NO adsorption on Ge(100) studied by TPD

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Abstract

We present temperature-programmed desorption studies of the adsorption of submonolayer coverages of nitric oxide on a Ge(100) surface at low temperatures, followed by electron irradiation which alters the surface chemistry. Desorption peaks near 180K indicate the non-dissociative nature of the adsorption, in addition to evidence for dissociation and recombination-desorption as N₂ molecules. Desorption after electron dosing of the surface indicates that this system exhibits electron-stimulated associative desorption of N₂, and the likely involvement of NO dimers on the surface which also produce N₂O desorption.

Keywords:  Adsorption; Germanium; Nitric oxide; Electron Stimulated Desorption (ESD); Temperature Programmed Desorption (TPD)

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1. Introduction

Renewed interest in passivating or insulating layers on germanium has been motivated in part by development of new devices based on SiGe alloys or on strained-layer superlattices during the last decade. In the case of silicon-based devices, silicon nitrides and oxynitrides have been investigated as possible alternatives to silicon dioxide. Germanium nitrides and oxynitrides require a relatively high thermal budget, which conflicts with other process requirements. Low thermal budget approaches to the atomic-scale control of nitride layer growth on germanium may therefore be useful. Previous studies have investigated the possibility of using electron irradiation to assist in the formation of nitrides on germanium at low temperature, using ammonia as a precursor [1,2]

In this study, electron beam enhanced oxynitridation of germanium was investigated using nitric oxide (NO) as adsorbate and precursor in the growth of ultrathin layers on germanium substrates. This was motivated in part by a previous study of this process on silicon substrates [3]. Reaction products were detected using temperature-programmed desorption (TPD) of neutrals and electron-stimulated desorption (ESD) of ions and neutrals, and the composition of the surface was analyzed using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), and low-energy electron diffraction (LEED).

2. Experimental Details
This study used an ultra-high vacuum system which has been described in detail elsewhere [4,5]. Additional details and drawings may be found in several Ph.D. dissertations [6-8]. New aspects of the experimental procedure used in this study are described here. The Ge(100) sample was cleaned in situ by a thermal anneal in a vacuum of $2 \times 10^{-10}$ torr. Typical temperature ramp rates were 3 K/s for heating and 2 K/s for cooling, with a 2 minute dwell at between 800 K and 870 K, as measured by an infrared optical pyrometer (Raytek Thermalert 30 with sensing head RAYSHMTCF2). Upon advice from the manufacturer, we used an emissivity setting of 0.8 for the wavelength used by the pyrometer (3.9 µm). This procedure resulted in the appearance of a sharp 2x1 LEED pattern at low temperature. An occasional Argon ion sputter was used to remove nitride from the surface. TPD data was obtained at a heating rate of 3 K/s, as measured by a thermocouple attached to the back of the silicon-tantalum-silicon sandwich which served as the heater and mount for the Ge sample. Electron irradiation was from a Kimball Physics electron gun (model EFG-7) at beam energy 600 eV and current density 1.2 µA/cm², incident on the sample at an angle of 60° with respect to the sample normal. Gas dosing through a tubular array doser located 1 cm from the sample was quantified by measuring the pressure with an ionization gauge. A voltage output from the ionization gauge controller was then measured and integrated using a PC. The exposure is calculated as the pressure-time product (ptp), which is equal to the [uncorrected ion gauge pressure during the dose (in Torr)] x [duration of dose (in seconds)] x $10^6$. The ptp is considerably greater than the conventional exposure given in Langmuir because of the significant dose amplification from the tubular array doser.
3. Results and discussion

Temperature-programmed desorption (TPD) results

Fig. 1 shows a series of TPD spectra for NO on Ge(100) with no electron irradiation. As NO doses increase, the desorption of mass 30 increases, producing a weak peak at about 180 K as the dose reaches 0.7 ptp. Also seen is an increase in the desorption peak of mass 28, which is due to molecular nitrogen. The mass 28 peak is stronger than the mass 30 peak, increases with NO dose, and occurs at approximately the same temperature as the NO peak.

