Photogenerated-Charge-Carrier–Induced Surface Reaction: NO on Si(111) 7×7

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Photodesorption and photodissociation of NO molecularly adsorbed on Si(111)7×7 at 90 K have been observed at wavelengths in the range from the visible to near-uv. An enhancement in the photodesorption intensity with photon energies above the transition energy of the first direct band gap of Si clearly shows that photogenerated carriers in Si initiate the reactions. Detailed data analysis suggests that the reactions are induced by hot carriers.

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Recent experiments have shown that reactions of molecules adsorbed on solid surfaces can be selectively induced by irradiation with photons in the range from ir to uv.[1-11] Several reaction mechanisms other than substrate heating have been reported. Photoexcitation of adsorbate electronic states was found to be effective in the initiation of dissociation of CH_3Br on LiF(100),[1] and $Mo(CO)_6$ on Si(100)[2] and Si(111).[3] Similarly, vibrational excitation of adsorbates caused desorption of CH_3F from NaCl,[4] and pyridine from KCl[5] and Ag.[6] The desorption of HD from LiF(100) was attributed to the creation of phonons from ir absorption.[7] In semiconductors, photogenerated electron-hole pairs in the bulk can migrate to the surface and induce reactions. Results from the photoenhanced etching of Si by XeF_2 suggested the relevance of this mechanism.[8] On ZnO surfaces the enhancement of the photodesorption of CO_2, produced from the oxidation of C impurity, was observed near the ZnO band-gap transition energy and was attributed to the mechanism of carrier-adsorbate interaction.[9,10] Analysis of the results from laser-induced oxidation of GaAs(100) under aqueous and moderate gas pressures led to the further assertion that it was the photogenerated hot carriers which were responsible for the observed reactions.[11]

We have studied, under well-controlled experimental conditions, the photoreactions of NO adsorbed on Si(111)7×7 at 90 K over a wavelength range from the visible to near-uv, which allowed direct observation of the effects of a band-gap transition in Si and the role of photogenerated carriers in the reactions. The adsorbed species were probed with high-resolution electron-energy-loss spectroscopy (HREELS) and thermal-desorption spectroscopy. Photon-induced desorption spectroscopy was used to detect the photodesorption products. For comparison, the wavelength dependence of the desorption intensity of CO from the photodissociation of $Mo(CO)_6$ on Si(111)7×7 at 90 K is given to show the clear contrast with a system where the adsorbates absorb the photons directly.[3]

The experiments were performed in ultrahigh vacuum. Two 0.5-mm-thick Si(111) samples of phosphorus-doped (10^{14} cm^{-3}) n type and boron-doped (10^{16} cm^{-3}) p type were used. All data reported in this paper were obtained from the n-type sample, except where otherwise noted. The samples were cleaned by repeated cycles of Ne^+ sputtering and annealing. Saturation monolayer coverage was achieved with exposures of 1.0-L NO or 3.0-L $Mo(CO)_6$ at 90 K [1 L (langmuir)$=10^{-6}$ Torr s]. An Ar^+ laser provided up to 4 W/cm^2 of 514-nm radiation and $\simeq 3$ mW/cm^2 of the frequency-doubled radiation at 257 nm. A Xe arc lamp and appropriate combinations of glass filters provided radiation in the wavelength range of 300–450 nm with incident powers of 10–50 mW/cm^2. Almost all the front surface of the sample was irradiated with the laser or the lamp. A rise in the sample temperature by as small as 0.2 K can be measured.[3,12]

The HREEL spectrum with saturation NO adsorption at 90 K, shown in Fig. 1, curve a, indicates both molecular and dissociative adsorption on Si(111)7×7. The two well-resolved loss peaks at 188 and 224 meV are assigned to the N-O stretching modes of molecular NO adsorbed in the bridge and atop sites, respectively.[13] The intensities of the peaks at 46 and 78 meV are correlated with the molecular N-O stretches and are identified as the vibrational modes of NO against the Si surface in the bridge and atop sites, respectively.[12] The 102-meV peak is the N-Si asymmetric stretching mode[14]; its presence indicates that NO also adsorbs dissociatively. The relatively small peak at 115 meV is attributed to the O-Si stretching mode; however, its energy is shifted down by $\simeq 10$ meV compared to the value when O is adsorbed alone.[15] The remaining lower-intensity peaks have not been assigned and are not significant in the analysis. Molecular adsorption is consistent with the observation of thermal desorption of NO at temperatures as low as 107 K. Recent photoemission studies of NO on Si(100)2×1 at 90 K have also shown the coexistence of both molecular and dissociated states.[16]

