Molecule Formation During Sputtering by Two-Body Associative Ionization with Diabatic Curve Crossing

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Optical emission was observed from N_2^+ molecules formed during ion bombardment of nitrogen-implanted silicon. A proposed two-body ionized-molecule formation mechanism which invokes inverse predissociation of the corresponding neutral, followed by a Franck-Condon ionization, quantitatively explains the data. The ionization step proceeds either by resonant electron tunneling to a vacant state in the nearby solid, or, for neutral molecule states above the first ionization limit, by autoionization.

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The basic dynamical processes responsible for the sputtering of monatomic particles are now well elucidated.[1] These principles have also been applied to the ejection of molecular species. Central to these sputtered-molecule theories is the assumption that the sum of the potential and relative kinetic energies possessed by the constituent nuclei is less than zero (i.e., they are bound) throughout the evolution of the ejection trajectory.[2-4] In this Letter we report evidence for an additional source of molecules, i.e., for the formation of N_2^+ molecules from independently sputtered, unbound N atoms. This observation is also the first evidence for the occurrence of associative ionization via a diabatic curve crossing. Previous to this work, only two-body associative ionization on a single curve was known.[5]

We have bombarded a single-crystal silicon target [(111) face, 99.999% purity] in ultrahigh vacuum with mass-analyzed ion beams in the energy range 500 eV to 6 keV, and observed the radiation emitted above the target for the geometry illustrated in Fig. 1. The photon spectrum seen up to 10 mm above the target surface during N_2^+ bombardment of silicon is presented in Fig. 1. An identical spectrum is obtained with use of N^+ and Ne^+ (for a nitrogen-implanted silicon target) as projectile, illustrating that the contribution to the spectral features from molecular projectiles which survive the collision with the surface is negligible. The position of spectral features at high resolution (Table I) exhibits no dependence on beam energy (500 eV to 6 keV) or incidence angle to the target surface. The spectrum also exhibits no meaningful correlation with known silicon or silicon nitride molecular bands,[10] but above 5000 Å correlates well with the gas-phase single-collision-excited N_2^+ $A^2\Pi_u$–$X^2\Sigma_g^+$ bands, provided we assume that an unusually extensive range of rotational and vibrational levels of the N_2^+ $A^2\Pi_u$ state are populated in the ion-surface collision formation process. The lower-wavelength (3000–4200 Å) portion of the ion-surface collision spectrum, when studied at higher resolution (8 Å full width at half maximum), reveals a discrete line spectrum (Table I) superimposed on a continuous background, both of which correlate well in position with N_2^+ $B^2\Sigma_u^+$–$X^2\Sigma_g^+$ transitions. Such an interpretation, however, requires that low vibrational states of N_2^+ $B^2\Sigma_u^+$ are rotationally populated both unselectively (leading to the apparent continuum) and, for spe-

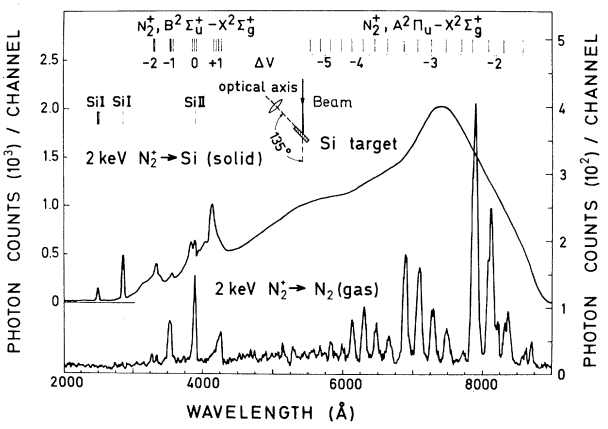

FIG. 1. Spectra of radiation emitted by excited N_2^+ molecules formed during ion-surface and gas-phase collisions. The single-collision gas-phase spectrum was obtained by replacing the solid target by an N_2 thermal gas target. Band-head wavelengths (Ref. 6) of the N_2^+ A–X and B–X systems, and positions of observed SiI and SiII lines are indicated. (No optical-system quantum-efficiency correction has been made to the data. Resolution is 25 Å full width at half maximum; multichannel scaler channel width is 7 Å; second order and primary beam excitation components have been subtracted.)

