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Abstract. The secondary-ion intensity of sputtered Si has been measured as a function of the emission energy using a previously calibrated mass analyser. From the Sigmund–Thompson energy distribution for neutrals, the ionization probability R^+ for Si$^+$ ions is inferred. It is found that the behaviour of R^+ at high emission energies is consistent with neutralization via the electron tunnelling mechanism (resonant electrons tunnelling from the substrate to the outgoing ions). The possibility of electronic excitations induced by the collision cascade in Sroubek's model is also considered.

1. Introduction

When solid surfaces are bombarded with ion beams, atoms and molecules are ejected from the surface in various charge states. In the case of a clean metal surface the fraction of particles escaping as singly charged positive ions is very small, commonly ranging from 10^{-5} to 10^{-3}. The formation and escape of secondary ions is probably the least understood aspect of the sputtering process. Measurements of the dependence of secondary-ion intensity on emission kinetic energy have indicated that the ionization probability (R^+) approximately follows an exponential dependence on the escape velocity [1–4], of the form

$$R^+ \propto \exp\left(-\frac{A}{v_\perp}\right) \tag{1}$$

where A is a constant that is dependent on the electronic environment of the ion and substrate and $v_\perp$ is the normal component of the ion emission velocity. The value of A is typically in the range 1×10^3–1×10^5 m s^{-1} [1–4].

On the basis of observations on the emission energy dependence, various models have been proposed to describe the ionization process and hence to provide quantitative expressions for the ionization probability. The exponential dependence of R^+ is most consistent with the electron tunnelling model. This model describes ionization, on an atomic level, as resulting from resonance-like transitions of electrons between atomic electronic levels of the escaping sputtered atom/ion and substrate continuum states [5–8]. All electronic excitations generated by the ion bombardment are assumed to dissipate rapidly so that the substrate electron temperature (T_e) is equal to zero. The theoretical treatment in this model assumes that the sputtered particle leaves the surface as an ion, and calculates the probability of neutralization by electrons from the substrate. Hence, the first ionization potential (I_p) plays a major role in positive ion emission. Owing to the screening by electrons in the

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metal conduction band, the positive ion leaving the sample surface has its atomic level ($\varepsilon(z)$) shifted by an image potential, that is inversely proportional to the ion–image distance (z), with respect to its value in free space (the maximum shift taking place at small distances, while for very large distances $\varepsilon(\infty) = I_p$). As the sputtered ion leaves the surface there exists the possibility that $\varepsilon(z)$ coincides with any of the occupied electronic energy levels (below the Fermi energy). This allows resonant electron tunnelling between the outgoing ion and the target surface to occur, which leads to neutralization of the outgoing ion. The ionization probability based on this mechanism can be calculated from first principles for certain $\varepsilon(z)$ dependences. [5] and [6] have obtained R^+ in the form

$$R^+ \propto \exp\left(-\pi \frac{C(I_p - \phi)}{\hbar \gamma v_\perp}\right) \tag{2}$$

which is consistent with the experimental result in (1). The constant C accounts for the variation of the respective atom/ion and substrate electronic levels as the atom/ion moves away from the surface, ϕ is the work function, γ is the decay length for the half width of the atomic level, typically of the order of 2 Å^{-1}, and $v_\perp$ is the normal component of the ion emission velocity.

In this study R^+ has been determined for Si atoms sputtered from Si(100) via measurements of the energy distributions of Si$^+$ ions. The results indicate a strong dependence of the ionization probability on emission velocity that is in agreement with (2), particularly over the higher-emission-energy range. Deviation from this dependence is observed at lower emission energy and a possible reason for this is discussed.

2. Experimental details

A schematic view of the set-up is presented in figure 1. The UHV chamber is pumped by a 240 l s^{-1} turbomolecular pump, giving a base pressure of 10^{-9} mbar with the help of a titanium sublimation pump and baking. Primary Ar$^+$ ions are produced from a VG EX05 ion source with raster scanning of the beam. During operation of the ion gun, the analysis chamber is maintained at 1×10^{-8} mbar pressure. The angle of incidence of the primary beam used in the experiment is 45° with respect to the sample surface normal. The primary ion energy and current density are fixed at 4 keV and 0.33 μA mm^{-2} respectively. A mirror-polished B-doped Si(100) wafer is used as the sample.

