, while attempting to understand novel and unexpected hydrogen-bond arrangements. Only through such understanding would it be possible to advance confidently to the next step of structure prediction and design.

Acknowledgment. We thank the CSIR and DST for support of this research and Prof. J. Bernstein and Dr. J. A. R. P. Sarma, Ben Gurion University, for X-ray data collection. This work is taken in part from the M. Phil thesis of B.N.M. and the Ph.D. thesis of K.V.R.K. submitted to the University of Hyderabad in 1987 and 1988.

Registry No. **2**, 3240-10-6.

Supplementary Material Available: Table of thermal parameters (1 page); listing of F_o/F_c values for acid **2** (4 pages). Ordering information is given on any current masthead page.

(24) Hagler, A. T.; Leiserowitz, L. *J. Am. Chem. Soc.* **1978**, *100*, 5879.
(25) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, 1985; p 175.
(26) Sheldrick, G. M. *Program for Crystal Structure Solution and Refinement*, University of Cambridge, 1976.

Adsorption of Nitric Oxide, Nitrous Oxide, and Oxygen on Ion-Bombarded Gallium Arsenide(100)

J. M. Epp and J. G. Dillard*

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

Received December 1, 1989

Chemically cleaned (1:1 HCl(conc)/H_2O) GaAs(100) was ion bombarded with 3-keV Ne^+ and Xe^+ at 10^{17} ions/cm^2 and subsequently exposed to NO in the range 10^6–10^8 langmuirs and N_2O in the range 10^7–10^{11} langmuirs. Ion-bombarded GaAs exposed to N_2O yields only Ga_2O_3. However, when ion-bombarded GaAs is exposed to NO, both gallium and arsenic oxides are formed, with Ga_2O_3 being the major component. The extent of oxidation for ion-bombarded GaAs exposed to a series of gases is NO > O_2 > N_2O. The ion-bombarded surface is composed of defects consisting of singly occupied Ga bonds, Ga–Ga bonds, and As vacancies. The limited reaction of N_2O and the greater reactivities of O_2 and NO with ion-bombarded GaAs are due to the interaction of each of these molecules with the defects on the ion-bombarded GaAs surface.

Introduction

The experiments of Bertness et al.[1] for N_2O and O_2 adsorption and Bermudez et al.[2] for NO and O_2 adsorption on GaAs(110) suggest that dissociative adsorption is dependent upon the bond energies of the molecules. Nitrous oxide, with the weakest (N–O) bond energy, shows the greatest reactivity with GaAs(110).[1] Bermudez et al.[2] also observed that NO reacts more slowly than O_2 with GaAs in the exposure range 10^4–10^7 langmuir (1 langmuir = 1.33 × 10^{-4} Pa·s). Defects are thought to play an important role in the dissociation process on cleaved or annealed material.

Ion-bombarded GaAs(100) exhibits increased reactivity compared to chemically cleaned GaAs(100) upon exposure to O_2 or H_2O at 10^7–10^{13} langmuirs. The quantity of gallium and arsenic oxides increased with increasing en-

(1) Bertness, K. A.; Chiang, T. T.; McCants, C. E.; Mahowald, P. H.; Wahi, A. K.; Kendelewicz, T.; Lindau, I.; Spicer, W. E. *Surf. Sci.* **1987**, *185*, 544.
(2) Bermudez, V. M.; Williams, R. T.; Long, J. P.; Rife, J. C.; Wilson, R. M.; Tuttle, A. E.; Williams Jr., G. P. *J. Vac. Sci. Technol. A* **1987**, *5*, 541.

0897-4756/90/2802-0449$02.50/0

ergy[3] or mass[4] of the bombarding ion. Increased reactivity was attributed to a greater concentration of defects on the ion-bombarded surface. For the present study, it was reasoned that if defects on ion-bombarded GaAs are significant reaction sites, then differences in O_2 and NO reactivity might be more pronounced for ion-bombarded GaAs(100) than for chemically cleaned GaAs(100) or for cleaved GaAs(110). The latter two surfaces should have a lower number of surface defects. Since NO, N_2O, and O_2 exhibited different reactivities with GaAs(110)[1,2,5-8] and have different bond strengths, it was thought that additional insight into the chemical nature of the ion-bombarded surface and the mechanism of reaction could be gained by examining NO and N_2O reactions.

Recent detailed studies of NO interaction with GaAs were reported.[2,5] A principal thrust of these studies was to clear up the controversy regarding GaAs oxidation. It was proposed[2] that results for a similar reactive, heteroatomic, diatomic molecule could be compared with the large amount of data on the O_2 reaction and could possibly provide new insight into the oxidation mechanism. It was also suggested[1,2,9] that adsorption of N_2O on GaAs[1,2,9] might provide additional insight into the oxidation mechanism by providing atomic O without the need to dissociate O_2; N_2O requires only 1.7 eV to dissociate compared to 5.1 eV for O_2[1] and 6.5 eV for NO.[2]

Almost all investigators have noted that a rate-limiting step in O_2 chemisorption is the dissociation of oxygen and that this step is also controlled by the presence of defect sites. In the photoemission study of NO adsorption on GaAs(110), Bermudez et al.[2] report that defect sites might also be important in the NO reaction. At exposures below 10^7 langmuirs, NO dissociates and reacts more slowly than does O_2. They also report that NO and O_2 adsorb dissociatively on GaAs at room temperature. If the reaction-controlling step is the dissociation of the molecule, then comparing two diatomic molecules with different dissociation energies could help to elucidate the oxidation mechanism and the role of defects on cleaved as well as ion-bombarded GaAs.