TABLE I. Identification of discrete B-X transitions with those predicted by the proposed model (observed linewidth equal to instrumental linewidth of 8 Å full width at half maximum). Unless indicated, all wavelengths were calculated using the molecular constants of Huber and Herzberg (Ref. 7).

Inverse predissociation	Predicted B-X transitions (v',v'')	N' range	λ_{air} (Å)	Observed wavelength λ_{air} (Å)
$B^3\Pi_g - {}^5\Sigma_g^+$, $v''=12$	(1,2)	32–35	4177[a]–4169	4173
$B^3\Pi_g - {}^5\Sigma_g^+$, $v''=12$	(2,3)	32–35	4147–4140	4144
$B^3\Pi_g - {}^5\Sigma_g^+$, $v''=12$	(13,10)	32–35	3359	3361
$B^3\Pi_g - {}^5\Sigma_g^+$, $v''=11$	(1,2)	52–55	4125–4115	4119
$C^3\Pi_u - {}^5\Pi_u$, $v''=4$	(0,0)	≥ 28	≤ 3874[b]	3870
$C^3\Pi_u - {}^5\Pi_u$, $v''=3$	(0,0)	≥ 43	≤ 3840[b]	3833

[a]Reference 8. [b]Reference 9.

cific high N values, extremely selectively (to explain the linelike components).

None of the existing molecule-sputtering theories[2-4] predicts an enhanced formation of diatoms in specific highly rotationally excited states, let alone states which exhibit no rotational or vibrational dependence on projectile species or energy (in this energy range), or incidence angle to the target surface. Certainly such an extreme rotational preference as implied by the data is hard to envisage within a purely dynamical argument for the direct ejection of molecules. A broad rotational and vibrational distribution would, however, be conceivable.

The observed rotational specificity of the population of the N_2^+ $B^2\Sigma_u^+$ low vibrational states suggests that a potential curve crossing is involved in the molecule formation process. A possible known mechanism is two-body radiative recombination with or without a diabatic curve crossing. Such a formation mechanism for the observed levels of the $B^2\Sigma_u^+$ state, however, is energetically precluded by these levels being at lower energy than the lowest N_2^+ dissociation limit $[N(^4S^\circ)+N^+(^3P)]$. Among the possible rotational-quantum-number identifications, however, are correspondences with just those N values at which the $B^3\Pi_g$ and $C^3\Pi_u$ states of N_2 are known to predissociate.[6] Given a suitable mechanism, loss of a $1\pi_g$ electron from $C^3\Pi_u$ or a $1\pi_u$ electron from $B^3\Pi_g$ could result in the formation of the N_2^+ $B^2\Sigma_u^+$ state with little change in angular momentum of the molecule. The data therefore suggested that N_2 inverse predissociation processes may be involved in the formation of sputtered N_2^+.

The model which we propose is illustrated in Fig. 2 for the N_2 $B^3\Pi_g - {}^5\Sigma_g^+$ $v''=12$, $N''=33,34$

