

LOW TEMPERATURE ADSORPTION AND REACTION OF NO ON GaAs(110)

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We have used polarized surface infrared spectroscopy in the multiple internal reflection mode to study the chemistry of NO adsorption on GaAs(110) at 90 K. NO is found to be reactive on the surface at these low temperatures, adsorbing dissociatively and molecularly. The reaction products identified are molecular N₂O, oxygen end bonded with the molecular axis perpendicular to the surface, and a flat-lying hyponitrito species. Heating the surface above 200 K leaves an arsenic nitride on the surface.

The study of the chemical reactions of nitric oxide on metal and semiconductor surfaces has been stimulated by their implication to technology. Experiments with metal surfaces are focused on the catalytic chemistry of NO [1-5]; the reduction of nitric oxide to non-toxic gases with metal catalysts plays a dominant role in air pollution control. Reactive dissociative adsorption of nitrogen oxides on semiconductor surfaces might prove useful in the growth of dielectric layers such as oxides and nitrides [6-9].

Although on silicon surfaces dielectric films may be grown by dosing the surface with molecular oxygen or nitrogen (low probability reactions), the electronically important GaAs surfaces are almost non-reactive to the molecular gases. Less than 1 in 10⁸ oxygen molecules impinging on a clean GaAs(110) surface are reported to dissociatively absorb and react at room temperature [10]. Various techniques have been used to enhance the oxygen uptake, including illumination with visible light, electronic excitation, increased surface roughness, etc. [11]. An alternative approach is the use of heteronuclear oxygen containing molecules as a means of providing "reactive" atomic O. Potential candidates for this purpose are the nitrogen oxides [11]. Although there is a large number of studies on the adsorption of nitrogen oxides on Si surfaces, little work has been done on the reaction of GaAs surfaces with oxides of nitrogen [7,9,11].

In a separate paper we report on the dissociative adsorption and resulting oxidation of GaAs(110) with NO₂ [12]. An important part of the chemistry of this system is the interaction of the dissociation products with this surface. In this paper we report on IR vibrational spectroscopy of the chemical interaction of NO with the GaAs(110) surface. The experiments were performed under ultra-high vacuum (UHV) conditions at temperatures around 90 K. NO is found to be very reactive on the surface at these low temperatures, adsorbing both molecularly and dissociatively. In addition molecular N₂O and a hyponitrito species N₂O₂ are formed on the surface.

The key element in studying the vibrational spectra of adsorbed NO and its reaction products on GaAs(110) with high sensitivity is the use of the multiple internal reflection [13]. The sample geometry used here is shown schematically in fig. 1. 0.5 mm thick defect compensated p-type GaAs wafers are cut in pieces 4 cm long and 2 cm wide with 45° bevels at each of the short sides. The infrared radiation, normally incident on the input level, is internally reflected a total of ≈ 38 times on the front side. The 45° internal reflection angle gives roughly equal sensitivities to the various components of the electric field for both p and s polarizations [13]. While p-polarized light can probe modes polarized perpendicular (z direction) and parallel (x direction) to the surface, s-polarized light is only sensitive to

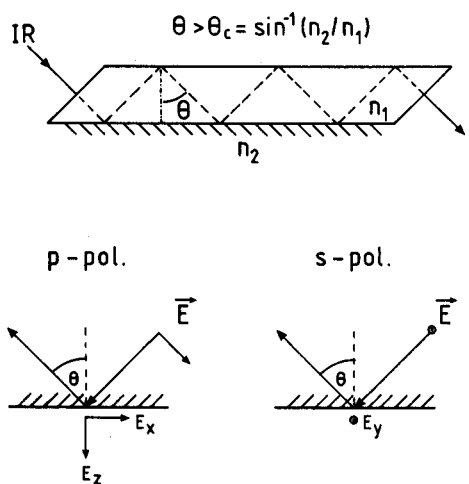


Fig. 1. Sample geometry for surface infrared spectroscopy in the multiple internal reflection mode. Electric field vectors are shown at the bottom for the two polarizations used ($\theta = 45^\circ$). For GaAs $\theta_c = 16.04^\circ$ and $E_z = 1.95 E$, $E_x = 1.31 E$ and $E_y = 1.66 E$.

modes parallel (y directions) to the surface.