Experimental Section

Materials. In this study n-type GaAs(100) with a Si doping density $\leq 5 \times 10^{17}$ cm^{-3} was used. All specimens were cleaned in 1:1 HCl(conc)/H_2O at room temperature for 10 min to remove surface oxides and were subsequently rinsed in deionized water. Samples so treated are referred to as chemically cleaned GaAs. The samples were transferred in air to the XPS chamber for ion bombardment and reactant gas exposure. Studies of chemically cleaned samples exposed to reactant gases were not of primary interest in this study.

Ion Bombardment. Ion bombardment was carried out in a Perkin-Elmer Model 5300 XPS system[3] equipped with a Model 04-300 differentially pumped ion gun, mounted at 45° with respect to a line perpendicular to the specimen surface. The gases used to produce the bombarding ions were ^{20}Ne (Isotec, 99.95%) and Xe (Airco, 99.9995%, natural isotopic abundance). Ion bombardment was carried out at 3000 eV using a 1-cm^2 rastered beam with currents in the range 20–30 μA. The time of bombardment was adjusted to give $(7.5 \pm 1.5) \times 10^{17}$ ions/cm^2. Ion bombardment was carried out for a sufficient time so that the O(1s) signal was below the detection level. The samples were oriented such that ion bombardment was in the (111) direction. Chamber pressure during ion bombardment was generally about 10^{-5} Pa.

Table I. Ga/As Atomic Ratios for Chemically Cleaned and Chemically Cleaned–Ion Bombarded GaAs (3 keV, 10^{17} ions/cm^2)

	Ga/As[a]	
	15°[b]	90°[b]
chemically cleaned	0.78 ± 0.05	0.89 ± 0.05
Ne^+	1.33 ± 0.04	1.37 ± 0.03
Xe^+	1.69 ± 0.06	1.71 ± 0.08

[a] Ga/As ratios determined from (peak area)/σ where peak area is the Ga(3d) or As(3d) photopeak area and σ is the experimentally measured sensitivity factor.[3,4] [b] Takeoff angle.

Gas Exposures. Following ion bombardment, the sample was immediately transferred under vacuum into a stainless steel ultrahigh-vacuum reaction chamber attached to the XPS system where exposure either to N_2O or to NO was carried out. Nitrous oxide (Scott Gases, SFC grade) was used as received. Mass spectrometric analysis of N_2O indicated no impurities or decomposition reaction products that would interfere[1] in the exposure experiments. Nitric oxide (Matheson, 99.0%) was purified by passage through 60–200-mesh silica gel (previously baked under vacuum) contained in a $^1/_4$-in. stainless steel tubing loop immersed in a dry ice/acetone bath.[2,10] Since NO is known to interact strongly with stainless steel,[2,11] the chamber was passivated following bakeout and before any NO exposures were performed by exposing the chamber to $<10^8$ langmuirs of NO. The NO gas flow was monitored by a mass spectrometer. No NO_2 was detected in NO itself or in the reaction chamber before or after NO exposure.

Nitric oxide exposures were from 10^6 to 10^8 langmuirs and N_2O exposures were in the range 10^7–10^{11} langmuirs. Care was taken to avoid exposure to excited gases during the experiments. Pressures were monitored by a thermocouple gauge (Hastings Vacuum Gauge).

Surface Analysis. The GaAs surfaces were analyzed by XPS using Mg Kα radiation ($h\nu$ = 1253.6 eV) as the excitation source. The chamber pressure was less than 4×10^{-6} Pa. Spectra were obtained immediately following ion bombardment and following ion bombardment–reactant gas exposure for the Ga(3d), As(3d), O(1s), and N(1s) core levels at various takeoff angles (TOA). The takeoff angle is measured as the angle between a line in the sample surface and a line to the entrance of the photoelectron analyzer. The photopeaks were analyzed by subtracting the X-ray source line width, smoothing, and curve-resolving using Gaussian peak shapes. Software routines available with the PHI 5300 system were used. The atomic concentrations were evaluated from photopeak areas using the appropriate sensitivity factors.[3,4]

Ninety-five percent of the observed photoelectron signal comes from a layer $3\lambda \sin\theta$ thick, where θ is the takeoff angle and λ is the mean free path of the photoelectron.[12] For the Ga(3d) and As(3d) core levels λ is approximately 22 Å; therefore, the analysis depths for the Ga(3d) and As(3d) photoelectrons at 15° and 90° TOAs are approximately 17 and 66 Å, respectively.[3]