Secondary ions are extracted perpendicularly to the sample surface and mass analysed by the Hiden Analytical EQS300 mass spectrometer which includes a 45° electrostatic energy analyser (ESA) for ion energy analysis. The resolution of the ESA is ±0.8 eV. The target is kept at earth potential and the energy scanning is performed at constant pass energy in the ESA, so that all ions enter the mass analyser at the same energy.

The measured secondary-ion energy distributions, $N_m^+(E)$, are divided by the instrument transmission function, $T(E)$, to correct for the increasing degree of discrimination that the instrument imposes on secondary ions of greater emission energies. Details of the secondary-ion energy calibration are described elsewhere [9] and the transmission function for our instrument has been found to take the form

$$T(E) \propto E^{-\beta} \tag{3}$$

for ion energies E above 6 eV with $\beta = 1.50 \pm 0.01$. This has been determined experimentally by using the method proposed by Garrett *et al* [2], which involves measuring the K$^+$ secondary-ion energy distribution of a potassium adsorbate sputtered off a Cu target surface, and also independently confirmed by simulating the trajectories of secondary ions emitted from the target surface to the analyser with the help of the SIMION [10] software.
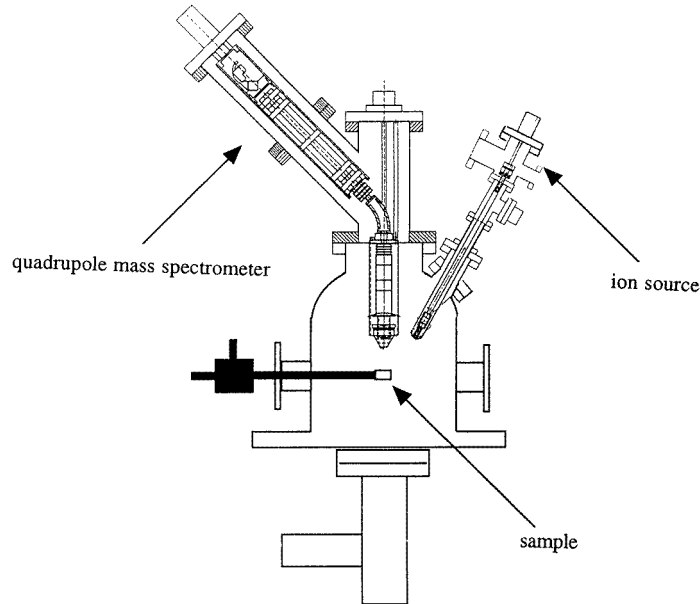
Figure 1. Schematic diagram of UHV–SIMS system.

3. Results

We have investigated the energy distribution of Si^+ from Si(100) under 4 keV Ar^+ bombardment at $45°$ incidence. The sample surface is first cleaned by prolonged Ar^+ bombardment before obtaining the energy spectrum, so as to remove adsorbed gases and other contaminants that might affect the secondary-ion yield. The uncorrected energy distribution of Si^+ ions is shown in figure 2 up to 25 eV. Above that, the spectrum contains too much noise to be useful. The most probable energy, E_m, occurs at about 4.5 eV, while the results of Wittmaack [11] show that $E_m \approx 5$ eV for Si bombarded with 4 keV Ar^+ at normal incidence.

The energy dependence of the ionization probability R^+ is simply determined by dividing the corrected ion energy distribution of Si^+, $N_c^+(E)$, by that of neutral Si, $N^0(E)$, i.e.

$$R^+(E) = \frac{N_c^+(E)}{N^0(E)} = \frac{N_m^+(E)}{N^0(E)T(E)}. \tag{4}$$

$N^0(E)$ is assumed to follow the well established Sigmund–Thompson relationship [12, 13]

$$N^0(E) \propto \cos\theta \frac{E}{(E+U)^3} \tag{5}$$

where θ is the angle of ejection with respect to the surface normal and U is the surface binding energy of the Si atom. This empirically derived relation has been shown to be capable of accurately predicting the secondary-neutral energy distributions for a number of elemental matrices such as Cu, Ag and Zr [14–16]. U is approximated in this study by the sublimation energy of silicon (4.67 eV).

