# Reaction of NO to form $N_2O$ and surface oxide on GaAs(100)

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Metastable quenching spectroscopy (MQS), temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (HREELS), and Auger electron spectroscopy (AES) were used to study the reaction of NO on GaAs(100) at 74–77 K. Adsorbed NO reacts nearly completely to form  $N_2O$  and surface oxide. A NO dose of about 200 L saturates the reaction, forming a complete oxide layer. The MQ spectra show that the product  $N_2O$  is adsorbed predominately with the O atom down on the oxide layer, resulting in a 30% higher saturation coverage than for  $N_2O$  adsorbed on the clean surface. Dosing the clean surface at 300 K with 200 L NO gave no measurable NO adsorption,  $N_2O$  production, or surface oxide formation.

#### 1. Introduction

Surface reactions that lead to oxidation of the surface can play a significant role in surface chemistry by enhancing some reactions and preventing others. The controlled oxidation of GaAs can either be used to passivate the surface or as an initial step for further, more complex reactions. Quite a number of studies with differing results have been published on the oxidation of GaAs with  $O_2$  [1–30]. Most of them focus on the GaAs(110) surface [1–24]. Only a few report results on GaAs(100) [26–30], which is more difficult to handle experimentally, but is of greater interest because of its practical application in electronic device fabrication.

Bartels and Mönch have recently given an overview of the oxidation of the (110) surfaces of III-V semiconductors [5]. Previous results show that the oxidation of GaAs by  $O_2$  at room temperature is very inefficient; it has been reported by many investigators that exposures  $\geq 10^6$  langmuir (L) are necessary to obtain monolayer oxidation of the surface. "Activated" oxygen has generally been used in UHV studies to enhance the reaction: this usually means oxygen which has been exposed to a hot filament or to electron bombardment.

Only a few studies have been published on the interaction of GaAs with nitric oxide (NO) [30-33]. Two studies have been made of the NO/GaAs(100) system [30,31]. Ekwelundu and Ignatiev [31] saw N and O contamination of the surface using Auger spectroscopy after exposure of the surface at 300 K to 10<sup>7</sup> L of NO. Epp and Dillard [30] studied the room-temperature oxidation of ion-bombarded GaAs(100) by 10<sup>6</sup>-10<sup>8</sup> L of NO and  $10^7 - 10^{11}$  L of N<sub>2</sub>O. They found that the extent of oxidation on such high-defect surfaces is  $NO > O_2 > N_2O$ . Bermudez et al. [32] compared the surface oxidation by NO and  $O_2$ on GaAs(110) at 300 K. They found the NO reaction to be *slower* than that of  $O_2$  for dosages below  $10^7$  L. Under these conditions the reaction involves defects and shows no photo-enhancement. For higher dosages NO reacts faster and the reaction becomes photo-enhanced. So and Ho [33] found NO to adsorb molecularly with a high sticking probability at 90 K on GaAs(110). They observed a small amount of nitrous oxide  $(N_2O)$  produced on the surface by reaction of NO.

In the present work we studied the thermal reaction of nitric oxide with GaAs(100) at 74–77 K. Temperature-programmed desorption (TPD), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), and metastable quenching spectroscopy (MQS) were used to identify the reaction products.

## 2. Experimental

The experimental methods used in this work are similar to those described in detail previously [34]. However prior to this work a new UHV chamber was installed, and a HREELS spectrometer was added to the system. In view of these and other changes, a general description of the experimental apparatus is given below.

The experiments were carried out in a UHV chamber with a base pressure of  $< 1 \times 10^{-10}$  Torr. The chamber is evacuated by a 300  $\ell/s$  turbopump which is backed by an oil diffusion pump and a mechanical pump. A titanium sublimation pump is installed at the bottom of the chamber, and is shielded to prevent contamination of the upper region where the experiments are carried out. The sample is connected to a liquid nitrogen cryostat which is mounted on a rotatable x-y-z manipulator on top of the chamber. The manipulator has 250 mm of vertical motion, which allows the sample to be located at the three working levels of the chamber where experiments are performed.

