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Basic mechanisms of energetic molecule ejection from surfaces

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Abstract - A description of the basic mechanisms of energetic molecule ejection from surfaces, both collisional and electronic, is presented. It is shown that the rotational and vibrational population distributions, and kinetic energy and angular distributions contain clear fingerprints of the ejection mechanism, and some information on the molecule bonding configuration on the surface. Use of this information should enable a definitive experimental determination of the last reaction step in the ion beam-reactive gas etching process.

INTRODUCTION

Both semiconductors and metals are eroded or etched by halogen containing vapours. Like its counterpart "wet chemical etching", this process is isotropic, and undercuts any structure defining mask, thus limiting the ultimate attainable device resolution (Fig. 1a). Directional etching, however, can be induced by combining a relatively unreactive halogen containing vapour with energetic particle bombardment. The bombarding species "catalyse" the reaction (Fig. 1b), and the etch rate is much faster than with either the particle beam or halogen vapour alone (ref. 1). This process is already being exploited in VLSI technology, but to allow full development of the potential of this technique, considerable effort is being devoted to fundamental studies whose aim is to identify the reaction mechanism, and optimize its efficiency.

It has been proposed that the energetic particle beam enhances the halogen-silicon reaction and that the product molecules thermally desorb (ref. 2-4), or alternatively, that the particle bombardment is itself directly responsible for the molecule ejection (ref. 5). In attempts to establish which mechanism is operative, extensive measurements of the mass and kinetic energy distributions of product molecules have been performed (ref. 2-5), and recently, the internal (rotational and vibrational) energy distributions of ejected molecules have been measured (ref. 6-7).

To assist the interpretation of these differential measurements, theoretical models describing molecule ejection following photon, electron, and ion or atom bombardment have been developed (ref. 8-13). The resulting calculations of rotational, vibrational, kinetic energy and angular distributions of ejected molecules provide us with fingerprints of these ejection processes, which we can then seek in experimental data.

In this paper, the general properties of molecules ejected following energetic particle bombardment of solids will be presented, and the microscopic mechanisms discussed. Specific examples of particular relevance to the etching of silicon by halogen containing vapours are presented.

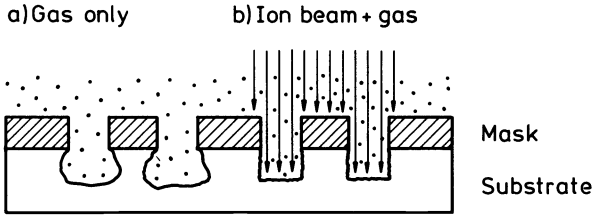

Fig. 1. Schematic etch pits generated by a) reactive gas only, and b) the combination of an ion beam and reactive gas.

BASIC MECHANISMS

Particles (either atoms or molecules) may be ejected from solids through momentum transfer following either vibrational or electronic excitation of the particle-surface bond (Fig. 2). The former process corresponds to the direct "collisional" energy transfer occuring in ion-beam induced desorption and sputtering (Fig. 3), the latter to the indirect energy transfer which occurs following electron or photon impact. We consider each of these processes separately.

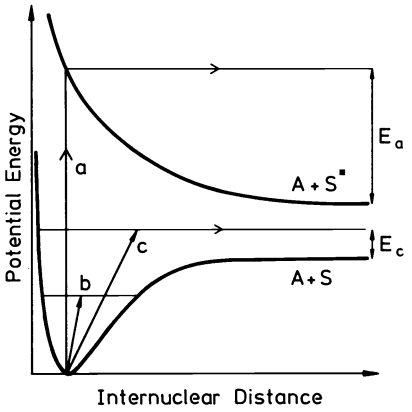

Fig. 2. Illustration of particle ejection from solids via a) electronic excitation of the particle-substrate bond via eg. electron or photon impact. If this state does not immediately decay, the atom or molecule A separates from the substrate S under the influence of the repulsive potential A+S*, and will be detected with a kinetic energy E_a; and b,c) vibrational excitation of the particle-substrate bond via collisional energy transfer. If insufficient energy transfer occurs, the atom or molecule will remain trapped, while for transfers exceeding the particle binding energy to the surface, ejection will occur with a final atom or molecule kinetic energy of E_c being observed.