Figure 3 also shows the behaviour of the experimentally derived R^+ as a function of $1/v_\perp$. The validity of the R^+ curves at low energies is limited because the transmission
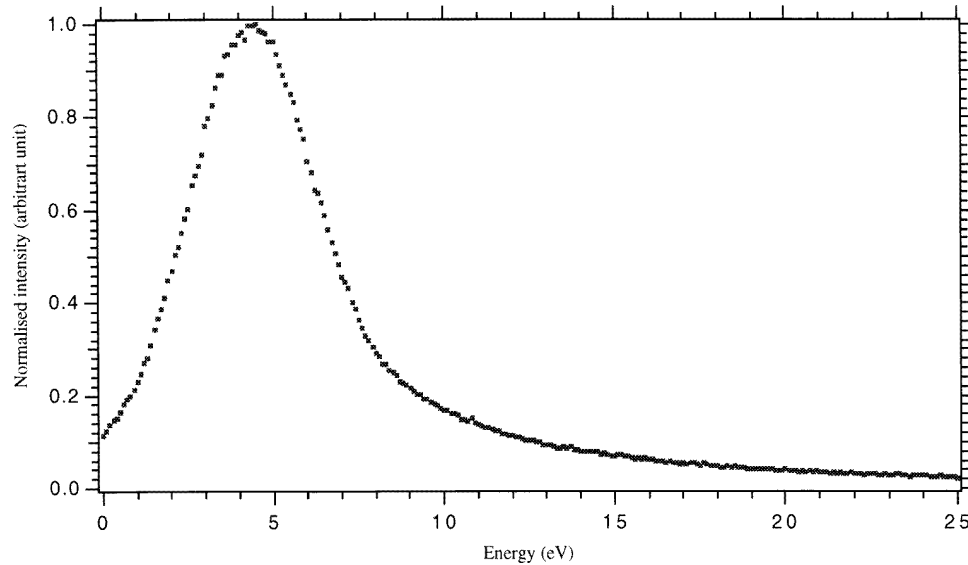
Figure 2. Uncorrected energy spectra of Si^+.

function of our analyser has been determined only for $E > 6$ eV [10]. In the region around 9 eV, a local minimum is observed. Similar results have been reported by Wucher and Oechsner [17] and were ascribed to the effect of the image charge potential energy which the sputtered ions must overcome before they finally reach the detector. The image force is a consequence of the attraction between the leaving ion and an equal induced charge of opposite sign in the metal, and acts to reduce the velocity of the leaving ion. Hence, there is a principal difference between the actual energy of the sputtered particle during ionization, i.e. close to the surface, and the experimentally obtained ion energy at a large distance from the surface. The effect of the correction leads to a shift in the observed secondary-ion energy spectrum relative to the neutral spectrum and is expected to be most prominent for the low-energy ions, but negligible for $E > 12$ eV [1].

4. Discussion

Fitting the data for R^+ to the electron tunnelling relations in (1) and (2), we obtain the full line in figure 3. R^+ is then seen to exhibit exponential behaviour for large velocities ($v > 1.1 \times 10^4$ m s^{-1} ≡ 19 eV) with $A = 2.1 \times 10^4$ m s^{-1}. The electron tunnelling process requires the $Si(I_p)$ level to lie in the energy region of the Si valence band where the density of electronic states is non-zero, to allow for electrons tunnelling from the target surface to the outgoing ions. Recent characterizations of the valence band structure of the clean Si(100) surface using XPS [18] have shown three peaks in the energy region of the $Si(I_p)$ level, corresponding to the $L_{3(I)}$, $X_{4(I)}$ and $W_2 + \Sigma_{1min}$ bands, which allows the possibility of electron tunnelling. A number of experimental results have shown that R^+ obeys the $\exp(-A/v)$ dependence in metals. Vasile [1] has found values of A ranging from 3 to 6×10^4 m s^{-1} for ions sputtered from Cr, Ag, Cu and Zr, while MacDonald and Garrett [19] report values in the range $(2.5-4) \times 10^4$ m s^{-1} for Fe^+, Ni^+ and Cr^+ from stainless steels.
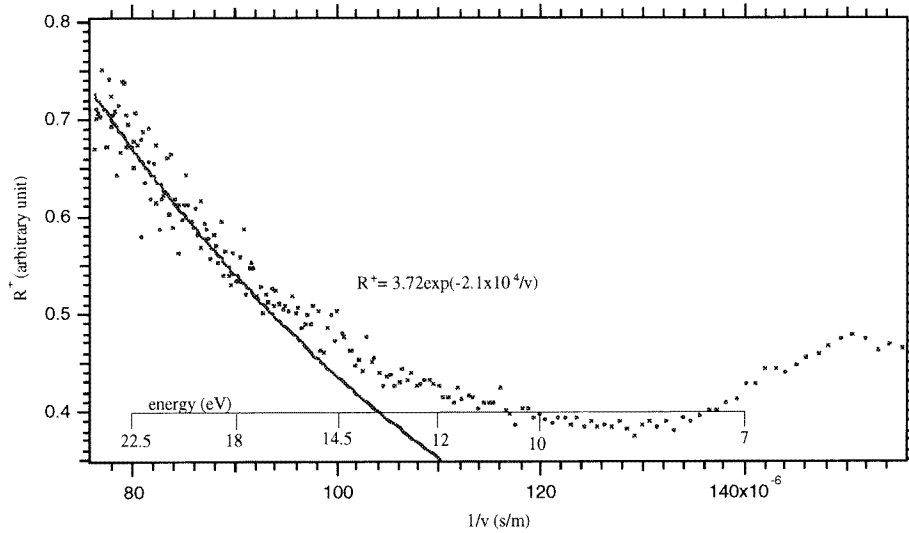
Figure 3. Ionization probability R^+ of Si atoms fitted according to (1).