The top level of the chamber is used for sample preparation. This level is equipped with a close-coupled multichannel capillary array (MCA) gas doser, metal dosers, and an ion gun for sample cleaning. The middle level is 76 mm below the top level. This is the main experimental level, and is equipped with a Physical Electronics 15155 electron gun and cylindrical mirror electron energy analyzer (CMA) for Auger electron spectroscopy (AES), a UTI 100C quadrupole mass spectrometer, a retarding potential difference (RPD) electron energy analyzer with hemispherical grids for MQS, UPS, and LEED measurments, and a Varian 981-2125 electron gun for the LEED electron beam source. The bottom level is 152 mm below the middle level, and houses an LK 2000 high-resolution electron energy loss spectrometer (HREELS). The spectrometer was operated in the specular mode. An

incident electron beam energy of 5 eV was used, giving a resolution of 10 meV FWHM. The Auger spectra were taken using an incident electron beam energy of 3 keV. For high-energy spectra the 100-1350 eV range was scanned at 8 eV/s with a modulation amplitude of 2 V. The low-energy spectra were taken over the 20-80 eV range at 0.8 eV/s with a modulation amplitude of 400 mV.

The mass spectrometer is used for TPD studies. The system for performing TPD has been described previously [35]. A RHK 310 temperature programmer provides a linear temperature ramp. An IBM AT computer provides control and data acquisition during the TPD experiments. The computer steps the mass spectrometer through up to 12 programmed masses during the temperature scan, providing up to 12 multiplexed TPD spectra from each scan. The mass spectrometer is mounted inside a copper shroud with a 3 mm diameter opening centered on the mass filter axis. The sample is moved to a position about 2 mm in front of the opening for the TPD runs. This arrangement minimizes the background signal due to desorption from surfaces other than the front surface of the sample.

In MQS, a beam of metastable rare gas atoms, usually He\* or Ne\*, is produced in a separate vacuum chamber and passed into the UHV chamber where it impinges on the surface. At the surface electronic transitions occur which give ejection of electrons from surface orbitals and leave the rare-gas atoms in the ground state [34,36]. The ejected electrons are energy analyzed to give an electronic spectrum characteristic of the surface. The principal advantage of MQS is that the metastable atoms interact only with the outermost orbitals of the surface layer (unlike the photons used in UPS), giving MQS a high surface specificity.

The metastable beam is produced in a separate double-chamber vacuum system, and the formation and characteristics of this beam have been described in detail previously [34]. The He beam is produced by expansion of He gas at a pressure of 2.0 atm into vacuum through a 50  $\mu$ m diameter orifice. After passing through an electroformed skimmer into a separately pumped vac-

uum chamber, the atoms are electronically excited by passing through a cold-cathode discharge. This produces both  $2^{1}$ S and  $2^{3}$ S metastable He<sup>\*</sup> atoms. The 2<sup>1</sup>S metastables are removed by passing the beam through radiation from a low pressure He discharge lamp [37]. leaving only 2<sup>3</sup>S metastable He\* and ground state He atoms. The RPD analyzer used for MQS is home made, and consists of three hemispherical grids followed by a planar draw-off grid, a 40 mm diameter Galileo 3040 chevron microchannel plate electron multiplier, and a Galileo fiber optic phosphorescent plate for observing the LEED pattern. The metastable atom beam enters the UHV chamber from the back of the RPD analyzer, and passes through axial holes in all the analyzer elements to impinge on the sample.