Collisional energy transfer

At the geometries generally employed for ion assisted etching (near normal incidence) direct beam induced desorption is prohibited by momentum conservation. At more glancing impact angles, such ejected atoms have a well defined energy E_1 in a particular observation direction θ to the primary beam direction, viz

$$E_1 = \frac{4m_1m_2}{(m_1+m_2)^2} E_o \cos^2\theta, \quad \theta \leq \pi/2 \qquad (1)$$

where m_1 and m_2 are the projectile and recoil atom masses, and E_o is the projectile energy. This technique has been termed ion impact desorption spectroscopy by Eckstein and coworkers (ref. 14). Molecules ejected via this process may have energies somewhat less than predicted by equation (1), due to excitation of rotational or vibrational degrees of freedom. Nevertheless, the approximate projectile energy, mass, and angular dependences contained in equation (1) permit easy identification of this process.

If the energetic projectile ion penetrates the surface layer, momentum transfer to atoms along its path sets up a "collision cascade" (ref. 15). This cascade can in general be described initially by a sequence of nonoverlapping binary collision sequences, which eventually intersect and thermalize. Particle ejection occurs in general early in the cascade development, when the average energy per moving atom is high. This requirement is imposed by the necessity for ejected atoms to overcome their binding energy to the surface. In solids like silicon, which are quickly amorphized by ion bombardment, the collision cascade is essentially isotropic and the atoms in the solid exhibit an energy spectrum close to E^{-2}. Through their diffraction by a planar surface barrier U, ejected atoms thus possess to first order the distribution (ref. 16)

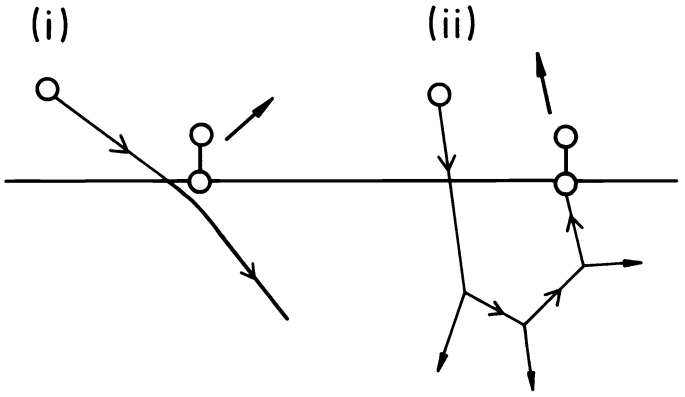

Fig. 3. Collisional energy transfer can occur (i) directly between the projectile and surface atom or molecule (direct beam induced desorption), or (ii) indirectly, via a complex collision sequence in the substrate (sputtering). Other molecule orientations and bonding configurations are of course allowed.

$$\frac{\partial^2 N}{\partial E \partial \Omega} = \frac{c_a E}{(E+U)^3} \cos\Theta, \tag{2}$$

where c_a is a constant containing the beam and substrate parameters.

This same collision cascade is of course responsible for molecule ejection. Let us consider the simplest possible model situation sketched in Fig. 4, and assume the molecule is ejected via a single binary collision between a substrate atom (atom 0) and one end of the molecule (atom 1). If we assume an energy transfer E_1 to atom 1, the energy of the centre-of-mass of the atom pair 1-2 is

$$E_{12} = \frac{m_1}{(m_1+m_2)} E_1 \tag{3}$$

where m_1 and m_2 are the masses of atoms 1 and 2 respectively. Since we already know the energy distribution of atom 1 (equation (2)), we can immediately write the atom pair kinetic energy and angular distribution, viz

$$\frac{\partial^2 N_{12}}{\partial E_{12} \partial \Omega} = \frac{c_{12} E_{12}}{(E_{12}+\kappa U)^3} \cos\Theta \tag{4}$$

where $\kappa = m_1/(m_1+m_2)$, the scale factor in equation (3). Since $\kappa<1$ always, the molecule energy spectrum will peak at a lower energy (namely $\kappa U/2$) than that of the atom 1 ($U/2$).