Spectra for model compounds, Ga_2O_3 (Alfa, 99.99%), As_2O_3 (Aldrich, 99.999%), and As_2O_5 (Fisher, 99.2%) were used for the determination of binding energies, full widths at half-maxima (fwhm), and atomic ratios.[3]

Results

Ion-Bombarded GaAs. The gallium [Ga(GaAs)] and arsenic [As(GaAs)] contents on GaAs following chemical cleaning and after chemical cleaning followed by 3-keV

(3) Epp, J. M.; Dillard, J. G., *Chem. Mater.* **1989**, *1*, 325.
(4) Epp, J. M.; Dillard, J. G.; Siochi, A.; Zallen, R.; Sen, S.; Burton, L. C. *Chem. Mater.* **1990**, *2*, 173.
(5) So, S. K.; Ho, W. *Appl. Phys. A* **1988**, *47*, 213.
(6) Bermudez, V. M. *J. Appl. Phys.* **1983**, *54*, 6795.
(7) Bertness, K. A.; McCants, C. E.; Chiang, T.; Spicer, W. E. *Bull Am. Phys. Soc.* **1986**, *31*, 536.
(8) Bertness, K. A.; Mahowald, P. H.; McCants, C. E.; Wahi, A. K.; Kendelewicz, T.; Lindau, I.; Spicer, W. E. *Appl. Phys. A* **1988**, *47*, 219.
(9) Barton, J. J.; Goddard III, W. A.; McGill, T. C. *J. Vac. Sci. Technol.* **1979**, *16*, 1178.
(10) Hughes, W. E., *J. Chem. Phys.* **1961**, *35*, 1531.
(11) Ibbotson, D. E.; Wittrig, T. S.; Weinberg, W. H. *Surf. Sci.* **1981**, *110*, 294.
(12) Briggs, D. In *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. P., Eds.; Wiley: New York, 1983; p 362.

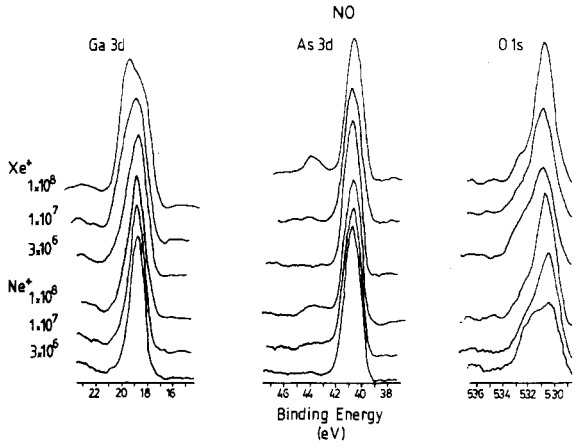

Figure 1. Representative XPS spectra taken at a 15° TOA for 3-keV Ne^+- and Xe^+-ion-bombarded GaAs exposed to NO.

Ne^+ and Xe^+ ion bombardment were determined by XPS measurements at 15° and 90° TAOs. The results are summarized in Table I. The XPS data reveal that the chemically cleaned GaAs surface is arsenic rich, in agreement with the measurements of others. The Ga(3d) and As(3d) photopeak shapes and binding energy values indicate only the presence of gallium and arsenic from GaAs. No spectral features characteristic of the oxides were detected. However, adsorbed oxygen (532.0 eV)[3,13,14] is detected (36 ± 9 atom % (15° TOA) and 16 ± 7 atom % (90° TOA)) on chemically cleaned GaAs.

Ion bombardment removes residual oxygen from chemically cleaned GaAs. Arsenic is preferentially sputtered from GaAs during ion bombardment, and the resulting surfaces are As-depleted with more As being removed by Xe^+ ion bombardment (see Table I). The respective Ga/As ratios for Xe^+ and Ne^+ ion-bombarded GaAs at the 15° and 90° TOAs are equivalent within the experimental error, indicating that As depletion extends to a depth of at least ≈60 Å (the maximum depth examined for the Ga(3d) and As(3d) levels by XPS).

Nitric Oxide Exposure. Representative XPS spectra obtained at a 15° TOA are presented in Figure 1 for the Ga(3d), As(3d), and O(1s) levels for Ne^+ and Xe^+ ion-bombarded GaAs following 3×10^6, 1×10^7, and 1×10^8 langmuir NO exposures. The Ga(3d) and As(3d) photopeaks both exhibit evidence for the formation of oxides by the appearance of photopeaks on the high binding energy sides of the respective substrate photopeaks. No signal from the N(1s) level (<2% atomic) was observed following any of the NO exposures.

