Interactions of low-energy (20–800 eV) nitrogen ions with Cu(100): A combined temperature programmed desorption and electron energy loss spectroscopy study of chemisorption and entrapment states

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The interactions of low-energy (20–800 eV) nitrogen ions with Cu(100) at room temperature have been investigated by using temperature programmed desorption (TPD) mass spectrometry and high-resolution electron energy loss spectroscopy. The desorption feature observed at 760 K can be attributed to adsorption of surface atomic nitrogen on fourfold-hollow sites. When the impact energy (IE) of the nitrogen ions used for the irradiation exceeded 75 eV, our TPD results further revealed a new desorption feature at 520 K, which can be tentatively assigned to ion-implanted atomic and/or molecular nitrogen. The intensities and temperatures of the desorption maxima of the surface (chemisorption) and ion-implantation (entrapment) features were found to greatly depend on the IE and the dosage of the ions. Other effects including the creation of defect sites as a result of the ion irradiation are also investigated.
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Given its enormous technological importance, the formation of a nitride film on metal and semiconductor surfaces continues to attract great interest in surface science.[1] In the case of a ''generic'' unreactive metal surface such as Cu(100), it is well known that molecular chemisorption of N_2 does not occur at room temperature (RT). Furthermore, although dissociative adsorption of N_2 on Cu(100) has not been observed at RT,[2,3] it has been shown to occur readily if activated by electron irradiation.[4–6] The resulting c(2×2) N overlayer on Cu(100) was found to be extremely stable, up to 770 K.[5] Studies by Mohamed and Kesmodel using high-resolution electron energy loss spectroscopy (EELS) further revealed that the Cu–N stretching vibrations in the perpendicular and parallel modes for N adsorbed on a fourfold-hollow site occur at 324 cm^{-1} and 750 cm^{-1}, respectively.[6] The bond length of the Cu–N bond has been determined to be 1.84 Å in an extended electron energy loss fine structure study.[7]

In addition to electron-activated surface processes, low-energy ion-activated surface reactions are also found to be effective in generating new surface species.[8] For instance, Heskett *et al.*[9] showed that the adsorption of atomic nitrogen on the (110) plane of Cu could be obtained by ion irradiation. The interactions of an ion beam with a solid surface have been studied extensively in the context of ion scattering[10,11] and ion beam processing.[12] The prominent effects of the interactions appear to greatly depend on the impact energy (IE) of the ion. According to studies of the interactions of rare-gas ions with a solid surface,[13] backscattering is generally believed to be the predominant process for an IE below 30 eV, while radiation damage and other sputtering effects become increasingly important when the IE changes from 30 eV to 1000 eV. Furthermore, the entrapment (implantation) effect also becomes more evident at a higher IE. When a reactive gas is used as the source of the ion, the activation of surface reactions also plays an important role in determining the resulting surface properties. Indeed, in practical applications such as ion- or plasma-assisted thin-film deposition,[14] reaction activation and sputtering are believed to introduce competing results. In the present work, we investigate the interactions of low-energy N_2^+ and N^+ ions with Cu(100) by using temperature programmed desorption (TPD) mass spectrometry and high-resolution EELS. We show that ''surface'' nitrogen atoms that form a c(2×2) overlayer on Cu(100) coexist with ''entrapped'' nitrogen species (that arise from N^+ or N_2^+ implantation) in the sub-surface region when the IE is greater than 75 eV. Of particular interest is the dependence of their relative concentrations on different experimental conditions (including, in particular, the IE and the ion dosage) used for the ion irradiation. Finally, the effects of radiation damage on the formation of the surface and entrapped nitrogen species are also investigated.

