Bond Breaking and the Ionization of Sputtered Atoms

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(Received 5 May 1986)

We have studied the static-mode ion-beam sputtering of Si^+ from a Si (100) surface during oxidation and nitridation. The data are consistent with the ionization of sputtered atoms resulting from the breaking of the local chemical bond during sputtering. A model is proposed to explain the dependences of the ionization probability of the ionization potential, emission energy, and isotopic mass.

PACS numbers: 79.20.Nc, 34.50.Fa, 61.80.Jh

During the impact of energetic noble-gas ions on solid surfaces, atoms are sputtered off by the transfer of momentum. It has been observed that charge exchange between these atoms and the surface can simultaneously occur. The fraction of them emitted as positive ions from clean metallic surfaces is usually small ($< 10^{-3}$) This fraction can be enhanced by several orders of magnitude if the metal surface undergoes chemical reaction with electronegative species such as oxygen or nitrogen, either by adsorption or by reactive-ion bombardment.[1] In fact, oxygen ion beams are routinely being used for sputtering in secondary-mass spectrometry to enhance detection sensitivities. The positive-ionization probability P^+ of the different atoms sputtered from an oxidized multielement metallic target frequently follows a Boltzmann-type dependence on the ionization potential[2-4] I:

$$P^+ = (Z_+/Z_0)\exp[-(I-\Phi)/k_B T_p]. \quad (1)$$

Here k_B is the Boltzmann constant. T_p has the dimension of temperature and ranges from 5000 to 10000 K. Z_+ and Z_0 can be either partition functions or multiplicities of the lowest-lying group of states of the positive ion and the neutral atom, respectively.[3] Φ is a fitting parameter. The physical basis of Eq. (1) is still unclear. A local thermal equilibrium plasma of temperature T_p has been proposed to exist at the sputtering site.[2] But so far the existence of a plasma has not been experimentally verified.[4] P^+ also shows little correlation with the work-function change introduced by the oxygenation.[5] Hence the use of the electron-tunneling model[6,7] developed for a free-electron-like metal surface is not appropriate. However, within the framework of the model, one hopping-matrix element between the atomic state of the sputtered atom and a particular *localized* substrate electronic state can dominate the electron transfer as in the case of the strong local chemical bonding. This physical picture is frequently called bond breaking,[8,9] reflecting the fact that the chemical bond between the sputtered atom and the substrate atoms is broken. In this paper we present experimental evidence and theoretical arguments for a local bond-breaking model for the ionization process.

If the interaction is indeed very local, the secondary-ion yield I_M^+ of element M would be the sum of the contributions from different bonding configurations (i) involving M:

$$I_M^+ = \textstyle\sum_i f_i P_i^+ Y_i i_p, \quad (2)$$

where f_i, P_i^+, and Y_i are the concentration, ionization probability, and partial sputtering coefficient of the M atoms bonded in the ith configuration. i_p is the primary ion beam current. In the first approximation, all the P's and Y's are constants specific to the chemical configuration and are independent of the concentration. The averaged sputtering yield Y per unit i_p usually determined by erosion measurements is simply $\sum f_i Y_i$. Since the f_i's change with the chemical composition of the surface, both I_M^+ and Y have in general nonlinear dependences on the concentration of the electronegative species, and these relations are hard to predict. Hence the validity of Eq. (2) is not obvious.

We measured the Si^+ and Ge^+ yields from Si and Ge surfaces partially reacted with oxygen and nitrogen. The apparatus is similar to that reported in our previous work.[6] Briefly, the sputtering experiment was performed in an ultrahigh vacuum with a base pressure of about 1×10^{-10} Torr. *In situ* x-ray photoemission spectroscopy was used to monitor the reactant coverage and the chemical states (i.e., f_i) of the surface. The surface reactions were thermally induced and sputtering was kept in the low-damage static mode with 1 nA, 500 eV of Ar^+ primary beam to minimize radiation damage and ion-beam–induced chemistry. The sputtered secondary ions were detected with a quadrupole mass spectrometer in series with an 0.5-eV–resolution energy filter. The simplest system we have studied is the enhancement, by over 2 orders of magnitude, of the sputtered Si^+ yield by nitridation of the Si (100) surface at 1000 °C. X-ray photoemission spectroscopy showed that only Si_3N_4 was formed. Hence Eq. (2)

simplifies to

$$I_{\mathrm{Si}}^{+} = (f_0 P_0^+ Y_0 + f_1 P_1^+ Y_1)\, i_p, \tag{3}$$

where the subscripts 0 and 1 represent unreacted Si and $\mathrm{Si_3N_4}$, respectively. Since the Si^+ yield from a fully nitrided surface ($f_0 = 0$, $f_1 = 1$) is over a hundred times that from a clean Si surface ($f_0 = 1$, $f_1 = 0$), $P_0^+ Y_0 << P_1^+ Y_1$. Hence I_{Si}^+ should be linear with f_1, which is proportional to the nitrogen coverage. Indeed, the nitrogen-enhanced Si^+ yield was found to be proportional to the nitrogen coverage up to a monolayer (Fig. 1). Our data for the sputtering of Si^+ and Ge^+ from oxygenated Si(100) and Ge (111) surfaces, respectively,[10] are also consistent with Eq. (2).

