Symmetric versus asymmetric collisions in ion-induced Auger emission from silicon

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We investigate the production of Si 2p Auger electrons during bombardment of Si surfaces by 1.0–5.1 keV Ar+ ions. Yields of Auger electrons emitted at $\sim 146^\circ$ with respect to the ion beam are measured as a function of ion energy. We observe a threshold of $\sim 3.8$ keV for formation of a double L vacancy in Si, which is due to Ar–Si collisions. This value is higher than those of previous studies, which were presumably influenced by contamination of the Ar+ beam with multiply charged ions, as follows from our measurements of the variation of the Auger yields with the energy of the electrons in the ion source. We conclude that Auger emission in our energy range is dominated by symmetric collisions involving a fast Si recoil, with excitation in asymmetric, Ar–Si collisions growing in importance above the $\sim 3.8$ keV threshold. The conclusion is also supported by the appearance of additional, Doppler shifted, Auger peaks at high projectile energies. Our threshold value for Ar–Si collisions is in good agreement with previous studies of gas-phase collisions, and should be used to reevaluate recent computer simulations which fail to predict the observations.

1. Introduction

When keV ions bombard solid targets of light elements, they may produce holes in shallow inner-shell (core) levels of atoms [1]. These holes can decay by X-ray emission but more likely by ejecting Auger electrons, easily identified in the high-energy tail of the energy distribution of ejected electrons. Auger transitions normally involve two outer electrons, one filling the core hole and the other being ejected, though a small percentage of the decays can be expected to involve three or more electrons.

Inner-shell excitations result from violent binary atomic collisions between the projectile (p) and a target (t) atom (asymmetric or pt collisions) or between a fast recoil and another target atom (symmetric or tt collisions). Depending on the nature of the colliding pairs, the core excitations can occur in the projectile and in the target atom. Excitations in the adiabatic region, i.e. for impact velocities much lower than those of orbital electrons, are explained by describing the slow collision as a time evolution of electronic states of the quasimolecule formed transiently during the encounter [2]. Excitation occurs by compression of the electron clouds during the collision and promotion of some molecular states due to the Pauli principle. Electron promotion occurs in many cases over a very narrow range of internuclear distances, $R_c$, which causes excitation cross sections to have a sharp kinetic energy threshold, which is that required for the distance of closest approach to equal $R_c$.

The lifetimes of 2p holes in the light elements (Na to Si) [3] are shorter than or comparable to the lifetime of collision cascades in solids. Therefore the Auger decay subsequent to the excitation collision can occur in the bulk or in vacuum (for scattered projectiles or sputtered atoms). Auger spectra will be different in these cases, and reflect the different distribution of valence electrons at the location of the core hole. An important consequence of Auger decay of excited projectiles outside the solid is a relatively high ion/neutral ratio for projectiles traversing thin foils [4], and backscattering from solids [5,6]. On the other hand, Auger emission from sputtered target atoms can produce high ion yields in secondary ion mass spectrometry [7–9].

In the case of second-row elements, the Auger spectrum from L-shell holes in target atoms consists of a broad structure, and sharp (1 eV wide or narrower) peaks. The broad structure is readily associated with Auger transitions in the bulk, very similar to those induced by electron bombardment. In the case of LVV Auger emission from the decay of L-shell holes, the spectrum is in a first approximation the self-convolution of the density of states of the valence (V) band, weighted by transition probabilities which depend on the energy and symmetry of the state. Therefore the
width of the LVV spectrum is large, close to twice the width of the valence band, or 10–30 eV, depending on the type of solid.

The understanding of the origin of the sharp peaks has not been so straightforward, and has been surrounded by some controversy. The clarification came from the analysis of Doppler shifts and broadening of the peaks [10,11], and from the observation of energy shifts accompanying work function changes induced by alkali adsorption [12]. It is now generally accepted that these sharp peaks correspond to atomic transitions in core-excited sputtered target atoms decaying in vacuum.

A topic still subject of controversy is the relative role of nt versus tt collisions in core excitations at keV energies. Here the evidence is indirect, and comes from comparison between experiments and computer simulations, which have reached a high degree of development. The Monte Carlo simulations of Be K emission [13] showed an excellent agreement with the experimental energy dependence of the Auger yields. This provided firm grounds to determine the relative importance of nt and tt processes in X-ray emission yields, more accurately than possible using analytical theory. Recent simulations of L-shell excitations in bombardment of solid Al targets with Ar ions [14] conclude that tt collisions are largely responsible for Auger yields at very low energies. This is consistent with the observation that Auger yields from Al [15] and Si [16] compounds vary with the square of the concentration c of the light element which is excited. At higher energies, nt collisions are expected to be dominant, and the growth of the yields with c are seen to include a linear component.