Significant changes in the vibrational spectra occurred after the surface was irradiated or heated, as shown in Fig. 1, curves b and c, respectively. The elastic peak exhibited a very broad angular distribution and its intensity

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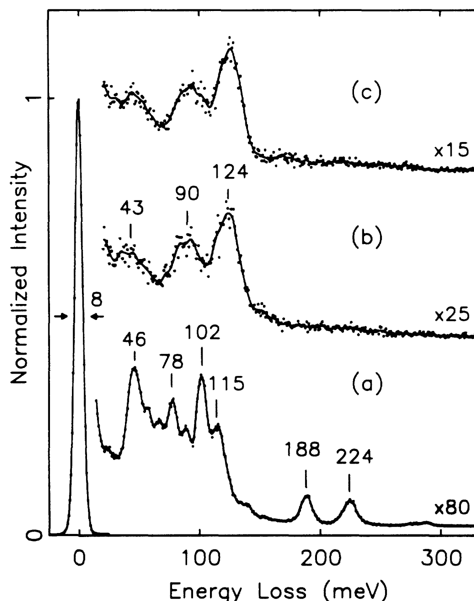

FIG. 1. HREELS of NO (curve *a*) adsorbed on Si(111)7×7 at 90 K, (curve *b*) after 10-min irradiation of Xe-lamp radiation filtered with a band-pass filter centered at 325 nm (the temperature rise of the sample was only 4 K), and (curve *c*) after heating the sample to 300 K for 3 min. Similar spectra were obtained after laser or lamp irradiation at all accessible wavelengths. The different multiplication factors in the spectra *b* and *c* reflect the effect of the significant disorder of the surface caused by irradiation or heating.

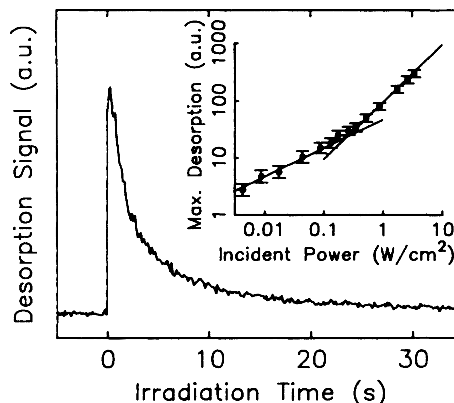

FIG. 2. A typical photodesorption spectrum of NO on Si(111)7×7 at 90 K. The spectrum shown was obtained with Xe-lamp irradiation filtered by the same filter used to obtain the spectrum in Fig. 1, curve *b*. Inset: Power dependence of the maximum photodesorption intensity measured with 514-nm laser.

was reduced by a factor of ≃50, indicating a very disordered surface. *Both* molecular N-O stretches disappear and the spectra are dominated by three broad peaks. The highest peak at 124 meV corresponds to the asymmetric stretching mode of O-Si, and its bending mode appears at ≃43 meV. The broad feature in between most likely contains two peaks: the O-Si symmetric stretch at ≃85 meV and N-Si asymmetric stretch at ≃95 meV. From these changes in the vibrational spectra it can be concluded that at least some of the molecularly adsorbed NO has dissociated, leaving O and N adsorbed disorderly on the surface. The remaining molecular NO is desorbed.