We shall attempt to formulate a quantitative description of the local bond-breaking mechanism for ionization. Let us consider the sputtering of neutral atom M^0 and positive ion M^+ from the surface X. Charge exchange can happen at the crossing of the diabatic covalent potential curve $M^0 + X^0$ and the diabatic ionic potential curve $M^+ + X^-$ (Refs. 8 and 9) at distance R_c from the surface. The probability P^+ that M is ionized is given by the Landau-Zener formula[11] expressed in atomic units:

$$P^+ = \exp(-2\pi H_{12}^2 / v|a|)_{R=R_c}, \tag{4}$$

where H_{12} is the transition matrix element, v is the velocity, and $|a|$ is the difference in the first derivatives of the potential curves. All quantities are evaluated at R_c. The sputtering of M^+ from the surface creates a cation vacancy that traps the electron left behind. We shall postulate that this electron remains localized in the vacancy within the sputtering time ($\sim 10^{-13}$ s).

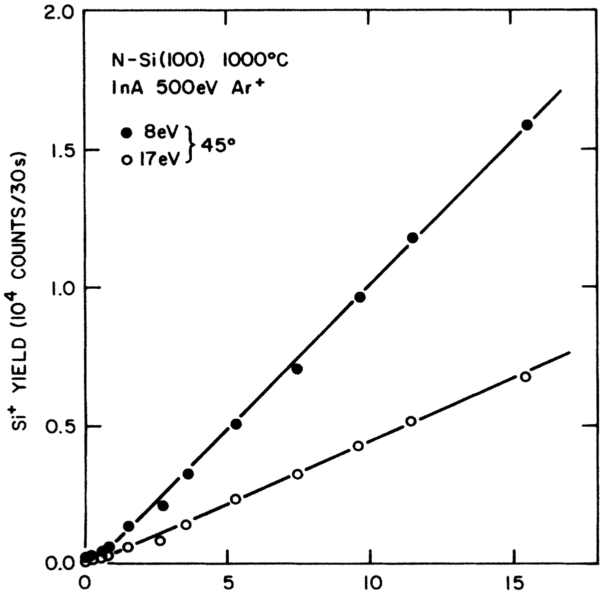

FIG. 1. The Si^+ secondary-ion yield as a function of nitrogen coverage at emission energies 8 and 17 eV. The maximum coverage was about $7 \times 10^{14}/\mathrm{cm}^2$.

Since the covalent force is very short ranged, we make the generally accepted assumption[12] that in the region of crossing the covalent curve (1) is independent of R, the distance of the sputtered atom from the surface, while the ionic curve (2) is given by the Coulombic attraction between M^+ and the electron left at the cation vacancy. At infinity the ionic curve lies above the covalent curve by $I - A$, where A is the electron affinity of the cation vacancy in the absence of M^+. Hence $R_c = (I - A)^{-1}$ and $|a| = R_c^{-2}$ in atomic units. For a sputtered ion of mass m and emission energy E_k, the velocity at R_c is given by

$$v(R_c) = [2(E_k + I - A)/m]^{1/2}. \tag{5}$$

Following Smirov,[13] H_{12} is given by

$$H_{12} = \tfrac{1}{8} R_c \Psi_1(\tfrac{1}{2} R_c) \Psi_2(\tfrac{1}{2} R_c), \tag{6}$$

where Ψ_1 and Ψ_2 are the normalized wave functions associated with the diabatic covalent and ionic potential curves. For Ψ_1, the electron is with M and since the outermost electrons for most metals are s electrons, we use the s wave function:

$$\Psi_1(r) = 2\alpha^{3/2} e^{-\alpha r}, \tag{7}$$

where $\alpha^2 = 2I$. Notice that both the shape and the amplitude of Ψ_1 depend on I. For Ψ_2, the electron is at the cation vacancy site. At present very little is known about the transient state of the vacancy during the sputtering event. Hence we assume that Ψ_2 has the same spatial dependence at R_c as the wave function for a negative ion in the field of M^+ which is at a distance R away[13]:

$$\Psi_2(r) = \left[\frac{R}{R-r}\right]^{1/\gamma} C \frac{(2\gamma)^{1/2}}{r} \exp\left[-\gamma r - \frac{r}{R\gamma}\right], \tag{8}$$

where $\gamma^2 = 2A$. α and γ explicitly relate the wave functions to I and A. We introduced C as a parameter for the amplitude to correct for the fact that Ψ_2 is for a solid-state cation vacancy. We also assume the electron affinity of oxygen (1.463 eV) for A in oxide systems. The total wave functions for curves (1) and (2) may have degeneracies g_0 and g_+, respectively. Simple statistical argument[14] shows that the right-hand side of Eq. (4) should be multiplied by a factor $G = g_+/g_0$, hence explaining the origin of Z_+/Z_0 in Eq. (1). In practice sputtered atoms and ions may have their low-lying excited states partially populated and a high-temperature partition-function ratio may be more appropriate.[3]