The remaining energy $E_i = E_1 - E_{12}$ is distributed over the internal degrees of freedom of the molecule. If we neglect electronic excitation, and treat rotation and vibration classically, we obtain

$$E_{vib} = E_i \cos^2\alpha \tag{5a}$$

and

$$E_{rot} = E_i \sin^2\alpha \tag{5b}$$

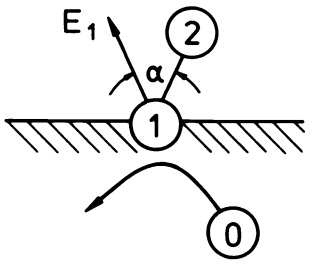

Fig. 4. Simple model of molecule sputtering in which a moving substrate atom 0 collides with atom 1 of the molecule. The atom 1 escapes the surface with energy E_1 and is moving initially in a direction at angle α to the 1-2 bond direction.

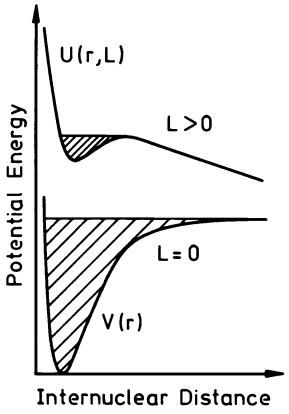

Fig. 5. Effect of non-zero angular momentum L on the ground state potential curve V(r) of a molecule. Atom pairs within the shaded regions are bound.

where α is the angle between the initial direction of motion of atom 1 and the molecule bond axis (Fig. 4).

Clearly, if E_i is large enough, the atom pair 1-2 may dissociate. These dissociating pairs must be removed from the spectrum (equation (4)) to give the true spectrum of sputtered molecules.

A diatomic molecule with angular momentum L has a potential curve

$$U(r,L) = V(r) + L^2/2\mu r^2 \tag{6}$$

where r is the internuclear distance, $\mu=m_1m_2/(m_1+m_2)$ is the reduced mass, and V(r) is the potential curve of the non-rotating molecule. Such a potential will have, in general, a maximum at some intermediate r value for non-zero L. This so-called "centrifugal barrier" can be seen in Fig. 5. If tunnelling through this barrier can be neglected, all molecules within the shaded regions of Fig. 5 are bound. This condition can be transformed into a limit on the maximum possible translational kinetic energy of a bound sputtered molecule (ref. 11). This limit has the upper bound

$$E_{12}^{max} = (m_1/m_2)D \tag{7}$$

where D is the dissociation energy of the ground state molecule. Thus the kinetic energy distribution of molecules ejected via this mechanism (equation (4)) will have a high energy cutoff. This cutoff is of the order of the dissociation energy for like-mass atoms, but can become very large for hydrides. This effect is illustrated in Fig. 6, and the corresponding rotational and vibrational population distributions are shown in Fig. 7. Notice that for typical sputtering parameters, between 50 % and 96 % of the molecules survive the ejection collision. This means that molecule sputtering can be an extremely efficient process.

Up to now we have considered an idealized, but nevertheless revealing, model of molecule sputtering. How would our predictions be influenced by assuming, for example, energy transfer to *both* atoms during ejection, or that *both* atoms are initially bound to other surface atoms (Fig. 8)?

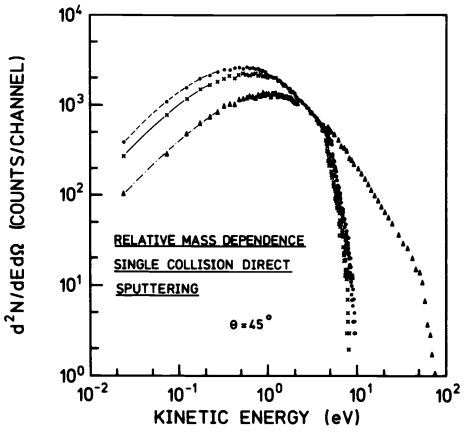

Fig. 6. Kinetic energy distributions of single collision directly ejected molecules of widely differing mass and molecular properties. We assume the N, Si, and Hg atoms of the molecules N_2, SiF, and HgH to suffer the direct collision, the second atom to be bound to no other surface atom, a binding energy of the first atom to the surface of 2 eV, and an isotropic initial molecule orientation distribution.