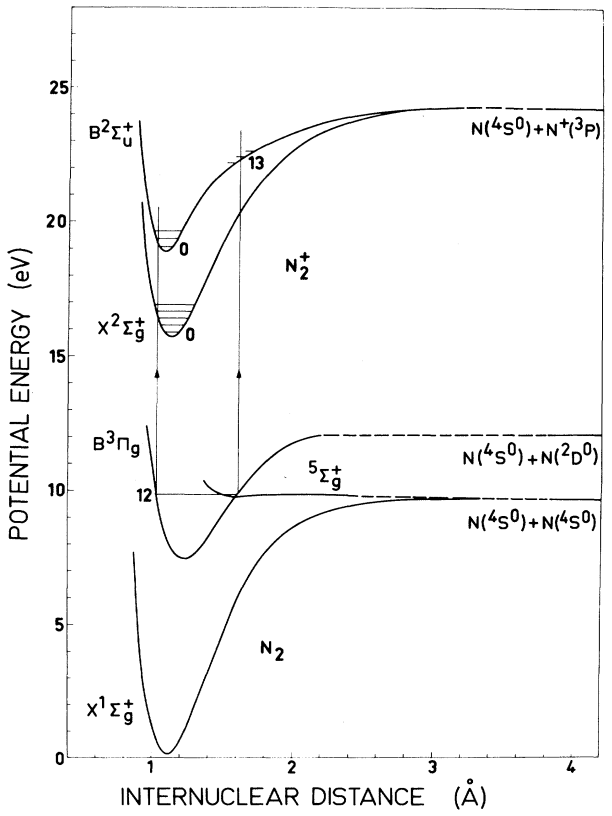

FIG. 2. Relevant potential curves for N_2^+ and N_2 for $N_{mol}=33$, $N_{ion}=34$ [full lines calculated with use of the curves of Loftus and Krupenie (Ref. 6) as a basis; broken lines serve only to indicate the respective dissociation limits], illustrating the N_2 $B^3\Pi_g - {}^5\Sigma_g^+$ inverse predissociation followed by a $1\pi_u$ ($\lambda=0$) electron loss to the nearby solid to produce N_2^+ $B^2\Sigma_u^+$. The Franck-Condon principle applied to the preionization implies $v''=1$, 2, and 13 will be most strongly populated.

inverse predissociation.[6] Two $N(^4S^\circ)$ atoms sputtered from the solid by the same impacting projectile ion (giving the required spatial and temporal coincidence) colliding on the $^5\Sigma_g^+$ potential curve can, for the appropriate relative kinetic energy and impact parameter, cross to the $v''=12$, $N''=33, 34$ states of the $B^3\Pi_g$ potential curve. If, during the lifetime (for predissociation) of the vibrational state ($\approx 10^{-13}$ s) a $1\pi_u$ electron tunnels to a vacant state in the solid, an N_2^+ ion is formed. Such adiabatic ionization processes can be of resonant, quasiresonant, or Auger type, and have an upper limit on their lifetime of 10^{-15} s.[11] This leads to a lifetime broadening of the participating energy levels of greater than 0.66 eV.

This broadening, coupled with the disturbance of the Si substrate electronic structure by the implantation of N, the existence locally of at least two surface defects (caused by the departing molecular constituents), and electronic holes created by ion-bombardment–induced electron emission, suggests that the ionization step which we propose should have finite probability even though the N_2 vibrational level energetically overlaps the occupied valence bands of pure, undisturbed bulk Si. Application of Kronig's selection rules and the Franck-Condon principle to this transition predicts the formation of N_2^+ $B^2\Sigma_u^+$ (plus several other N_2^+ states) primarily in the $N_{\text{ion}}=N_{\text{mol}}\pm 1$, $v''=1$, 2, and 13 vibrational states.

Among the observed spectral features, three can clearly be associated with strong transitions from these levels predicted by the approximate Franck-Condon factors[6,12] (Table I). The influence of the nearby surface on the gas-phase interatomic potential energy curves can be estimated with use of the theory of Mahanty and March,[13] and for recombination occurring outside the electron spillout region, the rotational quantum number at which the N_2 inverse predissociation occurs is perturbed by at most $\Delta N=1$. Similar application of the model to the remaining predissociations of N_2 quantitatively predicts all the remaining rotationally specific features (Table I).

The broad distribution observed in Fig. 1 could contain contributions from many alternative mechanisms and/or molecules formed during the sputtering process. A full analysis of the arguments for and against the various possibilities, including further experimental evidence, is presented elsewhere.[14,15] We note, however, that this spectrum can be explained by the general mechanism outlined above. The rotationally unspecific population of the (tentatively identified) N_2^+ $B^2\Sigma_u^+$ state occurs following loss of a $1\pi_u$ electron from the N_2 $a^1\Pi_g$ state formed via a curve crossing from the $^5\Sigma_g^+$ state, while that of the N_2^+ $A^2\Pi_u$ is due to an $o_4{}^1\Pi_u$–$C'^3\Pi_u$ inverse predissociation followed by loss of a $1\sigma_g$ electron. In the latter case, for $v'\geq 2$ (in the $o_4{}^1\Pi_u$ state), electron loss occurs via autoionization to the vacuum continuum above the N_2^+ $X^2\Sigma_g^+$ $v=0$ first ionization limit.