The experiments were conducted in a triple-level ultrahigh vacuum (UHV) chamber (base pressure $<8\times10^{-11}$ Torr), equipped with an ion(sputtering) gun, a four-grid retarding-field optics for low-energy electron diffraction (LEED) and Auger electron spectroscopic analyses, and a 1–300 a.m.u. quadrupole mass spectrometer (QMS) for TPD studies.[15] The EELS spectra were obtained at an IE of 4 eV in a specular reflection geometry (45° from the surface normal) using a home-built angle-resolved EELS spectrometer described elsewhere.[15,16] The Cu(100) sample (9.5 mm diameter × 2 mm thick) at 99.999% purity was obtained commercially from Monocrystals Company. The sample was cleaned by repeated cycles of Ar^+ sputtering [at 500 eV (IE) and 10 mA (electron emission current) in an ambient Ar pressure of

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2×10^{-5} Torr for 30 min] and annealing to 800 K, until a sharp (1×1) LEED pattern and no detectable Auger peaks attributable to the common impurities (such as C, O and S) were obtained. The sample could be heated to 900 K using a boron nitride heater in contact with the backside of the substrate (with a 0.05-mm-thick Ta foil placed between the heater and the Cu sample). The surface temperature of the sample was monitored by a type-K thermocouple (mechanically fastened to the front surface of the sample) to an absolute accuracy of ±20 K. During the TPD experiments, the front face of the crystal was positioned less than 0.5 mm from an orifice that provided the only entrance to a differentially pumped chamber that housed the QMS. Such an arrangement was found to be effective in reducing the background and preventing desorbed species in the surroundings from entering the ionizer region (of the QMS). The temperature was varied at a linear heating rate of 1 K/s with a precision better than ±1 K.

Unless stated otherwise, the ion irradiation experiments were performed at RT with the sample positioned at 5 cm from the front face of the ion gun. The direction of the ion beam is perpendicular to the sample surface. The ion gun was operated in a N_2 ambient pressure of 1×10^{-6} Torr with a typical ion flux of ~10 nA/mm^2. The IE of the ion beam could be controlled by adjusting a floating voltage applied on the sample with respect to a pre-selected beam voltage of the ion gun. Nitrogen gas at 99.9% purity was purchased from Matheson and used without further purification. All exposures were performed using a variable leak valve, with the pressure monitored by an uncalibrated ionization gauge. Unlike electron-activated adsorption,[5,6] where contribution from neutral nitrogen atoms is important, the species that could reach the sample in the present sputtering setup are predominantly positive ions (N^+ or N_2^+). Furthermore, because the ionization cross section for N_2^+ is much larger than that for N^+,[17] the impact dissociation of N_2^+ upon collision with the surface may play an important role in the production and subsequent chemisorption of atomic nitrogen.[4,18]

Figure 1 shows the TPD profiles of mass 28 for a Cu(100) sample after ion irradiation with 12 kL [1 kL (kiloLangmuir) =1000 L; 1 L (Langmuir)=1×10^{-6} Torr s] of N_2 at RT as a function of IE. Mass 28 corresponds to the parent ion of N_2, which came from recombinative desorption of N adsorbed on the surface because no evidence for the adsorption of N_2 has been found.[5] The desorption maximum at 680 K for 20 eV IE [Fig. 1(a)] was found to shift gradually to a higher temperature of 760 K when the IE was increased to 200 eV [Fig. 1(e)]. Further increase in the IE to 800 eV did not affect the position of the desorption maximum [Figs. 1(f)–1(h)]. It should be noted that the IE used for the ion irradiation is directly related to the effective coverage because a higher ion deposition rate can be obtained at a higher IE. This coverage-dependent shift of the desorption maximum [Figs. 1(a)–1(e)] was confirmed by a similar shift to a higher temperature found for a sample prepared with a longer irradiation time at 20 eV IE (not shown). The shift in the desorption maximum to a higher temperature below 200 eV IE would suggest a zeroth-order desorption kinetics process, contrary to the second-order kinetics expected for recombinative desorption.[19] A plausible explanation is that the steady-state approximation may not be applicable in the present case and that the observed desorption process involves a coverage-dependent activation energy.[20] Above 100 eV IE, a second desorption peak appeared at a (lower) temperature of 510 K [Fig. 1(e)]. As the IE was increased, this lower temperature feature became more intense and its desorption maximum shifted to a higher temperature, which provided support for the hypothesis that a higher effective ion dosage and deeper implantation could be achieved with irradiation at a higher IE. In contrast, the intensity of the higher temperature desorption feature appeared to level off when the IE was above 200 eV [Figs. 1(e)–1(h)]. Furthermore, the higher temperature peak was found to be broadened with increasing IE and become a double-peak band above 200 eV IE, lending support for the onset of adsorption of atomic nitrogen on the less stable sites after the c(2×2) sites were saturated. These ''less stable'' sites may include adsorption sites related to surface defects.