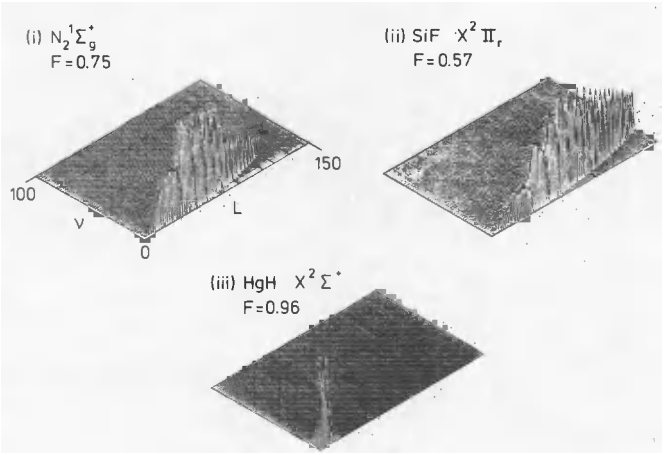

Fig. 7. Rotational L and vibrational ν population distributions corresponding to Fig. 6. The factors F represent the fraction of molecules which survive the ejection collision without dissociating.

We saw that for single collision ejection, the kinetic energy distribution cuts off sharply due to the energy difference between the ejected atoms eventually exceeding the molecule dissociation energy. This energy difference will be much reduced if we give *both* atoms 1 and 2 momentum in the vacuum direction. The sharp cutoff disappears and we obtain an asymptotic high energy dependence approaching $E_{12}^{-4.5}$, independent of the form of the surface potential barrier, provided we assume no energy or angular correlation between the two ejection collisions (Fig. 9). The rotational and vibrational excitation (Fig. 10) is not markedly dependent on the collision mechanism (single or double), but does exhibit some dependence on the way in which the atoms of the molecule were bound to the surface.

The way in which the molecule is bound to the surface also strongly influences the angular distribution of sputtered molecules (ref. 17). When only "one end" of the molecule is bound, we expect an atom-like θ distribution (equation (4)). When both atoms are "individually bound", this transforms approximately to the product of the atom θ distributions, and when it is more realistic to speak of binding of the molecule as a structureless entity, the θ distribution is once again atomic-like. This sensitivity to the model bonding type is clearly apparent for silicon fluoride in Fig. 11.

The vibrational energy distributions are also predicted to contain useful information on the atom separation distribution on the surface prior to sputtering of the molecule (Fig. 12). Very broad population distributions are indicative of broad separation distributions and vice versa (ref. 10). This information may tell us whether the molecules we sputter can be considered preformed, or whether the atoms only preferentially associate during ejection.

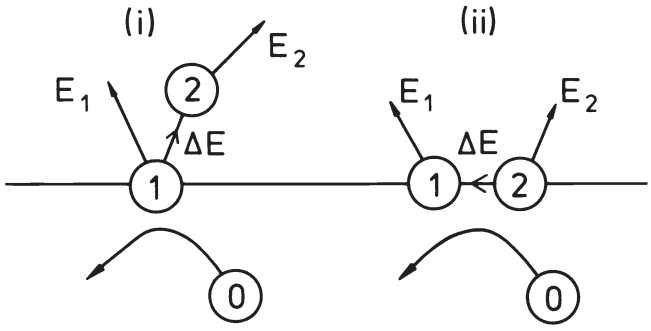

Fig. 8. Molecule sputtering in which energy transfer occurs directly to atom 1, and to atom 2 either (i) indirectly via atom 1 or (ii) directly via collision with atom O. Two possible bonding situations are illustrated. A further possible energy transfer mechanism is that two substrate atoms O and O' collide with atoms 1 and 2 of the molecule. This mechanism is expected to be of lesser importance for most sputtering situations, because the density of energetic atoms is low.