Evidence for the photodesorption of NO was obtained from photon-induced desorption spectroscopy; a typical spectrum is shown in Fig. 2. The desorption signal immediately jumped to the maximum intensity after opening of the shutter within the response time of the vacuum system of 0.4 s and decayed with further irradiation. This general line shape was observed for the desorption spectra at all accessible wavelengths and powers of laser or lamp irradiation. The desorption is not due to thermal effects because a much longer time constant was measured for the surface-temperature rise (≃5 s) than the rise time of the photodesorption signal. Furthermore, the maximum temperature rises were less than 5 K for all Xe-lamp irradiation and 257-nm laser irradiation. With 514-nm laser irradiation at high incident powers (> 200 mW/cm^2) the desorption signal decayed exponentially to about the half-maximum of the peak height and was then followed by an additional small peak. This second peak is attributed to laser-induced thermal desorption and will not be discussed in this paper. As laser power increases, the exponential decay time of the nonthermal peak decreases monotonically and its height increases linearly, as is shown in the inset of Fig. 2. HREELS and thermal-desorption spectroscopy showed that none of the molecular NO was left on the surface after 2-min irradiation. At low powers of laser irradiation at 514 nm, a square-root power dependence of the maximum desorption intensity was observed. In this regime the decay of the desorption signal showed a fast decrease followed by a slow exponential decay, but the exact profile is unclear because of the small signal-to-noise ratio. Thermal-desorption spectroscopy indicated that a substantial amount of molecular NO was left on the surface after 2-min irradiation.

The wavelength dependence of the photodesorption yield was studied with the Xe lamp over a wavelength range of 325–440 nm. The maximum desorption intensity in the different wavelength ranges is plotted in Fig. 3 versus the central wavelength of the filtered Xe lamp radiation (circles). All the data were taken in the linear power-dependence regime, judged by comparison of the decay times, and the intensities are normalized to the incident flux. An enhancement was observed above the first direct band-gap transition of Si at 3.37 eV (370 nm). The absorption coefficient[17] of Si is plotted by the solid line. As the wavelength decreases, the photodesorption signal increases and follows the absorption coefficient, but reaches a saturation value despite further

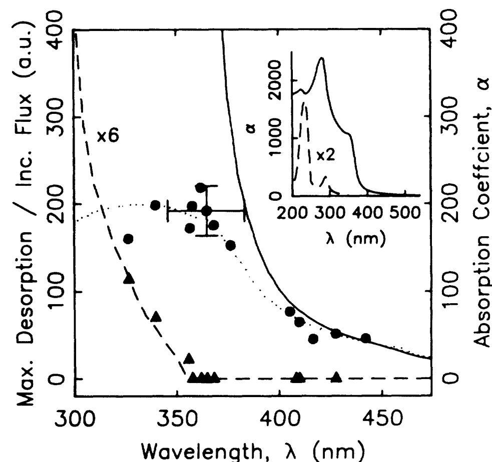

FIG. 3. Maximum intensity of the NO photodesorption (circles) and the CO desorption from the photodissociation of $Mo(CO)_6$ (triangles) on Si(111)7×7 at 90 K vs central wavelength of Xe-lamp radiation filtered with different filter combinations. All the data are normalized to the incident photon flux. Error bars show a typical bandwidth of the incident radiation and the uncertainty in the desorption intensity. The solid line is the absorption coefficient of Si (each unit is 10^3 cm^{-1}), and the dashed line is that of $Mo(CO)_6$ (each unit is 10^2 l mol^{-1} cm^{-1}). Inset: Corresponding absorption coefficient over a wider range (with the same units as those in the main figure). The dotted line is a model fit to the NO data (see text for discussion).

increases in the Si absorption coefficient.

The same wavelength dependence in the p-type sample was observed. However, the reaction cross section is smaller since the decay time in the photodesorption spectra was observed to be 1.5 times longer than the decay time for the n-type sample under the same irradiation conditions. Similarly, the enhancement in photoinduced etching by XeF_2 was observed to be smaller on p-type than on n-type Si.[8]

A completely different wavelength dependence compared with NO was observed for the desorption of CO from the photodissociation of $Mo(CO)_6$ adsorbed on Si(111)7×7 at 90 K. The desorption signal quickly reached the maximum intensity and then decayed with irradiation. The maximum intensity is plotted in Fig. 3 (triangles) versus the central wavelength of the filtered Xe lamp radiation. The desorption signal was nonvanishing only for wavelengths shorter than 360 nm. This wavelength dependence correlates with the absorption coefficient of $Mo(CO)_6$,[18] as is shown by the dashed line. The same decay time was observed for both the n-type and the p-type samples under the same irradiation conditions, indicating no significant substrate effects. These results further confirm the previous conclusion that the photodissociation of $Mo(CO)_6$ is due to direct excitation of the electronic states of adsorbed $Mo(CO)_6$.[2,3]