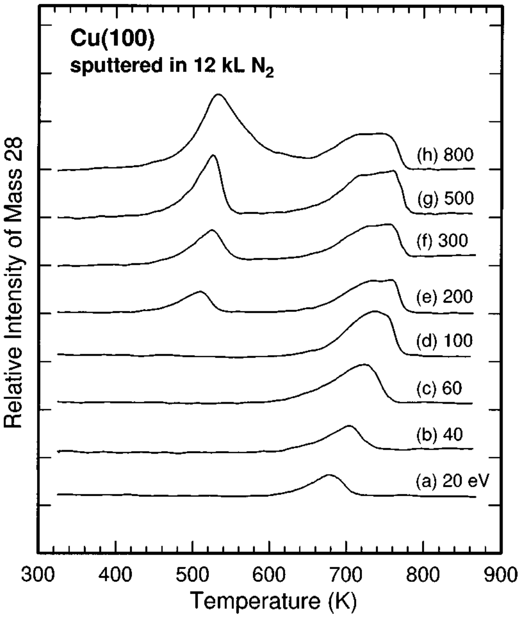

FIG. 1. Temperature programmed desorption profiles of the parent ion (mass 28) of N_2 for Cu(100) ion irradiated with 12 kL of N_2 at an impact energy of (a) 20, (b) 40, (c) 60, (d) 100, (e) 200, (f) 300, (g) 500, and (h) 800 eV.

For IE below 200 eV, the corresponding samples [Figs. 1(a)–1(d)] exhibited a diffused c(2×2) LEED pattern. The LEED pattern became a diffused (1×1) pattern at 200–500 eV IE [Figs. 1(e)–1(g)] and totally disordered above 500 eV IE [Fig. 1(h)]. The gradual degradation in the sharpness of the observed LEED spots with increasing IE was consistent with the increase in surface damage caused by ion irradiation. Upon annealing the samples to 600 K for 10 min, the LEED patterns of the samples prepared with different IEs [Figs. 1(a)–1(h)] all reverted back to a sharp c(2×2) pattern observed previously.[3,5] The ''sharpest'' c(2×2) LEED pattern obtained after the 600 K anneal was found for the sample prepared with an IE between 100 eV and 200 eV,

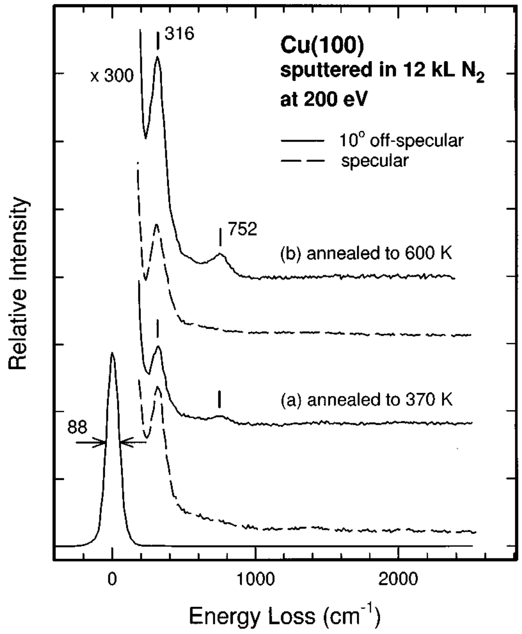

FIG. 2. Vibrational electron energy loss spectra for Cu(100) ion irradiated with 12 kL of N_2 at an impact energy of 200 eV followed by annealing to (a) 370 K and (b) 600 K, recorded in the specular (dashed lines) and 10° off-specular (solid lines) directions.

