Low-energy Auger electron emission from titanium induced by ion bombardment

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Abstract. Measurements are reported of the low-energy electron emission spectrum from a solid titanium target bombarded with Ar and Kr ions with energies in the range 2 keV to 5 keV. The ion-induced electron spectrum shows considerable structure which is not present in electron-beam-excited spectra. The ion-induced spectrum is interpreted as arising from atoms sputtered free of the surface in excited states. However, comparison with the free-atom electron spectrum shows both similarities and significant differences. Possible excitation processes are discussed and tentative labels assigned to the observed peaks.

1. Introduction

Ion-excited Auger spectroscopy (IAES) has proved a fruitful technique for examining details of the excited states produced when the atoms of a solid target are struck by incoming ions, usually rare gas ions, with energies ranging from a few hundred eV to many keV. Comparison with electron- (or x-ray-) excited Auger spectra (EAES) often shows striking differences, with IAES spectra having a great deal of structure absent in EAES [1]. The differences in the spectra are explained in terms of the electron promotion model of Barat and Lichten [2]. In this model level crossing in a compound atom formed by the close proximity of incident/target or target/target atoms gives rise to electron emission from the decay of auto-ionizing states in neutral atoms sputtered into the vacuum.

Most work on IAES has been performed on targets with low Z, particularly the elements at the start of the third period, and little data have been published for elements in the fourth period. Viel *et al* [3] examined a range of elements using 60 keV argon ions to excite electron emission spectra and they reported low-energy peaks, presented in the derivative mode, for transition metals Ti to Ni which they identified as arising simply from $M_{23}M_{45}N_1$ processes in the solid. The peaks were without structure except that the derivative curve for Ti showed a small but sharp peak below the main peak. Xu *et al* [4] recorded similar spectra in the $N(E)$ mode using 14 keV Ar-ion excitation and they published low-energy spectra for Ca to V; they compared their data with electron-excited spectra and concluded that they were essentially similar at low energies although significantly different in the energy region immediately above the low-energy peak. Polak [5] showed that there were differences between the low-energy peaks recorded with IAES and EAES in the case of titanium and he reported a sharp peak present at 26.5 eV in the derivative ion-excited spectrum, which was not found in the electron-excited spectrum.

The presence of transitions in EAES from solids originating from auto-ionizing states has been identified by Bertel *et al* [6] and by Bader *et al* [7]. These give rise to electron

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emission at energies above the low-energy MVV transition. Zajac *et al* [8] have published a set of such data for Sc to Cu and in the case of titanium the auto-ionizing transitions give rise to a broad peak, centred at approximately 39 eV, about 13 eV above the main MVV peak. All reports of ion-excited Auger spectra [4,5,9] stress the absence of this peak. In contrast to the rather featureless Auger spectra reported for solid first transition metals, the vapour phase data [10] show considerable structure with groups of distinct peaks identified as arising from both ionized initial states (Auger peaks) and from transitions from neutral excited initial states (auto-ionizing states).

The present paper presents new data for the ion-excited Auger spectrum of titanium and shows, in contrast to previous reports, that the spectrum contains a great deal of structure. This structure can be explained as arising from transitions in free atoms by a process similar to that which gives rise to the well-documented spectra from Mg, Al and Si.

2. Experimental details

2.1. General methods

Spectra were recorded with a concentric hemispherical analyser with a retarding input lens, operated in the constant pass energy mode. Ions were produced by a Kratos Minibeam 1 ion gun. The angle between the ion beam and spectrometer input axis was fixed at 145°; the ion beam, the spectrometer input optic axis and surface normal lay in a horizontal plane and the specimen could be rotated about a vertical axis. The acceptance half angle of the spectrometer input lens was approximately 2°.

The titanium target was cut from a 0.1 mm thick foil of 99.99% purity. The specimen was cleaned by 2 keV argon-ion bombardment using EAES to monitor the surface composition. After prolonged bombardment the oxygen Auger signal disappeared and the initial large signal from amorphous carbon was also removed, although an extremely small carbon signal characteristic of a carbide persisted even after many hundreds of hours of bombardment. The cleaned titanium Auger signal showed the characteristic signal of metallic Ti [11]. Both Ar and Kr ions were used to excite spectra and the spectra obtained were essentially identical except that the signal from Kr excitation was more intense and therefore of better signal-to-noise ratio. The titanium signal was found to depend strongly on the incidence angle of the ion beam (and hence on the emergence angle into the spectrometer), and the most intense spectra were obtained with the ion beam incident at about 25° to the surface and the angle between the surface and the spectrometer axis at about 10°. No changes in the measured energies of the peaks were found with change of incidence angle. Measurements were performed in a UHV system with a base pressure of 3×10^{-10} mbar; during ion bombardment gas was admitted to a pressure of 2×10^{-6} mbar.