Electron irradiation of the NO-covered Ge(100) surface produces desorption of neutrals, which our group had not previously studied. In this study, we found that some useful information could be obtained by monitoring the desorption during irradiation. Fig. 2 shows a series of desorption curves obtained during a 2 minute irradiation. The electron gun was gated on at a time of about 30 s, and kept on until 2 min 30 s, when it was gated off. The top set of curves corresponds to mass 30 desorption for increasing doses from 0.02 ptp to 0.7 ptp, with the curves offset vertically for clarity. At low doses, the desorption is approximately constant during this 2 min period, but for a dose of about 0.5 ptp and above, the NO desorption displays a peak during the first 15 seconds of irradiation. [Also note that the sloped background on the mass 30 data for 0.7 ptp is due to a steadily decreasing background partial pressure of residual NO from the dosing process. It was difficult to maintain a constant time period between the end of dosing and the beginning of data collection, and so it varied from about 2 to 5 minutes delay.] The second set of curves in Fig. 2 reveal similar behavior for mass 28, except that there is no sloping background of N₂ partial pressure after the dosing. In particular, note the
existence of very similar behavior in the 15 s peak at the beginning of irradiation for the higher doses. This behavior suggests the presence of a second species of NO on the surface for doses higher than about 0.5 ptp. For mass 16, which we attribute to atomic oxygen, the curves (not shown) show a consistently slow rise at the beginning of dosing, in contrast to the quick rise in the mass 28 and 30 curves. This slow rise is most evident for doses of 0.30 ptp and less, but the data is noisy and not conclusive, which suggests further studies to identify the time development of the surface concentration. Curves for mass 14 (not shown) are at low level and quite noisy, but display behavior similar to the mass 28 and 30 peaks, with the initial 15 s burst at higher doses. We attribute the mass 14 data to nitrogen ions produced in the mass spectrometer ionizer from cracking of the mass 28 and mass 30 neutrals, and hence mass 14 data should display behavior similar to those two species. Mass 44 desorption, shown in the third set of curves, however, displays an initial rise to an approximately constant rate, even for higher doses, in contrast to the presence of the initial 15 s peak in the NO and N₂ data. This suggests that the mass 44 desorption is associated with the species of NO or related products that are present at the low doses, and not with the species of NO that contributes to the 15 s peak at higher doses.

On the assumption that the initial 15 s peak is due to a second species of NO on the surface at higher coverage, we choose to present a set of TPD data for a dose of 0.3 ptp, which is just before the onset of the appearance of the 15 s peak. Fig. 3 shows a set of TPD curves for 0.3 ptp NO on Ge(100) after irradiation periods of 0 min, 2 min, and 10 min. Masses 28 and 30 show almost identical behavior, with peaks at about 180 K for 0 and 2 min irradiation, and the elimination of the peaks after 10 min of electron
irradiation. The mass 44 data shows a broader desorption peak than the others, extending from 140 to 270 K in the unirradiated data, but moving to higher temperature with irradiation, extending from 130 K to about 310 K for 2 min irradiation, and over a broad range starting at about 200 K for the 10 min irradiation. Note also a small feature at 130 K which appears in some of the mass 44 data. Increasing irradiation appears to be suppressing the desorption of mass 44 in the low temperature range from 150 to 200 K, and leaving some to desorb in the higher range from 200 to 300 K.

AES and XPS results

Auger electron spectroscopy was attempted in order to determine the concentration of nitrogen on the surface. The N peaks were too weak to be useful in a quantitative analysis, in part due to an unfavorable ratio of atomic sensitivities for N and Ge [9], and the fact that we were keeping the doses under a monolayer coverage. In addition, we believe that the focused electron beam used for Auger spectroscopy was causing desorption of the NO before a useful Auger signal could be obtained.