indicating that there were more complete c(2×2) domains on the sample so prepared than those irradiated at a lower IE but less radiation damage than those irradiated at a higher IE. If the samples [Figs. 1(a)–1(h)] were further annealed to 800 K for 10 min, the LEED pattern changed from a c(2×2) pattern [corresponding to N/Cu(100)] to a sharp (1×1) pattern [corresponding to clean Cu(100)]. Evidently, the c(2×2) LEED pattern corresponds only to the higher temperature desorption feature observed above 600 K. A similar desorption profile with two desorption peaks has also been reported by Heskett *et al.*[9] for a Cu(110) surface bombarded with a nitrogen ion beam at 200 eV. In particular, a (2×3) LEED pattern was attributed to the corresponding higher temperature desorption feature of the nitrogen overlayer while no assignment was given for the lower-temperature desorption feature.[9]

In order to determine whether the lower temperature desorption band was caused by a different chemisorption state or by entrapment of N^+ or N_2^+ during ion irradiation, we performed EELS experiments on a typical sample reported in Fig. 1. Figure 2 shows the EELS spectra, recorded in both the specular and 10° off-specular geometries, for a Cu(100) surface ion-irradiated with 12 kL of N_2 at 200 eV IE for two different annealing temperatures. It should be noted that the peak intensities of the energy loss features are relative only to the corresponding elastic peak in a single EELS spectrum, and the elastic peaks in all the spectra have been normalized identically to one another. Since the desorption maximum of the lower temperature feature occurs above 370 K [Fig. 1(e)], annealing the sample to 370 K should only produce the effect of surface smoothing, resulting in a more ''reflective'' surface to enhance the signals in our EELS experiments. On the other hand, annealing the sample to 600 K would remove the nitrogen associated with the lower temperature desorption feature [Fig. 1(e)]. All four EELS spectra in Fig. 2 depict a prominent vibrational feature at 316 cm^{-1}, which has been previously assigned to a Cu–N stretch in the perpendicular mode by Mohamed and Kesmodel.[6] An additional weak feature at 752 cm^{-1} can also be discerned in the off-specular spectra in Fig. 2. In accord with the dipole selection rules for surface electron scattering[21] and with the previous work,[6] this feature is attributed to the parallel modes of the Cu–N stretching vibration. Evidently, there is no notable difference (between the specular spectra and between the off-specular ones) for the sample after annealing to the two different temperatures. The changes in the relative peak intensities are likely caused by differences in the surface reflectivity as a result of the different annealing temperatures. Because vibrational EELS is a surface-sensitive technique, the lack of any substantial difference between the EELS spectra for the 370 K and 600 K anneals suggests that the lower temperature desorption feature at ~520 K [Fig. 1(e)] does not correspond to a new chemisorption state. The lower temperature desorption band may therefore be due to implantation of N^+ or N_2^+ into the sub-surface region during the ion irradiation process. This hypothesis is also supported by the fact that the desorption intensity of the lower temperature desorption feature increases with increasing IE, in contrast to that of the higher temperature feature (Fig. 1). Furthermore, the implanted nitrogen species were likely dominated by the atomic form rather than the molecular form, because the IE employed was sufficiently high to overcome the dissociation energy of N_2 (9.8 eV).[5] The different extent of implantation in the sub-surface region as a result of different IEs would lead to a zero-order desorption kinetics for the entrapped species,[19] which is consistent with the observed shift of the lower temperature desorption peak to a higher temperature shown in Figs. 1(e)–1(h). Finally, in accord with the conclusion made by Tibbetts,[5] our EELS results also do not reveal any features that could be attributed to molecularly adsorbed nitrogen species, which were previously proposed by Lee and Farnsworth.[3]