The determination of chemical species from the photopeaks was accomplished by curve resolution. Curve resolution was carried out using Gaussian-type peaks. The peak positions and the fwhm's used in the curve resolution were determined by measuring XPS spectra for standard oxide compounds.[3,4] The fwhm and peak positions for Ga(3d) and As(3d) due to GaAs were determined from the spectra for ion-bombarded GaAs. Oxygen peak intensities were selected on the basis of knowledge of the oxygen/gallium or oxygen/arsenic ratio for the respective gallium (Ga_2O_3) and arsenic (As_2O_3, As_2O_5) oxides.

Representative curve-resolved spectra are shown in Figure 2 for Ne^+ and Xe^+ ion-bombarded GaAs exposed to 10^8 langmuirs of NO. These spectra are characterized by the species Ga(GaAs), As(GaAs), $Ga(Ga_2O_3)$, $As(As_2O_3)$, $O(As_2O_3)$, and O(ads). Table II summarizes the binding energies obtained for the surface oxides on GaAs following NO exposure. The binding energies for surface oxides on GaAs compare favorably with the literature values.[3]

Table II. Binding Energies (BE) for Surface Components

component	BE, eV	fwhm, eV
Ga(GaAs)	18.8 ± 0.1	1.2 ± 0.1
As(GaAs)	40.8 ± 0.1	1.5 ± 0.1
$Ga(Ga_2O_3)$	19.8 ± 0.1	1.5 ± 0.1
$As(As_2O_3)$	44.0 ± 0.2	1.6 ± 0.1
$O(Ga_2O_3)$	530.7 ± 0.2	1.6 ± 0.1
$O(As_2O_3)$	530.0 ± 0.3	1.3 ± 0.1
$O(O_{ads})$	532.2 ± 0.4	1.6 ± 0.2

The relative amounts of gallium and arsenic oxides produced following NO exposure were determined from curve-resolved spectra and are shown in Figure 3 for Ne^+ and Xe^+ ion-bombarded GaAs as a function of NO exposure. The relative quantities of gallium or arsenic oxide are represented as

$$Ga(Ga_2O_3) \text{ or } [As(As_2O_3 + As_2O_5)]/[Ga(\text{total}) + As(\text{total})] \quad (1)$$

Following NO exposure at 10^6 langmuirs, only Ga_2O_3 was formed on ion-bombarded GaAs. At 10^7- and 10^8-langmuir NO exposures, both gallium and arsenic oxides were produced, with Ga_2O_3 being the major component. The relative amount of Ga_2O_3 produced following NO exposure is greater for Xe^+ ion-bombarded samples than for Ne^+ ion-bombarded samples. This supports previous conclusions that the reactivity is directly related to the mass of the bombarding ion and the greater concentration of surface defects on Xe^+ ion-bombarded GaAs(100).[4]

The O(1s) photopeak exhibits distinct peaks separated by approximately 2 eV (see Figure 2). The lower binding energy photopeak corresponds to oxygen due to gallium and arsenic oxides. The higher binding energy photopeak at 532.4 ± 0.3 eV exhibits the same binding energy that was attributed to molecularly adsorbed oxygen for ion-bombarded GaAs exposed to O_2.[3] The higher binding energy photopeak is in the area where molecularly adsorbed NO would be expected;[15] however, this peak cannot be attributed to NO due to the lack of a corresponding N(1s) signal. The intensity of the O(1s) photopeak at ~532 eV is sufficiently intense (5–10 atom %) to produce a detectable N(1s) signal based on the relative sensitivities for the N(1s) and O(1s) levels.[3,4,16] The adsorbed oxygen peak is formed upon initial exposure to NO (10^6 langmuirs), and the intensity does not appear to grow with increasing exposure. The photopeaks due to oxides increase with increasing NO exposure.

The absence of signal from the N(1s) region suggests that room-temperature adsorption of NO on ion-bombarded GaAs is dissociative and that nitrogen is desorbed from the surface during the reaction. Dissociative adsorption was also observed by Bermudez et al.[2,6] on Ar^+ sputtered/annealed, clean GaAs(110) in which a small amount of nitrogen (≈15% of the oxygen coverage) was observed. So and Ho[5] studied the adsorption of NO on Ne^+ sputter/annealed GaAs(110) at 90 K and reported molecular adsorption of NO with the possibility of some dissociative adsorption. Vibrational bands in the HREELS (high-resolution electron energy loss spectroscopy) spectra provided evidence for the presence of GaO, AsO, and AsN species on the surface following NO adsorption (2.0 langmuirs).[5] They observed some reaction of adsorbed NO

(13) Bertrand, P. A. *J. Vac. Sci. Technol.* **1981**, *18*, 28.
(14) Brundle, C. R.; Seybold, D. *J. Vac. Sci. Technol.* **1979**, *16*, 1186.
(15) Roberts, M. W. In *Adv. Catal.* **1980**, *29*, 70.
(16) Scofield, J. H. *J. Electron Spectros. Relat. Phenom.* **1976**, *8*, 129.