However, and in contrast with these work, recent theoretical studies by Shapiro and Fine [17] have re-opened the question proposing that tt collisions are unimportant and that nt collisions are responsible for the Auger emission from Al near the excitation threshold.

To study the effect of oxidation on the Auger spectra we needed to produce stable oxidized silicon surfaces. This was achieved by replenishing the oxygen removed by sputtering with adsorption from an ambient of oxygen at 1.6 × 10⁻¹ Torr maintained during ion bombardment.

3. Results

Typical spectra are shown in figs. 2–4. The main features have been identified before: the broad structure corresponds to Si decaying in the bulk, whereas the sharp peaks correspond to transitions in sputtered 

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exp(-\(d/L \cos \theta_e\)), where \(L\) is the attenuation length and \(\theta_e\) the angle of emission with respect to the surface normal. For grazing observation conditions (\(\theta_e \approx 90^\circ\)) most of the bulk emission is eliminated and the spectrum is due mainly to Auger processes in sputtered atoms [19].

The Auger yields increase very sharply with energy, but the shape of the spectra is not affected much until the impact energy exceeds \(\sim 4\) keV. Then, as illustrated in fig. 3, a tail appears on the low energy side of the sharp atomic lines, the peak at \(\sim 90\) eV grows in relative importance and a peak due to double 2p excitation becomes visible at \(\sim 104\) eV.

Oxidation causes a dramatic change in the Auger spectra and on its dependence with angle, as shown in fig. 4 for spectra taken at a 2° take-off angle to the surface, for clean and oxidized surfaces. No atomic peaks appear over the broad LW feature when bombarding oxidized samples near normal incidence.

We measured relative Auger yields for different ion energies. To avoid problems of changes in the beam size with energy, we scanned the beam over an area of constant size and larger than the acceptance area of the electron spectrometer. The spectra were normalized to the ion beam current after suppressing secondary electrons. Since we suspected that previous yield measurements by other workers were influenced by the presence of multiply charged projectile ions we measured spectra with 50 eV bombarding electron energy in the ion source, a condition known to produce a negligible fraction of \(\text{Ar}^{2+}\) [20].

The yields were defined as the area of the peaks, after the subtraction of a background, divided by the incident beam charge used to record the data. The background was calculated by fitting a function of the form \(A + B/E^n\) to the high-energy side of the spectra, where \(A\), \(B\) and \(n\) are constants. In fig. 5 we present yields for the single L-shell Auger transitions (between 80 and 95 eV to minimize uncertainties in background subtraction). In fig. 6 we plot yields for the double L-shell Auger decay. A very different kinetic energy dependence is observed for the these two lines. We can estimate thresholds by extrapolating the measured data. These are \(\sim 1.0\) keV for single L-shell excitations and \(\sim 3.8\) keV for double L-shell excitations.

We also measured L'MM yields using 235 eV electrons in the ion source, which is a typical operating condition for this type of ion source. These yields are also shown in fig. 6. They suggest lower apparent thresholds as a result of contamination of the ion beam with \(\text{Ar}^{2+}\) of twice the energy, consistent with results
Fig. 5. Auger yields from single L-shell vacancies in Si. (a) Linear scale, and (b) logarithmic scale. The data were measured with the ion source operated in conditions to produce a negligible Ar$^{2+}$ contamination. Angle of incidence is 74° with respect to the surface normal.

by Valeri and Tonini [21] obtained with a conventional ion source.

4. Discussion

4.1. Analysis of threshold data

Fig. 6 demonstrated that low thresholds as obtained in previous experiments can result from contamination by doubly charged ions. With the values obtained in the absence of contamination by Ar$^{2+}$ we can now derive the distance of closest approach required for excitation, once we identify the collision partners: Ar–Si or Si–Si.

This identification can be done for the double core excitation, which occurs when the distance of closest approach $R_o$ in the collision is equal or smaller than $R_c$, the distance at which the promoted molecular orbital (MO) crosses empty MOs. The threshold occurs when $R_o = R_c$, and should be essentially the same for single

Fig. 6. Auger yields from double L-shell vacancies in Si as a function of $E$, the energy of bombarding Ar$^+$ ions. (a) Linear scale and (b) logarithmic scale. The energy of the electrons in the ion source is: • 50 eV and ○ 235 eV. In the latter case, the ion beam is contaminated by a significant fraction of Ar$^{2+}$ ions of energy $2E$. Angle of incidence is 39° with respect to the surface normal.
and for double excitation. In both asymmetric (Ar–Si) and symmetric (Si–Si) collisions, one or two Si 2p vacancies can be produced by electron promotion in the 4fo MO \[22\]. However, as pointed out previously \[23\], if two vacancies are produced in a symmetric collision, they will end up one in each collisions partner, rather than two vacancies in one atom. This is easily understood by noticing that the formation of a Si\(2p^\text{2}\) + Si final state is \(-23\) eV more metastable than that of a Si\(2p^\text{1}\) + Si\(2p^\text{1}\) final state \[24\].