Figure 3 shows the effects of ion dosage on the TPD profiles at a fixed IE of 200 eV. At this IE, the higher temperature desorption feature (corresponding to atomic nitrogen chemisorption) could be observed at a relatively low ion dosage [Fig. 3(a)]. The intensity of this higher temperature feature became saturated at higher dosages [Figs. 3(b)–3(c)], in contrast to that of the lower temperature feature (corresponding to nitrogen implantation), which continued to increase with increasing ion dosage. Moreover, the broadening of the higher temperature desorption peak at a higher dosage also lends support to the proposed adsorption of nitrogen on other (e.g., surface defect) sites after saturation of the fourfold hollow sites.

When the IE was below 200 eV, the lower temperature desorption peak could not be observed (Fig. 1), which is consistent with the notion that less energetic ions are less

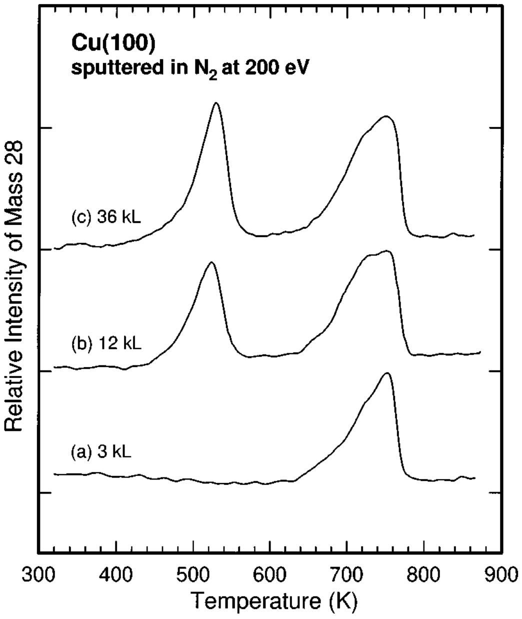

FIG. 3. Temperature programmed desorption profiles of the parent ion (mass 28) of N_2 for Cu(100) ion irradiated at an impact energy of 200 eV with (a) 3 kL, (b) 12 kL, and (c) 36 kL of N_2.

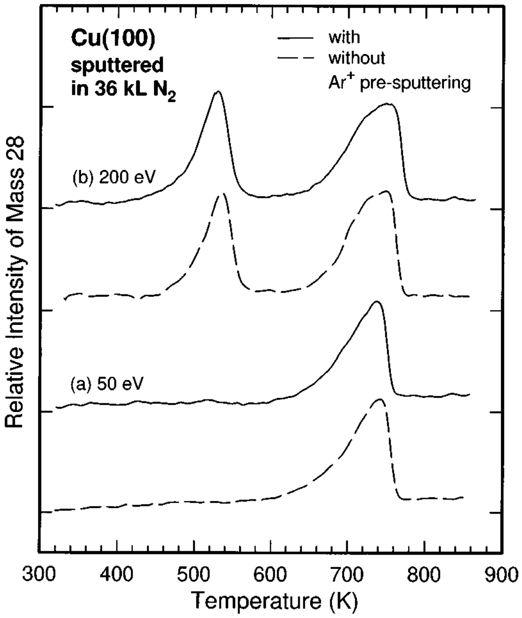

FIG. 5. Temperature programmed desorption profiles of the parent ion (mass 28) of N_2 for a clean Cu(100) surface ion irradiated with 36 kL of N_2 at an impact energy of (a) 50 eV and (b) 200 eV, with (solid lines) and without (dashed lines) Ar^+ pre-sputtering at 500 eV.

likely to implant into the bulk. However, if the ion dosage was increased sufficiently by extending the irradiation time, the lower temperature desorption band could again be obtained. Figure 4 shows the TPD results of Cu(100) irradiated with a higher nitrogen ion dosage (i.e., six times that used in Fig. 1) for three typical IEs not exceeding 100 eV. Evidently, a weak desorption peak at ~500 K could be observed in the TPD profiles for 75 eV and 100 eV but not in that for 50 eV, which suggests that an upper bound of the minimum IE required for the implantation to occur is below 75 eV. Furthermore, the entrapment of nitrogen species did not appear to affect the adsorption of atomic nitrogen that gave rise to the c(2×2) overlayer on Cu(100). It apparently occurred only after the adsorption of atomic nitrogen was nearly complete, as depicted by the saturated intensity of the higher temperature desorption feature in Fig. 4(b).