The experimental arrangement consists of a commercial interferometer coupled to an ultra-high vacuum chamber with KBr windows. Liquid-nitrogen-cooled HgCdTe detectors have been used to investigate the spectral range $850\text{--}3000\text{ cm}^{-1}$. The vacuum chamber is equipped with a cylindrical mirror Auger spectrometer, an argon ion sputter gun and a mass spectrometer. Evacuation is done by a turbo molecular pump; after a 10 h bake out at 150°C the base pressure was 1×10^{-10} mbar. The front of the sample surface was cleaned by sputtering with keV Ar ions with the sample held at room temperature, followed by careful annealing at 800 K (the back-surface native oxide is not degraded during the cleaning and was checked to be inert to NO adsorption). High purity NO (99%) is adsorbed from the gas phase; during the dose the NO gas is admitted into the UHV chamber through a variable leak valve. All exposures given in the text are derived from a Bayert Alpert gauge without calibration.

All infrared spectra were taken in a differential mode, where the reference spectrum of the clean surface is ratioed to that associated with the adsorbate-covered surface.

Fig. 2 shows a sequence of typical p-polarized IR spectra at 94 K taken as a function of increasing NO

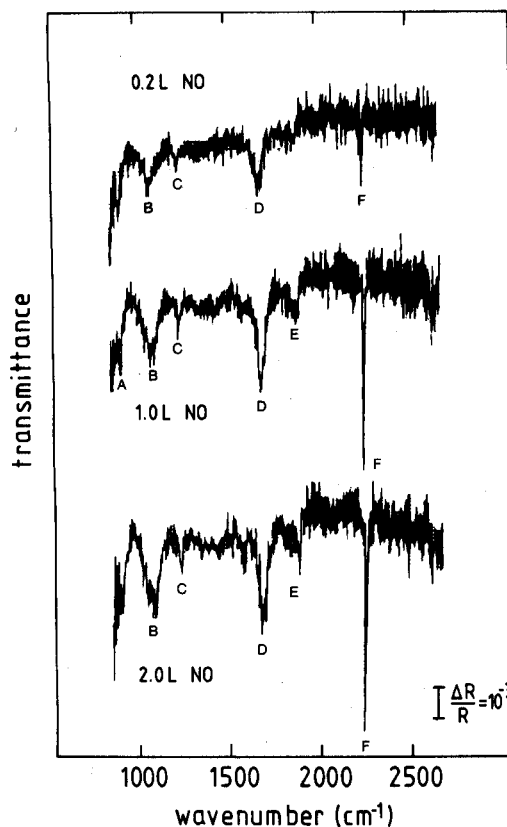




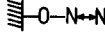
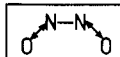
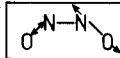


Fig. 2. Surface IR vibrational spectra taken with increasing ^{14}NO exposure on GaAs(110) at 94 K. The exposures are quoted in langmuir of molecular NO. All spectra are measured with p-polarized light. The indicated transmittance $\Delta R/R$ is per 38 reflections.

exposure. At low coverage (0.2 L) three vibrational bands at 1070 , 1670 and 2230 cm^{-1} are clearly visible; the presence of a fourth weaker mode at 1220 cm^{-1} can also be inferred. With increasing exposure all features gain in intensity and an additional adsorption peak at 1850 cm^{-1} develops. The assignment of these modes, based on results of isotopic shift experiments and on comparing the IR data to those of NO adsorption on metal surfaces [1-5] is given in table 1 and discussed below. The analysis reveals the coexistence of several molecular and atomic species on the GaAs surface.

Evidence for molecularly adsorbed NO is given by the modes at 1670 and 1850 cm^{-1} , both of which shift in frequency to 1650 and 1830 cm^{-1} in the

Table 1
Vibrational frequencies (cm^{-1}) of NO adsorption on GaAs(110) at 90 K

	^{14}NO IR data	^{15}NO IR data	^{14}NO EELS data [7]	Gas phase	Assignment
p polarization					
A	900	890	880		see text
B	1070	1040	1090	1068	As-N stretch 
C	1220	1205	1260	1268	N-O stretch of N_2O 
D	1670	1650			N-O stretch (bent terminal or linear bridge) 
			1790	1876	
E	1860	1830			N-O stretch (linear terminal) 
F	2230	2170	2250	2224	N-N stretch of N_2O 
s polarization					
G	1200	1170		1240 ^{a)}	symmetric N-O stretch of N_2O_2 
H	1255	1220		1285 ^{a)}	asymmetric N-O stretch of N_2O_2 

^{a)} Data from $\text{Pt}(\text{N}_2\text{O}_2)(\text{PPh}_3)_2$ complex.