2.2. Calibration of the spectrometer

One major problem in electron spectroscopy arises in the energy calibration of the instrument. Seah *et al* [12] have proposed calibration methods designed to produce uniformity of energy scales but these methods are applicable at rather higher energies than those reported here. In principle, an excellent calibration standard exists in the strong ^1D peak of neon which Olsen and Andersen [13] measured as 23.55 eV using a calibration method which could be referred to optical data. While the Ne peaks can be readily detected when the titanium target is bombarded with neon ions, the peak energies are strongly Doppler shifted. The measured values of the ^1D peak were 26.96 eV, 26.46 eV and 25.87 eV using 5.0 keV, 4.0 keV and 3.0 keV primary beams. Unfortunately, the intensity of the Ne peaks

fell sharply at energies below 3 keV and it proved impossible to obtain an accurate estimate of the rest-frame energy. The method used to calibrate the spectrometer involved using an electron gun to record the spectrum of the elastic peak at 2 volt intervals using energies in the range 20 to 30 eV. The potential with respect to ground on either side of the filament was measured and the mean value taken as the accelerating potential. Examination of the elastic peak data showed that the spectrometer was linear in this range and that the FWHM of the peak was constant at 0.56 eV, suggesting a spectrometer half-width of around 0.4 eV. Unfortunately the mean filament potential cannot be assumed to give the electron-beam energy because of space charge and contact potential effects. The electrons produced by the gun have their zero of energy at the space charge potential minimum in front of the filament; this value was estimated by measuring the difference between the mean potential and measured beam energy as a function of beam current and extrapolating to zero current. This gave a value of 0.75 V as the depth of the space charge minimum at the operating current for the gun; this value has to be added to the mean accelerating potential. A further correction has to be made for differences between the contact potential of the tungsten filaments and the titanium specimen, however the work functions of both metals are very similar [14] and this difference should be small.

If the corrections are made to the values for the Ne peak quoted above the values become 27.45 eV, 26.95 eV and 26.36 eV, respectively. Measurement of the Doppler shift for Ne on Al [15] showed that, using the same geometry, the Doppler shift could be represented by the equation

$$E_M = E_A + K\sqrt{(E_I - E_L)}$$

Using the corrected measured values and solving for K, E_L and E_A the values obtained are: $K = 0.060$, the same as for Ne/Al as expected; $E_L = 900$ eV much higher than Ne/Al and consistent with the much higher threshold; $E_A = 23.62$ eV remarkably close to the calibration value of 23.55 eV. While this close agreement may be fortuitous, it does suggest that the calibration method chosen is sensible.

3. Results and discussion

3.1. The electron-excited Auger spectrum

Figure 1 shows the low-energy Auger spectrum excited with a 500 eV electron beam. A smooth background has been subtracted since the $M_{23}VV$ structure appears on the side of a steeply ascending secondary electron background. The shape of the low-energy side of the $M_{23}VV$ feature depends on the background used, so too much credence should not be placed on details of the intensity distribution. However, the derivative of the $M_{23}VV$ peak agrees closely with that of Bertel *et al* [6]. The electron-excited auto-ionizing spectrum is seen at higher energy and this is similar to the data of Zajac *et al* [8] with a broad structureless peak extending from about 33 eV to 43.5 eV with a maximum around 38 eV. This peak has been identified [6, 7] as arising from excitations to auto-ionizing states in the neutral atom, followed by de-excitation and electron emission. The process in Ti is

$$3p^6 3d^2 4s^2 \rightarrow 3p^5 3d^3 4s^2 \rightarrow 3p^6 3d^1 4s^2 + e.$$
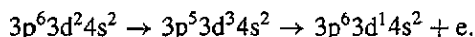
Processes of this type have been measured in free atoms by Meyer *et al* [10] and the vapour phase data differs significantly from that for the solid. The auto-ionizing part of the spectra for Ti vapour occurs at lower energy (26 eV to 34 eV) and consists of a number of sharp, well resolved peaks. Thus the spectrum in the solid has been shifted by 7 or 8 eV and has