Therefore, double I-shell excitation results from Ar–Si collisions, and the \(-3.8\) keV threshold energy is that required for the 4fo MO to cross empty MOs in the ArSi quasimolecule and end up with one or two 2p vacancies in the Si atom. Using the Molière interatomic potential, we obtain \(R_c = 0.358\) Å for Ar–Si excitation collisions, in excellent agreement with \(R_c = 0.344\) Å, the value calculated by Schneider et al. \[22\]. Based on the similarity of cross sections for Si–Ar collisions as compared to Ar–SiH collisions \[25\], we do not expect large solid state effects, though a slight increase in \(R_c\) can be expected due to enhanced screening in the solid.

These results then suggest that Auger emission below \(-3.8\) keV is essentially determined by symmetric Si–Si collisions initiated by fast Si recoils set in motion by the Ar projectiles. This conclusion, which is consistent with previous work in Al, disagrees with the simulations of Shapiro and Fine. The reason for this appears to be that these workers based the simulation on the assumption that the already artificially low threshold value obtained by Vrakking and Meyer \[26\] was due in part to asymmetric collisions.

Our interpretation also serves to explain the reason for the nonobservation of double excitations at normal incidence. The angular distribution of the doubly excited Si resulting from Ar–Si collisions lies in a cone near the incident direction. The aperture of the cone is determined by the deflection in a collision where the distance of closest approach equals \(R_c\). It increases with increasing Ar energy but is limited to 42° for 5.1 keV Ar (our maximum energy). Therefore, the primary excited Si recoils will move into the solid for incidence far from glancing. The small proportion which will be backscattered into vacuum will be further attenuated by Auger decay in the solid.

4.2. Double peaks

At our highest energies, additional atomic peaks or shoulders appear at the low-energy side of the atomic lines (e.g. 85 eV peak), as shown in fig. 3. We interpret the double peaks in terms of the Doppler shift of two distinct groups of excited Si. One, with low energies, leading to sharp peaks, present at all impact energies. This we assign to Si–Si collisions. The other group of excited Si have higher energies and produce a noticeable Doppler shift (to lower energies for our geometry). These faster Si recoils are assigned to Ar–Si collisions since they start to be noticed above \(-4\) keV.

The question that remains is, at what energy does the contribution of Ar–Si collisions to the total Si yield becomes comparable (or larger) to that from Si–Si collisions? Fig. 3 suggest a \(-15\)% contribution from pt collisions at 5 keV and 81.5° incidence. Our previous simulations for Al suggests a 20% contribution at around 9 keV, for 45° incidence. In fact, the very detailed measurements of Bonnano and co-workers at 10 keV \[27\] can be fitted with a model which includes only Ar–Si collisions, and which gives a fitted critical interatomic distance for excitation equal to 0.355 Å, in remarkable agreement with the findings of the present work. Thus, a consistent picture taking into account all previous experiments is one in which Si-L emission in Ar–Si collisions is dominated by symmetric Si–Si collisions involving fast recoils, below 3.8 keV incident energy. Above this threshold, direct excitation by the projectile grows in importance, possibly becoming dominant above 10 keV.

4.3. Emission from oxidized surfaces

By analogy with the work on silicides \[16\], it was expected that oxygen will lower the probability of Si–Si excitation collisions and that the Auger spectra would be dominated by Ar–Si collisions. We indeed observed a very strong reduction in Auger intensity upon oxidation (fig. 4). Furthermore, this also explains why we observe atomic peaks from sputtered Si only for ions incident obliquely. Although a recoil directed towards the interior of the sample can be backscattered and ejected outside the solid, the probability of doing so while retaining the core vacancy (without decaying in the bulk) will be low compared with a directly ejected recoil. This interpretation is also consistent with the absence of the sharper features attributed to recoils originating from Si–Si collisions.

5. Conclusions

Observations of electron spectral features, energy dependence of the yields and the effect of oxidation point to a consistent picture of ion induced Auger emission from Si. At low energies, from a threshold at \(-1.0\) to \(-3.8\) keV, excitation occurs only to single hole states, in collisions between a fast Si recoil and another Si atom. Above \(-3.8\) keV, direct excitation is possible in Ar–Si collisions which produces more energetic sputtered Si\(2p^\text{1}\) and also Si\(2p^\text{2}\) atoms. Oxidation suppresses most excitations from Si–Si collisions and produces drastic changes in the Auger spectra.
References

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[26] J.J. Vrakking and A. Kroes, Surf. Sci. 14 (1979) 153. The authors have acknowledged the presence of Ar 6+ contamination in their beam and their threshold energies are smaller than those for Al excitation obtained with charge/mass analysis of the primary beam and higher sensitivity (ref. [10]).

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