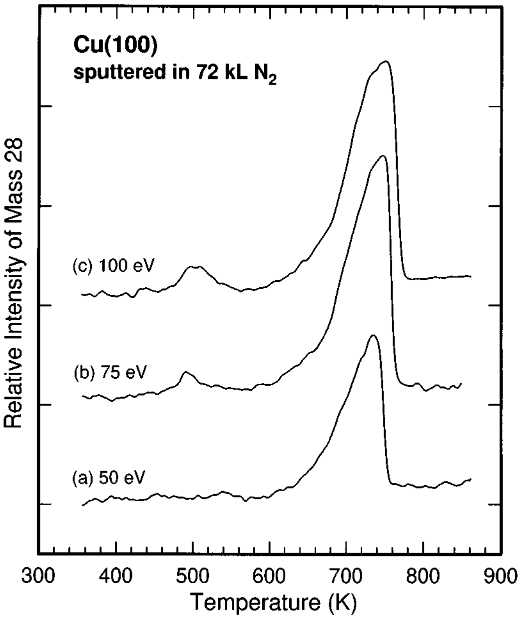

FIG. 4. Temperature programmed desorption profiles of the parent ion (mass 28) of N_2 for Cu(100) ion irradiated with 72 kL of N_2 at an impact energy of (a) 50 eV, (b) 75 eV, and (c) 100 eV.

It is well known that ion irradiation at an IE above 30 eV is sufficient to generate defect sites on a surface.[12,22] In order to examine the effects of defects, we compare the desorption of N_2 from an amorphous surface [obtained by Ar^+ sputtering a Cu(100) surface at 500 eV IE] with that from a clean surface at two different IEs of the nitrogen ions (Fig. 5). Evidently, there is no notable difference in the TPD profiles between the Ar^+ pre-sputtered surface and the clean Cu(100) surface for both 50 eV [Fig. 5(a)] and 200 eV IE [Fig. 5(b)]. If the lower temperature desorption band were due to nitrogen adsorbed on the defect sites of the surface, we would expect stronger lower temperature desorption on the Ar^+ pre-sputtered surface because of the high concentration of defect sites. The lack of any discernible difference in the TPD results between the two surfaces therefore provides strong evidence for our previous assignment of the lower temperature peak to implanted nitrogen species. In the case of the chemisorbed nitrogen (the higher temperature desorption feature), the similarities observed for the two different surface conditions suggest possible surface migration of N, whereby the nitrogen atoms, initially adsorbed at different sites of the amorphous surface with equal efficiency, underwent surface diffusion into the more stable fourfold-hollow sites [giving the c(2×2) reconstruction] when the temperature was increased.

In summary, we present the TPD and EELS results for a Cu(100) surface after different treatments of nitrogen ion irradiation. In addition to the desorption band at 760 K, corresponding to recombinative desorption of ''surface'' nitrogen atoms primarily adsorbed on fourfold-hollow sites, the TPD results reveal the onset of a second desorption band at 520 K. This new lower temperature desorption feature is attributed to ''entrapped'' nitrogen species in the sub-surface region, in good accord with the EELS results. Furthermore, nitrogen implantation appears to be insignificant when the IE is less than 75 eV. Depending on the IE and ion dosage, the ion irradiation process can also introduce different levels of damage to the surface. The surface defects do not appear to significantly affect the concentration of the implanted nitrogen species and that of the nitrogen atoms chemisorbed on the c(2×2) sites. Adsorption on these less stable defect sites occurs only after the saturation of the more stable c(2×2) sites.

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