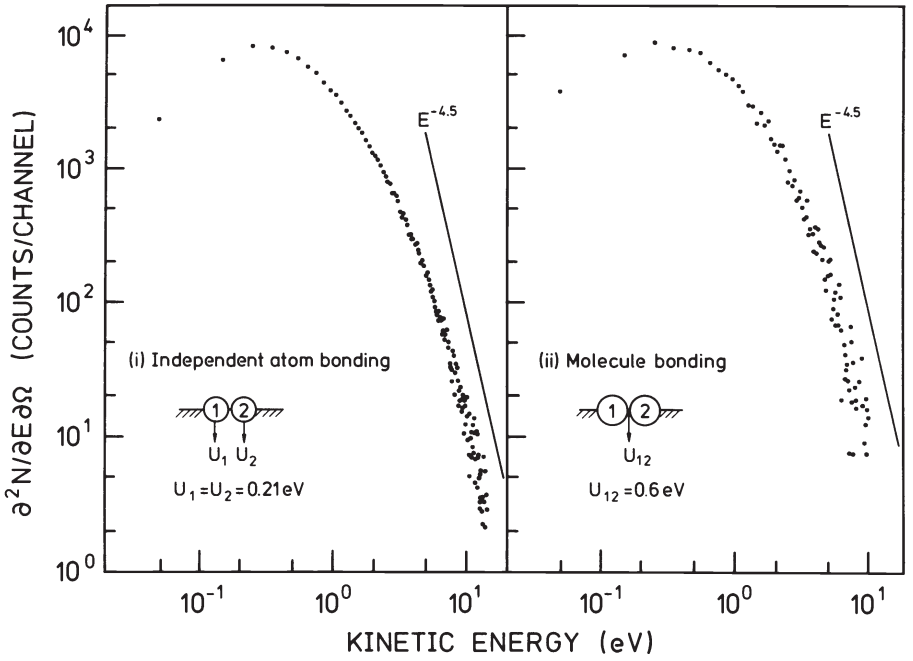

Fig. 9. Kinetic energy distributions of sputtered ground state SiF molecules for the types of surface bonding shown schematically in the insets. The high energy asymptotic dependence of the atom pair distributions are indicated. It was assumed that ejection was caused by collisions with both atoms of the molecule (ref. 17). The surface binding energies were chosen so that both distributions peak at the same energy (0.3 eV).

Electronic energy transfer

The erosion of solids following electron or photon impact proceeds via the indirect momentum transfer process illustrated in Fig. 2 (more complex variants for preparing the repulsive state are described in ref. 8. The electronic transition occurs on a time-scale short compared to that for nuclear motion. Provided this state does not decay within a time of order 10^{-14} s, the atom or molecule will desorb from the surface under the influence of the repulsive potential. The advantage of this erosion mechanism over ion or atom bombardment is that little sub-surface damage occurs. This is a particularly important consideration if an ordered crystal structure is important for successful operation of the component being constructed.

The same trajectory methods employed above for predicting the internal and translational energies of sputtered molecules can be employed for electron or photon induced desorption. Model calculations for the system CO adsorbed on Ru(001) have shown that the rotational, vibrational, kinetic energy and angu-

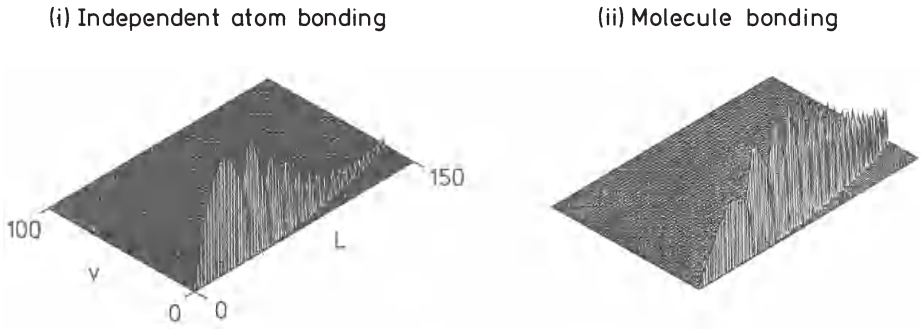

Fig. 10. Rotational L and vibrational ν population distributions corresponding to the kinetic energy distributions in Fig. 9. The L and ν axes are identical for both diagrams.