^{15}NO -isotope experiment (in the particular isotope spectrum shown in fig. 3c the 1830 cm^{-1} is not detected). These are assigned to N-O stretching modes. In the gas phase the N-O stretch frequency is 1876 cm^{-1} . Upon adsorption on metal surfaces this frequency is found to be substantially red-shifted, with the shift characteristic of the local bonding geometry. While adsorption in a terminal linear configuration only gives a slight shift, bridge-bonded or bent NO molecules can be shifted as much as 400 cm^{-1} to the red [14]. Accordingly, the 1850 cm^{-1} mode which appears at higher coverages is ascribed to the N-O stretch of NO molecules in a linear terminal bonding geometry. The IR absorption at 1650 cm^{-1} which grows from the beginning of the exposure is consistent either with a NO molecule in a linear bridge or a bent terminal configuration.

Besides molecular adsorption, NO is also found to adsorb dissociatively on the GaAs(110) surface at 94 K. The mode at 1070 cm^{-1} (1040 cm^{-1} for ^{15}NO) increasing in intensity from the beginning of the ex-

posure characterizes the As-N stretch^{#1}. On the other hand, no indication for formation of an As-O bond exists; no signal around 990 cm^{-1} characteristic for this species is observed^{#1}. The gallium-oxygen bond was not probed in this experiment, because its frequency of $\approx 770\text{ cm}^{-1}$ was in a region of poor sensitivity of the detector used. A very weak feature detected in some spectra at 900 cm^{-1} (red-shifted to 890 cm^{-1} for the ^{15}NO isotope) might be due to a Ga-N species. However, this IR band may be alternatively attributed to the bending-vibration of molecularly adsorbed NO, expected likewise to absorb in this frequency range.

Simultaneously with the dissociative and molecular NO adsorption, N_2O is formed in a surface reaction, as is evident in fig. 2. The strong and very sharp vibrational band at 2230 cm^{-1} (2170 cm^{-1} for ^{15}NO) is assigned to the N≡N stretch and the absorption at 1220 cm^{-1} (1205 cm^{-1} for ^{15}NO) is

^{#1} The diatomic molecules AsO, AsN and GaO are characterized by vibrational frequencies of 963 , 1068 and 766 cm^{-1} , respectively [15]. Exposing the clean GaAs(110) surface at 300 K to more than 1010 of an N_2/O_2 gas mixture gives indeed rise to vibrational bands around 770 , 990 and 1070 cm^{-1} in the IR spectrum.

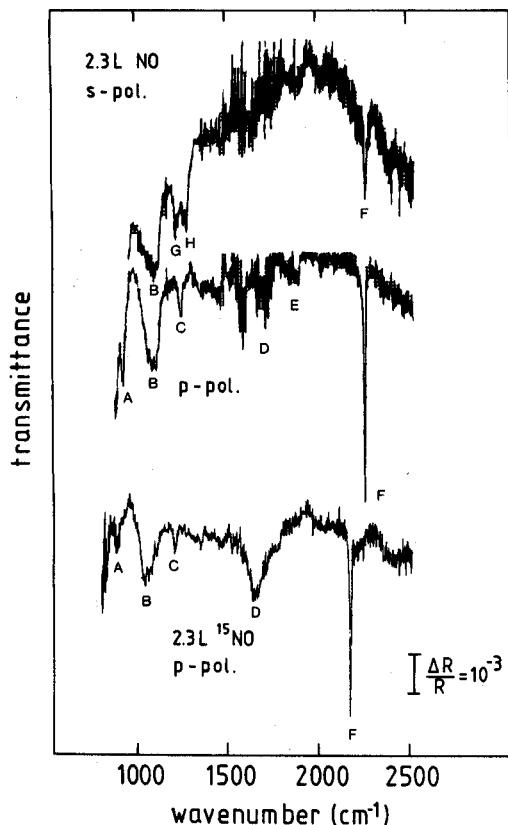


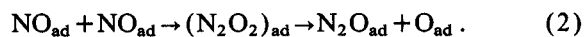
Fig. 3. Surface IR vibrational spectra of GaAs(110) exposed at 94 K to 2.3 L of NO. In the top two spectra the surface is exposed to ^{14}NO and the IR reflectivity changes are measured for p polarization and s polarization, respectively. At the bottom a p polarized IR spectrum of the GaAs(110) surface exposed to the ^{15}NO isotope is shown.