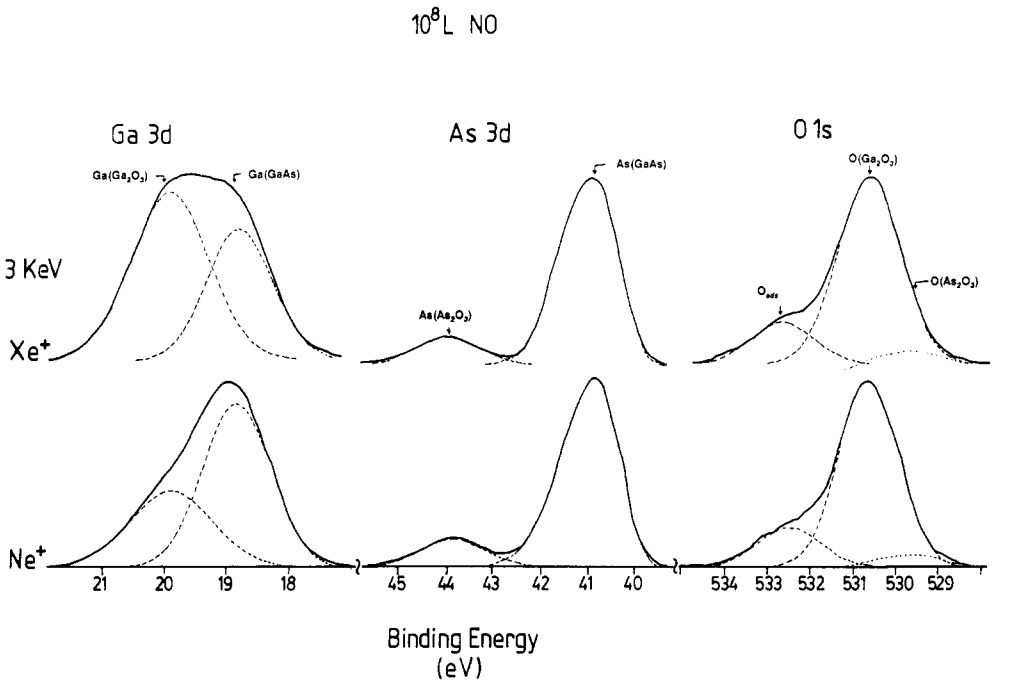

Figure 2. Representative curve-resolved spectra taken at a 15° TOA for 3-keV Ne^+- and Xe^+-ion-bombarded GaAs exposed to 10^8 langmuirs of NO.

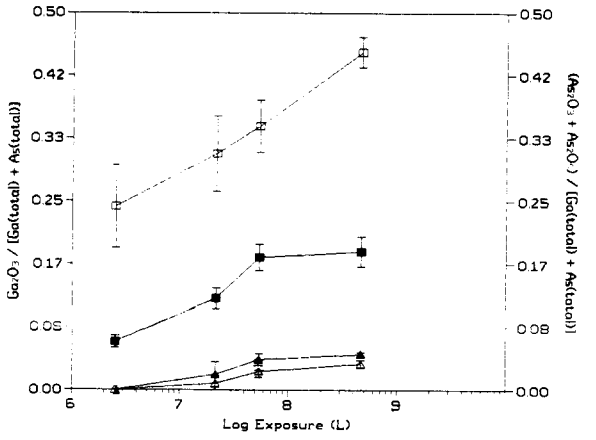

Figure 3. Relative amounts of gallium and arsenic oxides formed for 3-keV Ne^+ (■, ▲) and Xe^+ (□, △) ion-bombarded GaAs as a function of NO exposure. Squares represent gallium oxide, and triangles represent arsenic oxide.

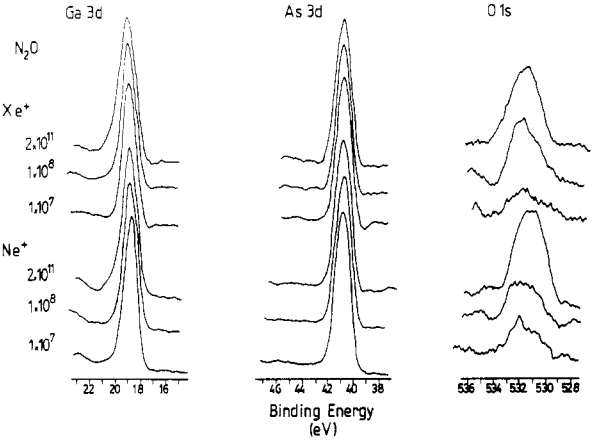

Figure 4. Representative XPS spectra taken at a 15° TOA for 3-keV Ne^+- and Xe^+-ion-bombarded GaAs exposed to N_2O.

with GaAs producing a small amount of N_2O.

In the present study, the quantities of gallium or arsenic oxides following 1.0×10^8 langmuir NO or O_2[4] exposure were

	NO	O_2
Ga_2O_3	0.45 ± 0.02	0.23 ± 0.03
$As_2O_3 + As_2O_5$	0.03 ± 0.01	0.01 ± 0.01

Approximately the same amount of arsenic oxide is produced upon exposure to NO or O_2. The quantity of gallium oxide following NO exposure is about twice that for an equivalent O_2 exposure.