Figure 3 shows a deviation of R^+ from the exponential dependence at lower velocities ($v < 1.1 \times 10^4$ m s^{-1} $\equiv$ 19 eV). The smaller velocity dependence observed is difficult to reconcile with (1) and (2) and cannot be fully explained by the image force correction to the measured energies, since the application of this correction on experimental results is only important for the low-energy particles (<8 eV) [1].

A possible explanation for this discrepancy could be that the electronic excitations induced in the semiconductor by bombarding particles may significantly influence the charge state of sputtered particles. Hence, the assumption $T_e = 0$ leading to (2) breaks down, making the model not applicable for lower emission energy. According to Sroubek [20], electronic excitations in real systems would only influence the charge state of sputtered atoms under conditions of high electronic temperature, i.e. $T_e \gg \hbar\gamma v/k$. By estimating the electronic energy density dissipated by the primary ions in the collision cascade and equating to the energy density of the excitations, he is able to obtain values of T_e. Such numerical results obviously depend on the choice of the thermal diffusion coefficient D. When D is taken to equal 1 cm^2 s^{-1}, the corresponding temperatures of T_e are around 1000 K for Cu, 2600 K for Si and 4400 K for GaAs. The key question is whether such high electronic temperatures can exist in the bombardment region. If so, the condition of $T_e \gg \hbar\gamma v/k$ in Si would be fulfilled for emission energies E well below 40 eV if we assume $\gamma = 2$ Å^{-1}.

By assuming that the electrons in the sputtering site are excited to a high electron temperature, Sroubek also formulated the semiphenomenological electronic excitation model of secondary-ion production [20–23]. He showed that the ionization probability can be approximately given by

$$R^+ \propto \exp\left(-\frac{2\Delta_0}{\hbar\gamma v_\perp}\right) + \exp\left(-\frac{\varepsilon(z^*) - \phi}{kT_e}\right) \tag{6}$$

where Δ_0 is the original width of $\varepsilon(z)$ and z^* is the distance from the surface where the positive ion is formed. As expected, the expression in (6) reduces to the functional form of (2) when $T_e = 0$. The first term decreases rapidly with decreasing $v_\perp$ and thus the

second term dominates at low $v_\perp$ when $T_e \neq 0$. By further assuming that $\varepsilon(z)$ has a linear dependence on z, the second term in (6) translates into a simple power law which has a weaker energy dependence. Rewriting (6) then gives

$$R^+ \propto \exp\left(-\frac{2\Delta_0}{\hbar\gamma v_\perp}\right) + \frac{Z^+}{Z^0}\left(-\frac{\hbar\gamma v_\perp}{2\Delta_0}\right)^n \propto \exp\left(-\frac{A}{v_\perp}\right) + C\left(\frac{v_\perp}{A}\right)^n \quad (7)$$

where

$$n = \frac{4\pi\varepsilon_0(I-\phi)^2}{kT_e e^2\gamma} \quad (8)$$

and Z^+, Z^0 are the partition functions of the ion and of the atom respectively.