In the MQS experiments, the kinetic energy  $E_k$  of an emitted electron with respect to the vacuum level of the sample is given by  $E_k = RPD$  $+\phi_a - \phi_s$ , where RPD is the retarding potential difference between the sample and the analyzer grids,  $\phi_a$  is the analyzer work function, and  $\phi_s$  is the sample work function. The  $\phi_a$  for our analyzer has been found to be very stable, with a value of 3.8 eV. For electrons ejected by the Auger deexcitation (or Penning) mechanism, the nominal  $E_{k} = E^{*} - E_{b} - \phi_{s}$ , where  $E^{*}$  is the excitation energy of the He<sup>\*</sup> atoms,  $E_{b}$  is the binding energy with respect to the Fermi level, and  $\phi_s$  is the work function of the sample. For electrons ejected from the Fermi level  $E_{\rm b} = 0$ : substituting  $E_{k} = E^{*} - \phi_{s}$  into the RPD equation above gives RPD =  $E^{*} - \phi_{a}$ , so the Fermi level is fixed on the RPD scale, independent of  $\phi_s$ . Since the gas-phase  $E^*$  value is 19.8 eV for He<sup>\*(3</sup>S) and  $\phi_a = 3.8$  eV, this puts the Fermi level at RPD = 16.0 eV. This assumes that the  $E^*$  value is not significantly changed by the potential energy interaction of the He\* initial state and He final state with the target at the moment of electron emission [34,38].

The GaAs(100) sample was cut from an ndoped (Si,  $(1.1-1.4) \times 10^{18}$  cm<sup>-3</sup>) wafer from MCP Electronic Materials Ltd. Before it was installed in the UHV chamber the sample was degreased in a boiling 1:1 mixture of acetone and trichloroethylene for 2 min and rinsed thor-

oughly with acetone, methanol and water afterwards. Then the sample was etched for 2 min in a 10:5:2 mixture of  $H_2O_2$ ,  $NH_4OH$  and  $H_2O_2$ . After it was rinsed with triply distilled water and dried with helium, it was indium-soldered to a molybdenum plate which was connected to the cryostat. To control the sample temperature, two chromel-alumel thermocouples were spot-welded to platinum foil which then was spot-welded to the molybdenum plate as close to the sample as possible. The sample was heated radiatively from the back (molvbdenum) side by four tungsten filament heaters. The heating can be controlled either manually or by the RHK 310 control unit. With this heating method and the liquid nitrogen cryostat the accessible temperature range was from 74 to 1100 K. A sample temperature down to 74 K could be reached by pumping on the liquid-nitrogen reservoir.

The sample was cleaned in the UHV chamber by an ion bombardment and annealing (IBA) treatment as described by Oelhafen et al. [39]. We sputtered the surface with  $1\mu A/cm^2$  of 250 eV Ar<sup>+</sup> ions at a temperature of 720 K for 30 min. The incident angle of the ions was 45° from the surface normal; at normal incidence no significant removal of the oxide layer was observed. After sputtering, the surface was annealed at 820 K for 2 min. This procedure was performed routinely every day before experiments were started, and also after experiments which led to significant surface contamination. The cleanliness was monitored by AES, which is very sensitive to the main contaminants O, C and N. The low-energy Auger peaks of As at 31 eV and Ga at 55 eV were monitored to ensure that the surface stoichiometry remained constant throughout the experiments. The surface cleanliness was also monitored using MQS; the MQ spectrum was found to be sensitive to both surface contamination and changes in stoichiometry of the clean surface. Later LEED spectra taken on GaAs(100) samples cleaned using the above IBA procedure showed a dominant  $8 \times 2$  pattern characteristic of the Garich  $c(8 \times 2)$  reconstructed (100) surface [40-42].

The surface gas exposures from the close-coupled MCA doser were measured in doser Torr  $\cdot$  s, i.e., the product of the reservoir pressure of the

dosed gas behind the MCA (typically 0.5 Torr) and the exposure time. A calibration performed by comparing TD spectra after molecular beam dosing and background dosing gave approximately 25 doser Torr  $\cdot s = 1$  langmuir (L). The doses for this work are given in langmuir, using this conversion factor.

### 3. Results and discussion

Fig. 1 shows the TPD spectra for NO<sup>+</sup> (mass 30) and N<sub>2</sub>O<sup>+</sup> (mass 44) following exposure of the sample at 77 K to 120 L of NO. The two spectra have the same temperature dependence, with the peak at 110 K and the tail extending up to 300 K. The ratio of the signal intensities at the peak,  $I_{44}/I_{30} = 3.8$ , is only slightly smaller than the ratio of 4.0 obtained from measuring the gas-phase mass spectrum in the chamber. Therefore the NO<sup>+</sup> signal from TPD is nearly all due to cracking of N<sub>2</sub>O<sup>+</sup>. This shows that at this exposure the adsorbed NO reacts nearly completely to form N<sub>2</sub>O on the surface. As will be discussed, the reaction that occurs is NO(ad) +



Fig. 1. TPD spectra of NO<sup>+</sup> (mass 30) and  $N_2O^+$  (mass 44) following exposure of the sample at 77 K to 120 L of NO. The NO<sup>+</sup> signal is due to the cracking of  $N_2O^+$ .