X-ray photoelectron spectroscopy results are shown in Fig. 4. XPS could be used to study Ge and oxygen, but not nitrogen due to the presence of X-ray-induced Ge-Auger features in the region of the N 1s peak around 400 eV. XPS spectra were obtained for doses of 0.10 ptp, 0.30 ptp, 0.50 ptp, and 1.0 ptp. The Ge 2p XPS peak (not shown) could be fit by a sum of two Gaussians, one centered at 1221.3 eV (0.1 ptp and 0.3 ptp) or 1221.4 eV (0.5 ptp and 1.0 ptp) with FWHM of 1.5 eV, and a second weaker Gaussian centered at 1221.6 eV and FWHM of 3.3 eV. (Note that these XPS spectra are not corrected for a work function of about 4 eV.) The O 1s region, shown in Fig. 4, contains a background which complicates the fit, but by taking a difference curve between the
curves for 1.0 ptp and 0.5 ptp, we can fit a Gaussian of center 535.6 eV and FWHM of 3.2 eV. This peak, which appears in the higher dosing region where the electron irradiation curves showed the 15 s burst of mass 28 and 30, may be related to molecular NO adsorbed above or on other sites than the NO and its products which were adsorbed at lower doses. In addition, the O 1s difference peak is shifted about 1 eV to lower binding energy than the 536.6 eV peak which appears in the lower NO dosing region.

**HREELS results**

HREELS spectra of the NO-dosed Ge(100) surface show no clear peaks corresponding to non-dissociative adsorption of NO, although the TPD results clearly suggested the non-dissociative adsorption of NO. There is no observed N-O stretch mode near 1800 cm$^{-1}$ on the Ge(100) surface, in contrast to the presence of a peak for NO adsorbed on Si(100) [7, 10, 11]. This suggests that adsorbed NO molecules are not dipole active. One possibility would be the adsorption of NO in a configuration parallel to the Ge surface. Depending on the site symmetry, parallel adsorption would have zero or small dipole moment. A second possibility is adsorption of NO in the so-called 'cave' site, in the valleys between 2x1 dimer rows, which would result in partial shielding of the NO dipole field. This adsorption site has been proposed for the Na/Si(100)2x1 system by Mangat et al. [12]. The NO$^+$ ion is, however, larger than Na$^+$ and may not fit in the 'cave' site. The dimerization of NO into N$_2$O$_2$ is a third possibility, considering that dimerization occurs in solid and gaseous NO. Several NO dimer geometries are possible, as indicated in a recent summary of theoretical work on the gas phase molecules [13]. The existence of dimers of NO on the surface of metals has been assumed in proposing a mechanism for production of N$_2$O on Ag(111) [14]. In the present work, it is difficult to
explain the near simultaneous desorption of mass 44 and also mass 30 from an initial coverage of NO at such low temperatures without postulating the existence of dimers on the surface. The results of Fig. 1 even suggest that it is more likely for such dimers to decompose into N\textsubscript{2} or N\textsubscript{2}O at low temperature than it is for them to desorb as single NO molecules. Only at 0.7 ptp, above the dose for the appearance of the "second species" (which presumably are single adsorbed NO molecules) does the NO desorption peak appear clearly at low temperature in Fig. 1.

4. Conclusions

The adsorption of submonolayer coverages of NO on a Ge(100) surface at low temperatures was studied by TPD and by electron stimulated desorption, followed by electron irradiation which alters the surface chemistry. Desorption peaks near 180K indicate the non-dissociative nature of the adsorption, in addition to evidence for dissociation and recombination-desorption as dinitrogen molecules. ESD of neutrals suggests the presence of a second species of NO on the surface for doses higher than about 0.5 ptp. Desorption after electron dosing of the surface indicates that this system exhibits "electron-stimulated associative desorption" (ESAD) of N\textsubscript{2}. The ESAD mechanism has been reported for ammonia on both Pt(111) [15] and Si(100) [16]. The TPD results also suggest the likely involvement of NO dimers on the surface which then decompose to produce desorption of N\textsubscript{2}O.
References


Figure captions

Fig. 1 TPD spectra for various doses of NO on Ge(100) with no electron irradiation.

Fig. 2 Desorption curves from various exposures of NO on Ge(100) obtained during a 2 minute electron irradiation.

Fig. 3 TPD spectra for various doses of NO on Ge(100) with various amounts of electron irradiation.

Fig. 4 XPS of O1s peaks vs. NO exposure. Lower panel shows Gaussian fits to the peak for 0.50 ptp NO exposure and to the difference curve attributed to a second NO species.
Fig. 1
Fig. 2
Fig. 3
Fig. 4