We have attempted to fit R^+ over the range of 12–25 eV according to (7) using C and n as fitting parameters. The value of A is retained as 2.1×10^4 m s^{-1} since at large velocities expression (7) approaches an exponential dependence. The best fit to the experimental data (see figure 4) is obtained for $C = 6.3$ and $n = 1.47$. Thus by including electronic excitation effects, the fit to R^+ is improved from 19 eV down to 12 eV. Further deviation of R^+ from (7) below 12 eV can then be attributed to the image charge effect as explained above.
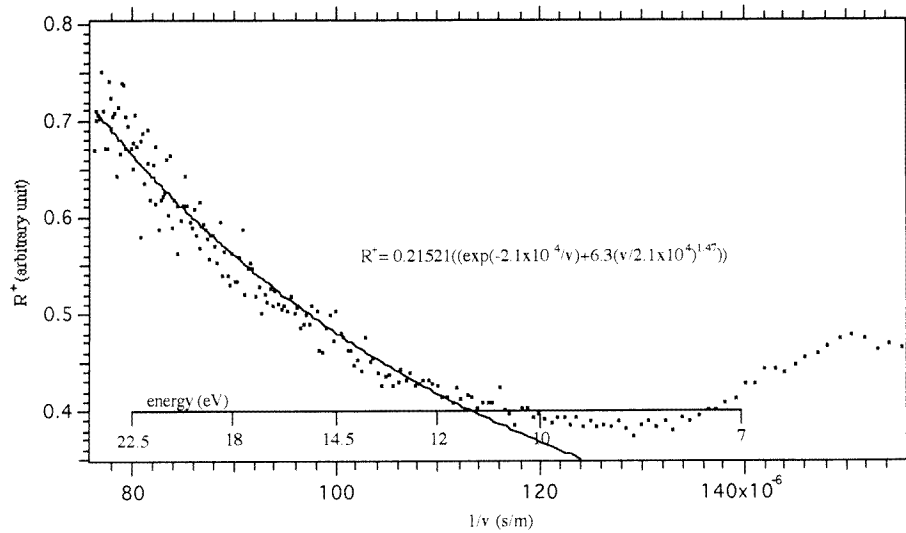
Figure 4. Ionization probability R^+ of Si atoms fitted according to (7).

Quite apart from improving the fit, the additional term due to electronic excitations also yields the electronic temperature T_e through the power factor n in expression (8). Using values for the ionization energy $I_p(\text{Si}) = 8.15$ eV, the work function $\phi(\text{Si}) = 4.91$ eV and $\gamma = 2$ Å^{-1} [5], we obtain $T_e = 2900$ K. This value of T_e is in good agreement with Sroubek's theoretical estimate which effectively means that the electronic excitation mechanism will have some influence at velocities much less than 2×10^4 m s$^{-1} \equiv 50$ eV, as seen from the condition $T_e \gg \hbar\gamma v/k$. This also agrees with the inclusion of electronic excitations to the fit for ion emission energies less than 19 eV.

It must be mentioned that the analysis of $R^+(E)$ is heavily dependent on the neutrals distribution $N^0(E)$ in expression (5) being correct. Although no direct measurement for Si has ever been made, early work by Zalm [24] on the sputtering yield under noble gas

ion bombardment seem to indicate that the sputtering process in Si conforms to the linear cascade theory. More recent angle resolved Si^+ emission by Pellet *et al* [25] also confirms the linear cascade behaviour to some degree. The linear cascade theory has been applied to several metals by Vasile [1] with a wide range of surface binding energies.

For the present set of data, the effect of the linear cascade expression on the ionization probability has been examined. Two other values for the power factor of the denominator in expression (5) have been used, namely 2.75 and 2.5. The procedure for fitting the spectrum is the same as before, i.e. by first fitting the high-energy part of the spectrum to expression (1) and obtaining the value of A in the exponential, and then fitting with expression (7) to obtain n. In both cases, the value of A obtained is 2.0×10^4 m s^{-1}, close to that obtained above. The lack of sensitivity in A to the neutral distribution has also been noted by Vasile [1]. However, the values of n obtained show quite a large variation. For the power factor of 2.75 the value of n is 1.16, giving $T_e = 3700$ K, while for the power factor of 2.5 the value of n is 0.73, giving $T_e = 5800$ K. Thus it appears that high temperatures persist in the electronic excitations and that Sroubek's estimate of 2600 K may be somewhat low.

5. Conclusion

In conclusion, the charge exchange process in Si^+ secondary-ion emission from Si(100) was found to exhibit a strong dependence on escape velocity, particularly over the high-emission-energy portion (>19 eV). Such a trend is consistent with the electron tunnelling model which is based on the electronic interaction of the sputtered ion with an undisturbed metal band structure ($T_e = 0$ K). At lower emission energies (<19 eV), the ionization probability for Si^+ exhibits a reduced velocity dependence. Agreement between experiment and theory can be improved if electronic excitations in the collision cascades are considered.

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