Fig. 2. The integrated TPD signal of  $N_2O$  at mass 44 as a function of NO dosage.

 $NO(ad) \rightarrow N_2O(ad) + O(ad)$ , which produces an oxide layer on the surface.

The integrated TPD signal at mass 44 as a function of NO dosage is shown in fig. 2. After a sharp onset, the curve appears to be approaching a saturation value at high dosage. To see if this corresponds to the saturation coverage of  $N_2O$  on the oxide layer, the surface was exposed to  $N_2O$  following desorption of the  $N_2O$  produced by reaction of NO on the surface. Fig. 3 shows the



Fig. 3. The integrated TPD signal of  $N_2O$  at mass 44 as a function of  $N_2O$  dosage on clean GaAs(100) (solid circles) and on oxidized GaAs(100) (open circles).



Fig. 4. MQ spectra following saturation doses of NO and N<sub>2</sub>O on GaAs(100) at 77 K. The four N<sub>2</sub>O peaks are identified by the orbital designations. See text for a discussion of the different N<sub>2</sub>O orientations on the two surfaces.

resulting curve for the integrated TPD signal. It is seen that the same saturation coverage of  $N_2O$ is produced, but with an exposure of only about 4 L versus about 200 L for NO on clean GaAs (fig. 2). Thus exposure of the clean surface to NO at 77 K produces a saturated monolayer coverage of  $N_2O$  on the oxide layer. Fig. 3 also shows that when  $N_2O$  is dosed on clean GaAs(100) at 77 K the saturation coverage is ~ 30% lower than on the oxide layer. The reason for this is discussed below.

Fig. 4 shows the MQ spectra following saturation doses of NO (trace a) and N<sub>2</sub>O (trace b) on the clean surface at 77 K. The four peaks can be assigned to the  $6\sigma$ ,  $1\pi$ ,  $7\sigma$  and  $2\pi$  orbitals of N<sub>2</sub>O by comparison with the gas-phase UP spectrum [43]. The spectrum of the N<sub>2</sub>O produced by reaction of NO on the surface (trace a) is shifted to 0.8 eV higher energy than that of N<sub>2</sub>O adsorbed on the clean surface (trace b): this is due to an increase of 0.8 eV in the work function, and shows that N<sub>2</sub>O is tied to the vacuum level, rather than the Fermi level. There is no evidence of the NO MQ spectrum [44] in trace a. This is consistent with the TPD results showing that adsorbed NO reacts almost completely to form  $N_2O$  below the onset of  $N_2O$  desorption at 90 K.

The differences between the MQ spectra of  $N_2O$  on the clean (trace b) versus oxidized (trace a) surfaces seen in fig. 4 can be explained in terms of different orientations of  $N_2O$  on the two surfaces. The Auger deactivation (or Penning ionization) mechanism for electron election depends on the overlap of the He\*1s orbital with the orbitals of the target molecule. This overlap requirement makes MQS sensitive to the orientation of the molecule on the surface [45].  $N_2O$  is a linear molecule, isoelectronic with CO<sub>2</sub>. The  $6\sigma$ orbital is dominant at the O end, the  $7\sigma$  orbital is dominant at the N end, and the  $\pi$  orbitals are dominant at the sides. We have previously observed MQ spectra of N<sub>2</sub>O on surfaces under conditions where the  $6\sigma$  peak dominates (N end down) and where the  $7\sigma$  peak dominates (O end down) [46]. The spectra of fig. 4 do not correspond to either extreme. However, on the oxidized surface (trace a) the  $6\sigma$  peak is only a weak shoulder, showing that there is a tendency for the  $N_2O$  to be oriented with the O end down. This is supported by comparing the ratio of the  $7\sigma/2\pi$ intensities for the two spectra: for product N<sub>2</sub>O on the oxidized surface (trace a) this ratio is 30% larger than for N<sub>2</sub>O on the clean surface (trace b), again indicating a greater propensity for the N end to be up. The spectrum of N<sub>2</sub>O on the clean GaAs(100) surface (trace b) is consistent with that expected for N<sub>2</sub>O lying flat. This explains the difference in the saturation coverage on the two surfaces observed in fig. 3. Since the  $N_2O$  tends to be oriented vertically on the oxidized surface, the molecules can pack more closely together.