The lowest electronic excitation energy and the dissociation energy of NO in the gas phase are 5.5 and 5.3 eV,[19] respectively. In the present experiments photoreactions were observed with photon energies as low as 2.4 eV, and the only onset of the reaction yield in the energy range studied with the Xe lamp (2.8–3.8 eV) occurred at about 3.4 eV (the Si direct band-gap transition). The lowest electronic transition of NO could shift to a lower energy upon adsorption; however, it is unlikely that the decrease is greater than 2 eV. Thus it can be concluded that the observed photoreactions, at least with photon energies less than 3.8 eV, are not due to the direct photoexcitation of the adsorbed NO.

We propose the following mechanism for the observed NO photoreactions. When the sample is irradiated with photons, electron-hole pairs are created. Most of the carriers lose their kinetic energies within 10^{-10} s by collisions with the optical phonons. These carriers remain at band edges and diffuse in the sample for $\simeq 10^{-6}$ s until they recombine. Only a small fraction of carriers undergo the reaction. An energy barrier is present so that the reactions are induced not by those carriers which have lost their kinetic energies after a number of collisions with optical phonons, but by hot carriers. These hot carriers have to be created within a distance comparable to their mean free path from the surface in order for them to induce reactions.

With use of this model the wavelength dependence of the photodesorption intensity can be explained. Under photon irradiation the generation rate of the electron-hole pairs varies exponentially in distance z ($z>0$) as $e^{-\alpha z}$, where α is the Si absorption coefficient. If we suppose, for simplicity, that carriers created within a distance δ from the surface have a constant probability of reactions and zero probability outside, the ratio of the number of the effective carriers to the total number of carriers created is $1-e^{-\alpha\delta}$, which is proportional to α for small values of α and approaches unity for sufficiently large α. The experimental data for NO in Fig. 3 are fitted by $a(1-R)(1-e^{-\alpha\delta})$, where R is the reflectivity[17] of Si and a is a constant. The best fit is shown by the dotted line, yielding a value for δ of 400 ± 80 Å, which is comparable to the mean free path of the carriers.

To explain the power dependence and time profile of the photodesorption spectra we utilize a simple model calculation, which was performed originally to explain the photodesorption of CO_2 from ZnO.[10] The average density of charge carriers within a distance of δ from the surface in the electric field set up by the adsorbates was calculated. The photoreaction rate was assumed to be proportional to this carrier density and was calculated for the case where only a small fraction of the adsorbates have reacted. The results gave a square-root power dependence and an inverse square-root time-decay profile. This time-decay profile was observed for the desorption of CO_2 from ZnO; however, a linear power dependence

has been reported.[9] We use this model to explain the photoreactions of NO on Si, but interpret the average density to be that for the hot carriers, and also extend the calculation to include the case where a substantial number of the adsorbates have reacted. The extension gives a linear power dependence of the maximum photodesorption intensity and an exponential time decay.[12] All these results are consistent with our experiments (see Fig. 2).

The cross section of the NO photoreactions varies with wavelength and sample doping. The highest value was observed on the *n*-type sample and in the wavelength region where the photodesorption signal saturates. Under these conditions, a decay time of 2.4 s was measured with an absorbed photon flux of 2.6×10^{16} cm^{-2} s^{-1}. The inverse of their product yields a cross section of 1.6×10^{-17} cm^2 for each photon. With use of the Si surface density of 7.83×10^{14} cm^{-2} as an upper limit of the density of molecularly adsorbed NO, the maximum reaction rate is 3.3×10^{14} cm^{-2} s^{-1}, or at most 1.3% of the total number of carriers created actually induce reactions.

In conclusion, we have observed that NO adsorbs both molecularly and dissociatively on Si(111)7×7 at 90 K. Photodesorption and photodissociation of molecularly adsorbed NO have been determined to be initiated by the interactions with photogenerated carriers. It is suggested that only those energetic carriers created within a distance in the order of their mean free path from the surface are effective in inducing the reactions.

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