N_2O Exposure. Representative XPS spectra obtained at a 15° TOA are presented in Figure 4 for Ne^+ and Xe^+ ion-bombarded GaAs following 1×10^7, 1×10^8, and 2×10^{11} langmuir N_2O exposures. No signal from the N(1s) level was observed for any of the N_2O exposures. This finding suggests that N_2O dissociates into N_2 (which desorbs) and atomic oxygen.[1] The relative amount of oxide produced as a function of N_2O exposure is presented in Figure 5. Ion-bombarded GaAs exposed to N_2O at the

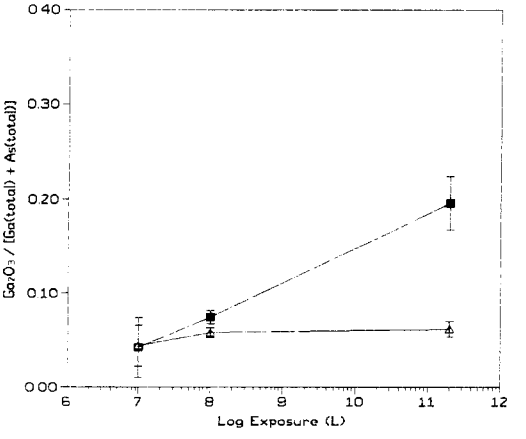

Figure 5. Relative amounts of gallium oxide formed for 3-keV Ne^+ (△) and Xe^+ (■) ion-bombarded GaAs as a function of N_2O exposure.

exposure levels indicated produces only Ga_2O_3, and the amount of Ga_2O_3 is greater for Xe^+ than for Ne^+ ion-bombarded GaAs following N_2O exposures above 10^7

langmuirs. The O(1s) photopeak can be resolved into two characteristic oxygen peaks, one due to the oxygen from Ga_2O_3 (~531 eV) and the other due to adsorbed oxygen (~532 eV).

Except for the observation that nitrogen is not detected on the surface following N_2O exposure, the results for oxidation of ion-bombarded GaAs by the adsorption of N_2O are unlike those presented by Bertness et al.[1] for cleaved GaAs(110) exposed to N_2O. Bertness et al. observed oxidation below 10^6-langmuir N_2O exposure, with As being the predominant oxidized species. For ion-bombarded GaAs, oxidation is discernible at 10^7–10^8-langmuir N_2O exposure, and oxidized gallium (Ga_2O_3) is detected. The extent of oxidation for GaAs(110) exposed to N_2O was greater than that for an equivalent O_2 exposure.[1] In this study the amount of oxide formed is much greater for an ion-bombarded surface exposed to O_2 than for exposure to N_2O at equivalent exposures.[3,4]

Discussion

Distinct differences were observed in the relative amounts of oxides produced for ion-bombarded GaAs exposed to NO and N_2O, as presented in this study and to O_2 studied previously.[3,4] The quantity of Ga_2O_3 produced upon equivalent exposure of xenon-ion-bombarded GaAs to NO, O_2, and N_2O varied in the manner NO > O_2 > N_2O. Differences were also noted among the results obtained for ion-bombarded GaAs and results reported for NO exposure of GaAs(110) by Bermudez et al.[2] and O_2 and N_2O reaction with GaAs(110) by Bertness et al.[1] In previous studies of GaAs(110)[1,2,17,18] arsenic oxide was the predominant oxide formed. The preferential formation of arsenic oxide in the oxidation of GaAs(110) is most likely due to the configuration of the GaAs(110) surface. The dangling bond on the surface As atom of GaAs(110) is the most accessible site for a reaction, and the reactant molecule interacts with the lone pair, resulting in the preferential oxidation of surface As atoms.[18] In comparison of the results of previous studies with the present experiments, a number of differences exist in sample preparation procedures and the surface chemical composition of GaAs. In the current work GaAs was ion bombarded and immediately exposed to NO, O_2, and N_2O, and as a result of ion bombardment the surface exposed to the reactant gases was disordered and gallium-rich.

In the study of O_2 and N_2O reactions with cleaved GaAs(110)[1,17] dissociation of the reacting molecules upon adsorption was the limiting step in the chemisorption reaction. The X–O strength (X = N, O, and N_2) for NO, O_2, and N_2O are 6.5, 5.1, and 1.7 eV, respectively. Bertness et al.[1] observed more oxidation following N_2O adsorption than for O_2 adsorption. On the other hand, Bertness et al.[8] note that enhancement of oxygen adsorption by visible light on atomically clean GaAs(110) is a result of energy released in a surface recombination process of photogenerated electron–hole pairs, which provide sufficient energy to dissociate adsorbed molecules. For reactions with ion-bombarded GaAs(100), exposure to O_2 yields a more highly oxidized surface compared to an equivalent N_2O exposure.