When  $N_2O$  is adsorbed onto the oxide layer after thermally desorbing the reactively produced  $N_2O$ , the  $6\sigma$  peak in the MQ spectrum is comparable in intensity to that of  $N_2O$  on the clean surface. Since the coverage of  $N_2O$  on the oxidized surface is the same whether it is produced by reaction of NO or by dosing  $N_2O$ , we believe that the  $N_2O$  tends to be aligned perpendicular to the surface in both cases. The reactively pro-



Fig. 5. MQ spectra of clean GaAs(100), GaAs(100) exposed to 80 L of NO at 74 K, and the same surface heated to 90 and 310 K.

duced  $N_2O$  is preferentially oriented with the O end down. The MQ spectrum of the dosed  $N_2O$ on the oxidized surface suggests that the molecules are oriented both with the O end down and with the N end down. We have observed this type of behavior previously on oxidized Ru(001) [46]. Another difference in the two spectra is that the up-shift in the energy of the spectrum relative to that of  $N_2O$  on the clean surface is less when  $N_2O$  is dosed on the oxide layer than when it is produced reactively, and the shift decreases with increasing  $N_2O$  coverage. This shows that the work function shift is not produced by oxidation of the surface alone, but by both oxidation and the oriented adsorption of  $N_2O$  on the oxide.

Fig. 5 shows the MQ spectra corresponding to conversion of the clean GaAs surface to an oxide layer by reaction of NO. The clean surface gives a broad band, as seen in trace a. As described in section 2, the Fermi level is at 16.0 eV on the

RPD scale. The spectrum extends up to about 15.0 eV, which corresponds to the valence band maximum. The only notable feature other than the main peak at 8 eV is the small peak 2.5 eV below the valence band maximum. In trace b, exposure of the surface at 74 K to a saturation dose of NO gives the same spectrum of N<sub>2</sub>O as seen in fig. 4. Trace c shows that most of the  $N_2O$ is desorbed by heating the surface to only 90 K. the onset of the TPD spectrum. Trace d shows that there is no  $N_2O$  remaining on the surface when it is heated to 310 K. The MQ spectrum results from the broad electronic band of the oxide layer at this temperature. MOS shows that  $N_2O$  is not reactive with clean GaAs(100) under these conditions: deposition of a saturation N<sub>2</sub>O layer at 77 K followed by heating to 200 K resulted in complete desorption of the N2O and restoration of the clean surface.

Auger spectra taken of the clean surface showed only Ga and As peaks. After NO adsorption followed by heating to 310 K to desorb the product N<sub>2</sub>O, strong oxygen peaks and no nitrogen peaks were observed. This shows that there is no nitride formation on the surface. The amount of surface oxygen qualitatively follows the amount of N<sub>2</sub>O produced in TPD; it increases with NO exposure to saturate at high dosage. The oxygen Auger peak was also monitored while slowly heating the GaAs sample. The peak stayed constant up to 870 K and then rapidly disappeared at higher temperature.