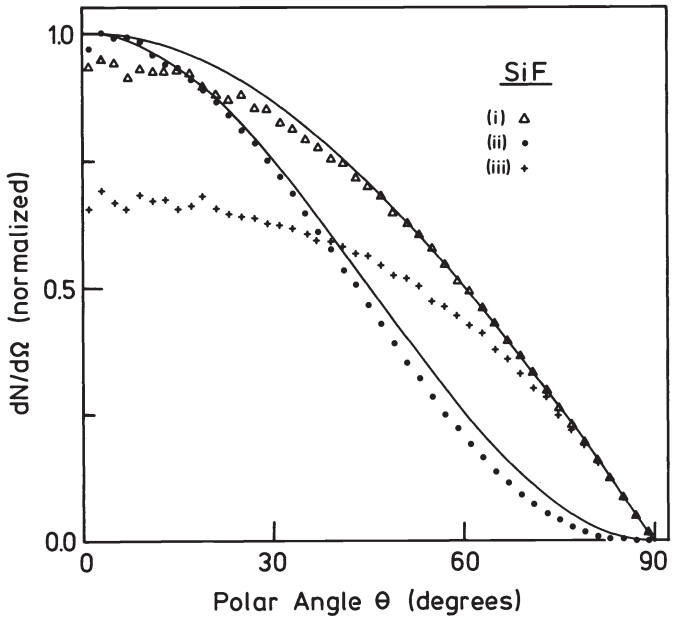

Fig. 11. Polar angular distributions of SiF corresponding to the ejection mechanisms and bonding configurations of (i) Fig. 6, (ii) Fig. 9(i), and (iii) Fig. 9(ii). The lines represent $\cos\Theta$ and $\cos^2\Theta$ distributions.

lar distributions of ionized and neutral carbon monoxide contain information on the molecule-substrate bond-length distribution, on the strength of the repulsive state formed following electron or photon impact, and on the molecule orientation distribution (Fig. 13). This means that unambiguous identification of electronic energy transfer as the product molecule ejection mechanism should be possible experimentally.

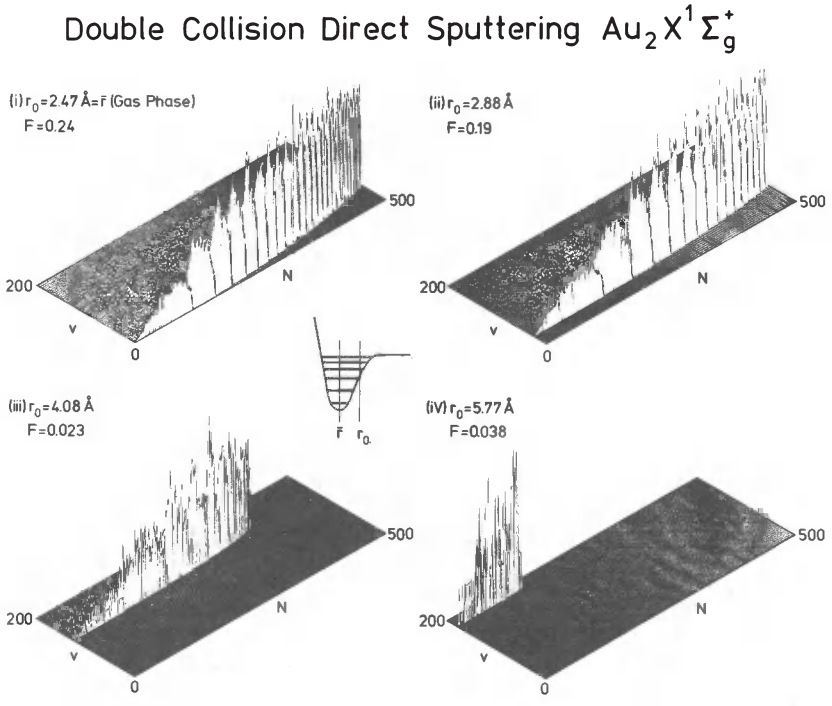

Fig. 12. Rotational N and vibrational v population distributions of sputtered Au_2 molecules as a function of initial separation r_o on the surface (ref. 18). The r_o values chosen represent (i) the gas phase equilibrium value, and (ii)-(iv) nearest, next nearest, etc. neighbours for the face centred cubic crystal. F has the same meaning as in Fig. 7.