assigned to the N–O stretch of molecularly adsorbed N_2O . These values have to be compared to the gas phase frequencies of 2224 and 1286 cm^{-1} respectively [16]. While the $\text{N}\equiv\text{N}$ stretch frequency is almost unchanged, the N–O stretch is shifted to the red. This suggests a bonding of the linear N_2O molecule to the GaAs surface via the oxygen end. This oxygen down orientation is consistent with the bonding geometry of N_2O on Si(111) (7×7) [8] but in contrast to the bonding on Ru(001) [17] and in metal complexes [18]; in the later cases N_2O was found to bond via the nitrogen end.

A possible mechanism which produces N_2O would be the reaction of adsorbed nitrogen atoms with molecularly adsorbed NO:



An alternative reaction pathway for the N_2O formation from adsorbed NO would be via an intermediate hyponitrito species:



An indication that mechanism (2) may take place to some extent is provided by the IR spectra taken with s-polarized light shown in fig. 3a. Note that with s-polarized light vibrations with displacements parallel to the surface are probed exclusively. While the As–N vibration at 1070 cm^{-1} is less effected the strong N–N absorption at 2230 cm^{-1} in the p spectrum declines substantially in the s spectrum. This suggests an almost vertical alignment of the N_2O molecule with respect to the surface. Furthermore, the N–O stretch of the N_2O molecule, present in the p spectrum at 1220 cm^{-1} , is not seen in the s spectrum. Instead a doublet with absorptions centered at 1200 and 1260 cm^{-1} appears. A doublet in this frequency range is indeed characteristic of a hyponitrito species. The hyponitrito ligand complex $\text{Pt}(\text{N}_2\text{O}_2)(\text{PPh}_3)_2$ has strong symmetric and antisymmetric stretches of the terminal NO at 1285 and 1240 cm^{-1} [19]. We therefore tentatively interpret the adsorption state characterized by the bands at 1200 and 1260 cm^{-1} in the s spectrum as a hyponitrito species. The measured IR absorption accordingly represents the symmetric and antisymmetric N–O stretch. Both modes are exclusively polarized parallel to the surface indicating that the hyponitrito species is lying flat on the surface.

The major difference between the possible N_2O formation reactions is that mechanism (1) involves atomic nitrogen while mechanism (2) produces atomic oxygen. The IR data presented here give direct evidence for the presence of atomic N on the surface but are unable to prove the generation of atomic oxygen due to the limited spectral range on the low frequency side. The As–N bond being energetically more favorable than the As–O bond, arsenic sites are likely to be blocked by the atomic nitrogen. Atomic oxygen, if present, should be bonded to the Ga atoms. On the oxidized (110) surface of GaAs the Ga–O stretch is characterized by an IR band at 770 cm^{-1} [12]. In a recent EELS study of the NO adsorption on GaAs(110), sensitive to this

frequency range, So and Ho [7] did not observe any energy losses around 770 cm^{-1} (however, the background in the EELS spectra is strongly rising in this wavenumber range), which might indicate the absence of gallium oxygen bonds. We may thus conclude that although a hyponitrite species is present at the surface, mechanism (1) might be the dominant reaction pathway for the N_2O formation.

When the GaAs(110) surface, which had been exposed to NO at 90 K, is heated above 200 K substantial changes in the vibrational spectrum are observed. All vibrational bands due to molecularly adsorbed species disappear except the As-N stretch at 1070 cm^{-1} which is detected with almost unchanged intensity, indicating an arsenic-nitride covered surface. The passivating nitride layer can be removed by heating the sample to 800 K for several minutes.

In conclusion, we have shown that at 90 K NO is very reactive on GaAs(110), adsorbing both molecularly and dissociatively. We have identified as reaction products nitrogen atoms, molecular NO with linear terminal and bent terminal (or linear bridge bonded) configurations and adsorbed N_2O and N_2O_2 which are formed from NO reactions on the surface. In particular the latter two products call for a detailed time-resolved study to elucidate the reaction dynamics and mechanisms.

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