The HREEL spectrum of the surface after dosing with NO or  $N_2O$  is shown in fig. 6. The loss peaks at 157, 280, and 314 meV can be assigned to excitation of the  $n_1 = 1$ ,  $n_3 = 1$  and  $n_1 = 2$  vibrations of N<sub>2</sub>O which appear in the gas phase at 159, 276, and 318 meV, respectively. [47] The excitation of  $n_2 = 1$  which in the gas phase appears at 73 meV cannot be resolved, because it coincides with the first overtone of the GaAs phonon loss at 72 MeV. Three more peaks are seen at 108, 198 (with N<sub>2</sub>O dosing) or 207 (with NO dosing), and 233 meV. The 108 and 233 meV peaks are much stronger on the NO-exposed surface. The 233 meV peak is the NO vibration, which has the same energy in the gas phase. The peak at 108 meV tends to increase with NO



Fig. 6. HREEL spectra of GaAs(100) after exposure of the surface to 20 L NO and 4 L N<sub>2</sub>O at 77 K.

exposure. After desorption of  $N_2O$  at 350 K this peak is gone, showing that it is not characteristic of the oxide. The peaks in the 198–207 meV region have different shapes but approximately the same intensity on the two surfaces. These peaks may be due to ionic oxide species on the surface, but we do not have sufficient data to assign them.

No significant HREELS oxide band was observable on the surface from the oxide layer formed at low temperture. When the sample was annealed at 500 K, which desorbed the  $N_2O$  and allowed the oxide layer to thermally reconstruct, a small double-peaked oxide band appeared between about 50 and 120 meV. The thermal development of this band has been studied more fully in our subsequent work on the oxidation of GaAs(100) by NO<sub>2</sub> [48].

With the clean surface at 300 K, NO doses of 200 L gave no measurable NO adsorption,  $N_2O$  production, or surface oxide formation. Dosing

the clean surface at 77 K with 40 L of  $O_2$  also produced no sign of surface oxidation. With an  $O_2$  exposure of 400 L there was a significant change in the MQ spectrum, indicating a relatively small amount of oxidation. The bond strength of NO is 6.50 eV versus 5.12 eV for  $O_2$ [49]. The fact that NO is much more reactive with the surface than  $O_2$  can be rationalized in terms of the open-shell character of NO. This is expected to enhance the sticking coefficient, and leads to dimer formation on the surface which provides a low-energy reaction path: (NO)<sub>2</sub>(ad)  $\rightarrow$  N<sub>2</sub>O(ad) + O(ad).

The present results for NO/GaAs(100) at 74-77 K can be compared with those obtained by So and Ho for NO/GaAs(110) at 90 K [33]. Both GaAs samples were Si-doped with  $n \approx 10^{18}$  cm<sup>-3</sup>. NO was found to reach saturation coverage on (110) at 90 K with 2.0 L exposure, whereas about 160 L was required for saturation exposure on (100) at 77 K. With the former system NO adsorbs mainly in the molecular state, whereas with the latter it mainly reacts to form  $N_2O_1$ , oxidizing the surface. It would be interesting to see how much of this difference is due to the temperature. In fig. 5 it was shown that when the NO-saturated (100) surface is heated to 90 K most of the product N<sub>2</sub>O desorbs. A small amount of N<sub>2</sub>O was observed to form on the (110) surface at 90 K. It is possible that at 77 K the (110) surface would adsorb more NO, promoting the formation of  $N_2O$  and oxidation of the surface.

#### 4. Summary

We find that when NO is adsorbed on the gallium-rich  $c(8 \times 2)$  reconstructed surface of GaAs(100) at 77 K, it reacts to form N<sub>2</sub>O and surface oxide. HREELS shows that the conversion of NO to N<sub>2</sub>O is nearly complete for dosages greater than 40 L, and this is confirmed by the TPD and MQS spectra. With a NO dosage of ~ 200 L the reaction saturates after forming a complete surface oxide layer. With the clean surface at 300 K, NO doses of 200 L gave no

measureable NO adsorption,  $N_2O$  production, or surface oxide formation.

The MQ spectra show that the N<sub>2</sub>O which is formed by the reaction  $2NO(ad) \rightarrow N_2(ad) + O(ad)$  is adsorbed predominately with the O end of the molecule down on the oxide layer. This tendency of the N<sub>2</sub>O molecules to be aligned vertically on the oxide layer results in closer packing, which gives a 30% higher saturation coverage of N<sub>2</sub>O on the oxide layer than for N<sub>2</sub>O adsorbed directly on the clean surface.

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