We thus report the first experimental observation of N_2^+ formation via the processes

$$N(^4S^\circ)+N(^4S^\circ)\rightarrow N_2(^5\Sigma_g^+)\rightarrow N_2(B^3\Pi_g)\rightarrow N_2^+(B^2\Sigma_u^+)+e^-, \quad (1)$$

$$N(^4S^\circ)+N(^4S^\circ)\rightarrow N_2(^5\Sigma_g^+)\rightarrow N_2(a^1\Pi_g)\rightarrow N_2^+(B^2\Sigma_u^+)+e^-; \quad (2)$$

and the possible observation of

$$N(^4S^\circ)+N(^2D^\circ)\rightarrow N_2(^5\Pi_u)\rightarrow N_2(C^3\Pi_u)\rightarrow N_2^+(B^2\Sigma_u^+)+e^-, \quad (3)$$

$$N(^4S^\circ)+N(^2D^\circ)\rightarrow N_2(C'^3\Pi_u)\rightarrow N_2(o_4{}^1\Pi_u)\rightarrow N_2^+(A^2\Pi_u)+e^-. \quad (4)$$

The ionization step proceeds either via an electron tunneling to a vacant electronic state in the nearby solid [Eqs. (1)–(3)], or, where energetically permitted, by autoionization to the vacuum continuum, independent of the presence of a surface [Eq. (4)]. We call these processes two-body associative ionization with a diabatic curve crossing.

This newly observed mechanism for ionized molecule formation may have significant implications for catalysis, gas-phase chemical reactions (including upper atmosphere and interstellar chemistry), molecule-sputtering theory, and the explanation of continuum optical emission observed in the sputtering of many metals.

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Stress-Induced Electronic Transition (2.5 Order) in Al

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The effect of uniaxial stress (σ) on the superconducting transition temperature (T_c), resistivity (ρ), and magnetothermopower of Al has been measured. It has been found that $[\partial T_c/\partial\sigma]_{\sigma=0} = (9.6 \pm 0.5) \times 10^{-11}$ K/Pa. Further, it is found that an anomaly exists in $\partial T_c/\partial\sigma$ and $\partial\rho/\partial\sigma$ near $\sigma = 0.5$ GPa, and that the magnetothermopower oscillations associated with the α orbit in the third-zone electron surface disappear at $\sigma = 0.54$ GPa.

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In 1960, Lifshitz[1] described the consequences of a change in the Fermi-surface topology, showing that there would be singularities in the third derivatives of the thermodynamic potentials proportional to $z^{-1/2}$ (2.5 order). Here z is the difference between the chemical potential of the electrons and the electron energy at which the topology change occurs. In the case of stress, z is linearly related to stress near $z = 0$. The clearest method of experimentally demonstrating the existence and character of an electron transition is to observe the cross section of the part of the Fermi surface undergoing a change in connectivity. This can be done by observing de Haas–van Alphen,[2] de Haas–Shubnikov,[3] or magnetothermopower oscillations, or any other thermodynamic or transport property which is related to the Landau levels. As Lifshitz showed, properties which average over the Fermi surface, such as T_c, will show characteristic anomalies. To make sure that these anomalies are due to an electron transition is not an easy task; simultaneous observations of the relevant portion of the Fermi-surface cross section are the best proof.

Such transitions are thought to occur as a function of pressure or stress in As,[4] $AuGa_2$,[2] Bi,[5] Cd,[6], In and In alloys,[7-9] $LaSn_3$,[10] Re and Re alloys,[11] $(SN)_x$,[12] Tl,[13] and Zn.[6] We believe that this is the first time, however, that a change in a thermodynamic derivative (in this case, $\partial T_c/\partial\sigma$) has been directly correlated with a known Fermi-surface topology change.

Al whiskers were grown by depositing 99.999% Al on steel washers, stacking the washers on a bolt, compressing them on the bolt, and then heating the compressed stack in vacuum at about 800 K for periods of six months to one year. A few whiskers of length up to 2 mm and cross section about 1 μm^2 grew at the surface of the Al deposit. Rotating crystal x-ray photographs showed the whiskers to be single crystals; the samples reported here have their axes along a $\langle 110 \rangle$ crystal direction. The whiskers were mounted on a low-temperature stressing apparatus previously described,[14] which was modified to allow the temperature on one end of the whisker to be raised by about 1 K above that of the other end. The resistive superconducting transition