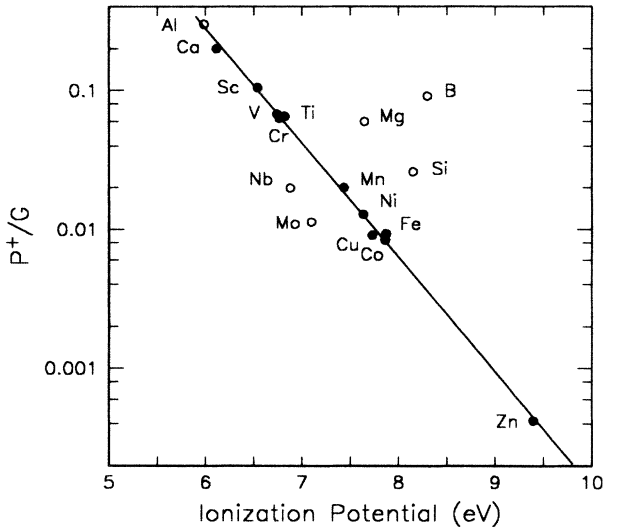

FIG. 2. Calculated P^+/G as a function of ionization potential for $C = 0.25$ and $A = 1.463$ eV. The best-fit line for the eleven fourth-period elements (filled circles) has $T_p = 6116$ K. Open circles are elements not in the fourth period.

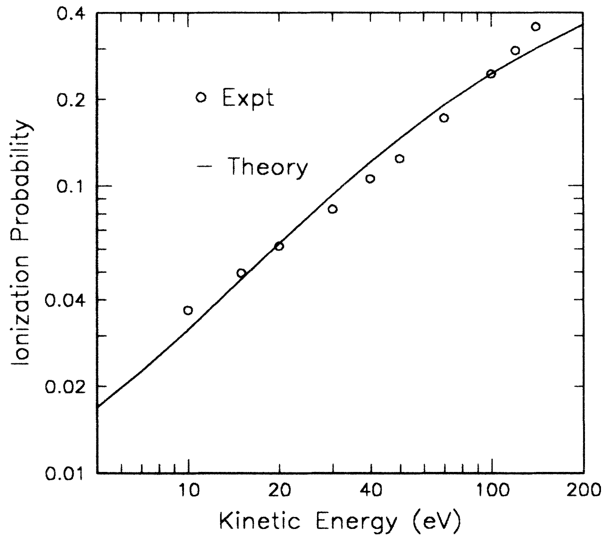

FIG. 3. Comparison between the experimental (Ref. 17) and theoretical values of P^+ for sputtered Be as a function of emission kinetic energy.

We calculated P^+/G for the twelve metallic elements (filled circles in Fig. 2) with $4s$ outermost electrons in the fourth period of the periodic table and with E_k equal to 10 eV. These elements have been studied most in relation to Eq. (1).[2-4] We found that the result follows the Boltzmann-type dependence on I [Eq. (1)] very well. We simulate the usual experimental situation that these elements are dilute components in a common metal matrix and the sample surface is uniformly oxidized. We shall assume the same values of C and A for the sputtering of all these elements. Again as a first approximation, A is taken to be the same as the electron affinity of oxygen (1.463 eV). C is adjusted to give the correct value for T_p. For $C = 0.25$ and $E_k = 10$ eV, the best-fit straight line (Fig. 2) gives 6116 K for T_p, in good agreement with observations.[2-4] P^+ of potassium is close to unity as expected from its low ionization potential. As I increases, the crossing point is closer to the origin. In general H_{12}^2 increases, causing P^+ to decrease. Since both Ψ_1 and R_c are functions of I, P^+ has a complicated dependence on the ionization probability. The apparent Boltzmann-type dependence of P^+ on I is only an approximate result for this small range of I, and has no thermal origin.

Our theory also predicts deviations from Eq. (1). We calculated P^+/G values for elements of other periods (Mg,Nb,Mo) and elements with non-s-like outermost electrons (B,Al,Si) assuming the same value for C. The results are shown by the open circles in Fig. 2. The lighter elements B, Si, Mg, with the exception of Al, have larger while the heavier elements Nb and Mo have smaller P^+/G values than the corresponding values for the fourth-period elements. These results are qualitatively consistent with the experimental data of Morgan and Werner[15] (B,Al,Nb,Mo) and Werner[4] (Mg) with the exception of Si.