Ion bombardment results in disruption of the GaAs surface structure.[4] It was found from XPS results that the ion-bombarded surface was arsenic-deficient, and evidence was obtained from optical and electrical studies to indicate that the disorder was caused by ion bombardment.[4] Figure 6 illustrates a model previously presented[4] indicating the

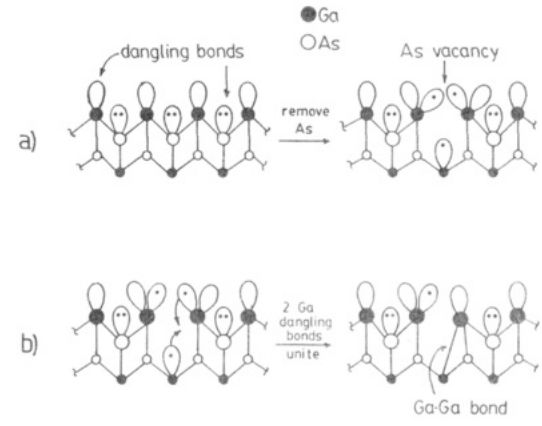

Figure 6. Schematic representation for (a) the removal of As from GaAs as a result of ion bombardment creating As vacancies and singly occupied Ga orbitals and (b) two singly occupied Ga dangling bonds uniting to form a Ga–Ga bond. These configurations could be possible defects that are active sites for reactions on the ion-bombarded surface. The ion-bombarded surface is more disordered than the structures indicated in this figure.

removal of arsenic as a result of ion bombardment. In this model active surface sites are represented as singly occupied gallium or arsenic orbitals, as deficiencies, and Ga–Ga bonds. If active sites are represented as just described, the reactivity of ion-bombarded GaAs exposed to NO, O_2, and N_2O suggests that an increased number of carriers (electrons) on the surfae may be involved. The presence of such defects at the surface could aid in the adsorption and dissociation of reactant molecules depending on the extent that each reactant molecule interacts with the defect.

Utilizing the proposed configuration of the ion-bombarded surface, a possible interaction of O_2 with ion-bombarded GaAs can be suggested. Diatomic oxygen is paramagnetic, possessing two unpaired electrons in degenerate π^* antibonding orbitals. An electron from one of these π^* antibonding orbitals could interact with singly occupied Ga orbitals to produce chemisorbed molecular oxygen. If dissociation occurs, chemisorbed atomic oxygen would be formed. If Ga–Ga bonds exist as a result of ion bombardment, oxygen could react at a Ga–Ga bond to form Ga–O bonds. Cleavage of Ga–Ga bonds is favored; the Ga–Ga and Ga–As bond energies are 1.43 and 2.17 eV, respectively.[19]

Reactivity of NO with ion-bombarded GaAs may take place in a similar way. Nitric oxide possesses a single unpaired electron in a π^* antibonding orbital and may also be expected to interact strongly with the defects on ion-bombarded GaAs.

Nitrous oxide exhibits a lower reactivity with ion-bombarded GaAs compared to O_2 or NO at equivalent exposures. The oxidation of GaAs by N_2O is expected to be greater if the reaction is controlled by the dissociation energy of the molecule; N_2O possesses the lowest dissociation energy among the molecules O_2, NO, and N_2O. The lack of N_2O reactivity may be due to relatively weak interaction of N_2O with defects on the ion-bombarded GaAs surface. Nitrous oxide is diamagnetic and thus has no unpaired electrons to interact with defects on the ion-bombarded surface. Thus, even if the reaction between N_2O and GaAs is thermodynamically favored, N_2O does not interact strongly with surface singly occupied gallium or arsenic orbitals or defects.

(17) Su, C. Y.; Lindau, I.; Chye, P. W.; Skeath, P.; Spicer, W. E. *Phys. Rev. B* **1982**, *25*, 4045.
(18) Lucovsky, G.; Bauer, R. S. *Solid State Commun.* **1979**, *31*, 931.
(19) *Handbook of Chemistry and Physics*, 61st ed.; Weast, R. C., Astle, M. J., Eds.; The Chemical Rubber Co.: Boca Raton, FL, 1980; pp F222–223.

The trends in reactivity for ion-bombarded GaAs exposed to various gases[4] (reactivity NO > O_2 > N_2O) are very similar to the results reported by others[1,2,5,8] for photoenhanced chemical reactions on GaAs. Both O_2 and NO exhibit photoenhancement reaction[1,2,6,8] with GaAs, whereas N_2O does not exhibit photoenhancement.[1] Photon-induced enhancement in reactivity is attributed to interaction of the adsorbed molecule with photogenerated carriers, i.e., electron–hole pairs that are created in the bulk by interaction of the photon with the semiconductor. The pairs migrate to the surface and react with the adsorbate–surface complex and induce reactions.[20] Photoenhanced reactions involve the interaction of the adsorbing species with an increased concentration of electrons at the surface. As a result of the present study, it is suggested that processes for ion-bombarded GaAs may be similar to those occurring in photoenhanced reactions where ion-bombardment generated singly occupied gallium orbitals (free electrons) and other defects are principal active sites for reactions with gases.