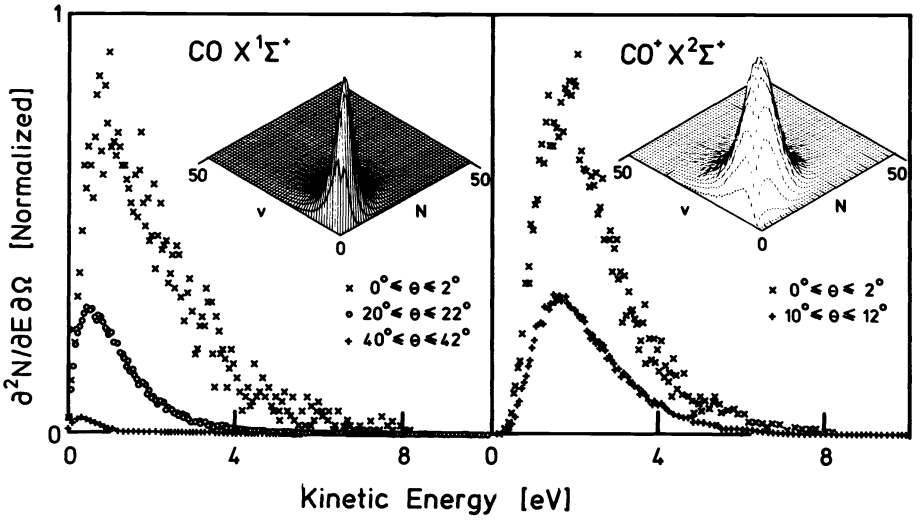

Fig. 13. Calculated kinetic energy and rotational N and vibrational v population distributions of CO and CO^+ ejected from Ru(001) following electron or photon impact (ref. 12).

CONCLUSION

Following extensive theoretical analysis of molecule ejection from surfaces via collision or electronic energy transfer, we find that clear fingerprints of the ejection mechanism exist in the internal and translational energy, and angular distributions. Measurement of these observables, and comparison with theoretical predictions, should therefore enable definitive identification of the final reaction step in the ion beam-halogen etching process.

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REFERENCES

1. H.F. Winters, Int. Conf. Ion Beam Modifications of Materials, Ithaca, USA (1984).
2. J.W. Coburn and H.F. Winters, J. Appl. Phys. 50, 3189-3196 (1979).
3. Y.Y. Tu, T.J. Chuang and H.F. Winters, Phys. Rev. B23, 823-835 (1982).
4. U. Gerlach Mayer, Surf. Sci. 103, 524-534 (1981).
5. R.A. Haring, A. Haring, F.W. Saris and A.E. de Vries, Appl. Phys. Lett. 41, 174-176 (1982).
6. K.J. Snowdon and W. Heiland, Z. Physik 318A, 275-284 (1984).
7. R. Walkup, Ph. Avouris, R.W. Dreyfus, J.M. Jasinski and G.S. Selwyn, Appl. Phys. Lett. 45, 372 (1984).
8. Proceedings DIET I, ed. N. Tolk et al., Springer New York (1983).
9. G.P. Können, A. Tip and A.E. de Vries, Rad. Eff. 21, 269-274 (1974).
10. K.J. Snowdon, R. Hentschke, W. Heiland and P. Hertel, Z. Physik 318A, 261-274 (1984).
11. K.J. Snowdon, Nucl. Instr. Meth. B, in press (1985).
12. K.J. Snowdon, Proceedings DIET II. To appear in Springer Series Chem.Phys.
13. R.A. Haring, Thesis, University of Leiden (1984).
14. P.J. Schneider, W. Eckstein and H. Verbeek, Nucl. Instr. Meth. 218, 713 (1983).
15. For a review see Sputtering by Particle Bombardment, ed. R. Behrisch, Topics in Applied Physics 47, Springer Verlag, Berlin (1981)
16. M.W. Thompson, Phil. Mag. 18, 377-414 (1968).
17. K.J. Snowdon and R.A. Haring, Submitted to Nucl. Instr. Meth. B.
18. K.J. Snowdon, B. Willerding and W. Heiland, Proceedings V Int. Workshop on Inelastic Ion-Surface Collisions (1985). To appear in Nucl. Instr. Meth. B.