The theory also predicts, through the factor $v(R_c)$ in Eq. (4), dependences of P^+ on E_k and the isotopic mass m. P^+ approximates a power-law dependence on E_k from about 1 to 200 eV. The exponent depends on m and increases with C. This E_k dependence has been observed in the sputtering of Ni^+ and Be^+ from oxidized Ni[16] and Be surfaces.[17] By choice of 0.276 for C of Be, our theory agrees reasonably well with the experimental Be^+ data (Fig. 3). At very low E_k, P^+ converges to a constant value corresponding to $v(R_c) = [2(I-A)/m]^{1/2}$. At very high E_k, P^+ approaches an exponential relation: $P^+ = G\exp(-v_0/v)$, where $v = (2E_k/m)^{1/2}$. The emission energy also affects the dependence of P^+ on I. For example, T_p in Fig. 2 rises to 10 800 K for ions with 50-eV emission energy, which is also in good qualitative agreement with observations.[15]

For a fixed E_k, Eqs. (4) and (5) predict a linear decrease of P^+ of an element with increase in the isotopic mass m. Lorin, Havette, and Slodzian[18] measured for Zr^+ sputtered from $\mathrm{ZrSiO_4}$ the deviation factor $D = R_{ij}^+/R_{ij}^0 - 1$ with $^{90}\mathrm{Zr}$ as the reference. R_{ij}^+ is the ratio of the secondary-ion intensities of the isotopes m_i and m_j, respectively, and R_{ij}^0 is the abundance ratio. The experimental value of −1.7%/u allows us to determine the values of C for this compound. If we assume A to be the same as that of oxygen (1.463 eV), C is

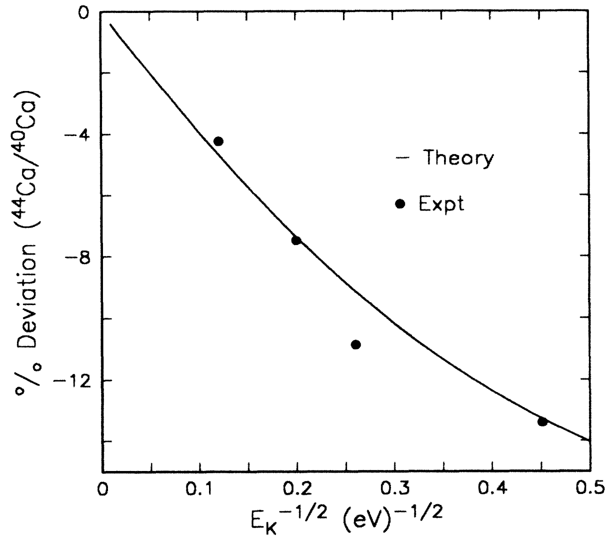

FIG. 4. Deviation from the isotope abundance ratio ^{44}Ca/^{40}Ca as a function of $(E_k)^{-1/2}$ for the sputtering of Ca$^+$ from calcium fluoride. The experimental values are taken from Ref. 18. The theoretical values are calculated for $C=1.1$ and $A=2.9$ eV.

about 0.23, again very similar to the values for Be and metals in the fourth period. Lorin, Havette, and Slodzian[18] also reported the dependence of D or E_k for ^{44}Ca$^+$ and ^{40}Ca$^+$ sputtered from CaF$_2$. Figure 4 shows that with $C=1.1$ and $A=2.9$ eV (electron affinity of F_2) for this compound, our calculated dependence of D on E_k fits the experimental data quite well.

The bond-breaking model in conjunction with the Landau-Zener formula gives a simple explanation of the dependences of the ionization probability on the ionization potential, emission energy, and isotopic mass.[19] The theory depends on the wave functions at the crossing point. The details of the chemical bond at the equilibrium position are reflected indirectly by the properties (C and A) of the cation vacancy created during the sputtering event. A complete quantitative theory of P^+ requires *ab initio* calculations of C and A for the cation vacancies, which are not available so far. C and A do not seem to vary much for the same class of compounds—for example, $C \simeq 0.25$ and $A \simeq 1.46$ eV for oxides—but they reflect changes in the chemical environment. For example, very different values of C and A are found for fluorides versus oxides.

We are delighted to acknowledge the useful conversations with Dr. J. Clabes, Dr. R. Kelly, Dr. N. Lang, Dr. W. Reuter, and Dr. G. Scilla. Our discussions with Professor P. Williams of Arizona State University and Dr. D. Simons of the National Bureau of Standards are particularly valuable.

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