The differences in the extent of oxidation for Xe^+ and Ne^+ ion-bombarded GaAs surfaces by either NO, O_2, or N_2O support previous results[4] where the effect of the mass of the bombarding ion on the chemical reactivity was investigated. Damage caused by Xe^+-ion bombardment is confined mainly to surface atoms, therefore imparting more defects at the surface. The penetration of Ne^+ into GaAs is greater than for Xe^+, and thus fewer defects are found at the surface. Hence, the concentration of defects at the surface is greater following Xe^+ bombardment, and thus Xe^+-ion-bombarded GaAs exhibits increased relative reactivity for all three gases.

Acknowledgment. We acknowledge the funding of this project by Texas Instruments and the Virginia Center for Innovative Technology. The National Science Foundation provided funds for an equipment grant.

Registry No. GaAs, 1303-00-0; N_2O, 10024-97-2; NO, 10102-43-9; O, 7782-44-7; Ne^+, 14782-23-1; Xe^+, 24203-25-6.

(20) Ying, Z.; Ho, W. *Phys. Rev. Lett.* **1988**, *60*, 57.

$Ca_4Bi_6O_{13}$, a Compound Containing an Unusually Low Bismuth Coordination Number and Short Bi···Bi Contacts

J. B. Parise,*,† C. C. Torardi,*,‡ M.-H. Whangbo,*,§ C. J. Rawn,⊥ R. S. Roth,*,⊥ and B. P. Burton⊥

Mineral Physics Institute, Department of Earth and Space Sciences, State University of New York, StonyBrook, New York 11794; Central Research and Development Department, E. I. du Pont de Nemours and Co., Inc., Experimental Station, Wilmington, Delaware 19880; Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695; and National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received February 12, 1990

Single crystals and powder samples of a new bismuth(III) calcium oxide, $Ca_4Bi_6O_{13}$, have been synthesized and studied by X-ray diffraction. This compound crystallizes in the orthorhombic space group $C2mm$ with $Z = 2$. The absence of a center of symmetry was confirmed by the presence of a second harmonic signal some 60 times that observed for quartz. The cell parameters are $a = 5.937$ (1), $b = 17.356$ (4), $c = 7.206$ (4) Å. A weak superstructure (2 × 3.6 Å), visible in long-exposure rotation and precession photographs, exists along c^* due in part to alternation of oxygen and vacancies along the c axial direction. The structure consists of ribbons of edge-linked BiO_5 square pyramids running parallel with the c axis. These chains are linked via a novel three-coordinate Bi atom to form semicylinders stacked along the a axial direction. Sheets of these units are then stacked along the b axial direction and are separated by Ca ions in 7-fold coordination with oxygen. Along the c direction, the three-coordinate Bi atoms form ···BiOBi···BiOBi··· chains. The Bi···Bi contacts of these chains are short, 3.341 (2) Å, and the bridging oxygen atoms are displaced by about 0.25 Å from the centers of the Bi–O–Bi bridges in the direction perpendicular to these bridges. Molecular orbital calculations suggest that this displacement of the bridging oxygen atoms reduces the extent of lone pair–lone pair repulsion that occurs in each short Bi···Bi contact.

Introduction

The frenetic activity devoted to determination of the structural properties of the alkali metal/bismuth oxide/copper oxide based superconductors has somewhat overshadowed a need for a better understanding of the phase relations in the binary and ternary oxide systems on which they are based. As part of an ongoing study of the structural characterization of compounds in these systems,[1] we report here the structure of $Ca_4Bi_6O_{13}$. With respect to copper-containing superconductors, we were particularly interested in obtaining precise information on the geometric nature of the Bi coordination, a topic of some discussion in the literature.[2-5] In $Ca_4Bi_6O_{13}$ the bismuth

† State University of New York.
‡ E. I. du Pont de Nemours and Co.
§ North Carolina State University.
⊥ National Institute of Standards and Technology.

(1) (a) Roth, R. S.; Rawn, C. J.; Ritter, J. J.; Burton, B. P. *J. Am. Ceram. Soc.* **1989**, *72*, 1545. (b) Roth, R. S.; Rawn, C. J.; Bendersky, L. A. *J. Mater. Res.* **1990**, *5*, 46. (c) Hwang, N. M.; Roth, R. S.; Rawn, C. J. *J. Am. Ceram. Soc.*, to be published. (d) Roth, R. S.; Burton, B. P.; Rawn, C. J. *J. Am. Ceram. Soc.*, to be published. (e) Roth, R. S.; Rawn, C. J.; Burton, B. P.; Beech, F. *J. Res. NIST*, to be published. (f) Roth, R. S.; Rawn, C. J.; Burton, B. P.; Beech, F. *Abstr. Am. Crystallogr. Assoc. Ser. 2* **1989** *17*, 41.

0897-4756/90/2802-0454$02.50/0