broadened sufficiently to remove all structure. Screening effects in the solid lower the final state energy 9.9 eV by around 5 eV (compare the 3d binding energy in the Ti atom to the peak in the conduction band binding energy). Furthermore the lifetime of the auto-ionizing state is much shorter in the solid since all the 3p–3d excited states in the metal lie above the 3p ionization threshold, and so quasi-atomic multiplets are unresolved.
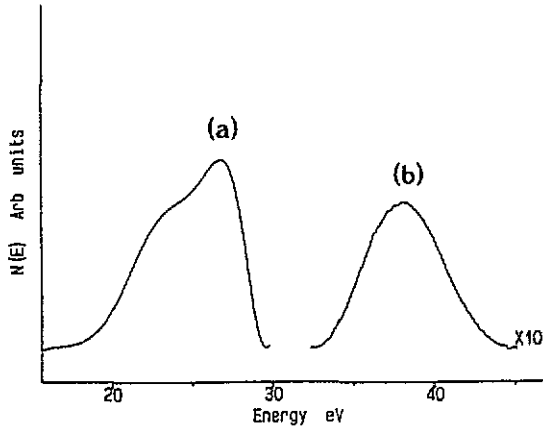

Figure 1. The low-energy Auger spectrum of clean Ti excited with an electron beam of energy 500 eV, a smooth background has been subtracted. (a) The MVV Auger spectrum (b) the auto-ionizing spectrum.

3.2. The ion-excited Auger spectrum

The spectrum excited by 3 keV krypton ions is shown in figure 2. The energy range is similar to that for figure 1. Very clear differences may be seen, the broad $M_{23}VV$ transition has been replaced by much narrower structure and the auto-ionizing structure is completely absent. The absence of the higher-energy auto-ionizing peak in the case of ion excitation is in agreement with previous observations [4, 5, 9] but the sharp features in the 20–27 eV range indicate emission which is mainly atomic in origin. At lower energies peaks due to processes in Kr and Ar were present; these features were very similar to those previously reported [16] with Al and Si targets, although their intensity was somewhat reduced.

Figure 3 shows the low-energy portion of the curve after subtraction of a smooth background. Five peaks can be clearly seen and a sixth peak, C, is measurable after peak stripping. The energies of the peaks are shown in table 1. The uncertainties quoted are standard deviations of 21 measurements obtained with both Kr and Ar excitation using primary beam energies from 2 to 5 keV. No systematic variation with ion-beam energy was observed and no Doppler shift was present. Apart from higher intensity in the case of Kr ions the spectra were independent of the means of excitation which suggests that excitation depended on target–target interaction. The vapour phase Auger emission peaks observed by Meyer *et al* [10] are also shown in table 1. The two most intense peaks, E in our data and peak 9 in the data of Meyer *et al*, have been aligned in this table. The initial and final state labels of Meyer *et al* are also shown. It may be seen that there is quite close agreement between the peaks we report from the solid and the vapour phase data apart from a systematic shift in energy with our values lying about 1.4 eV higher. The peaks in our data appear somewhat broader, as may be seen by the much reduced valley between peaks
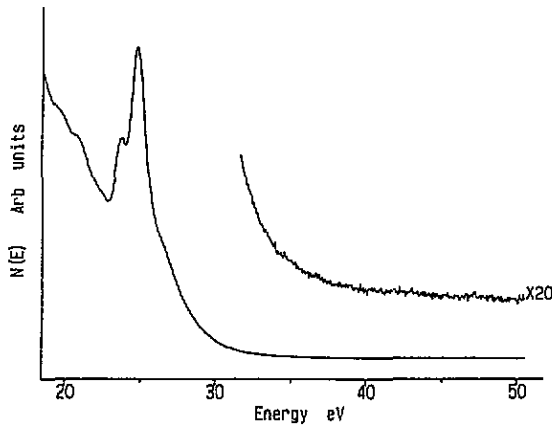
Figure 2. The low-energy electron spectrum of clean Ti excited with a 3 keV beam of krypton ions.
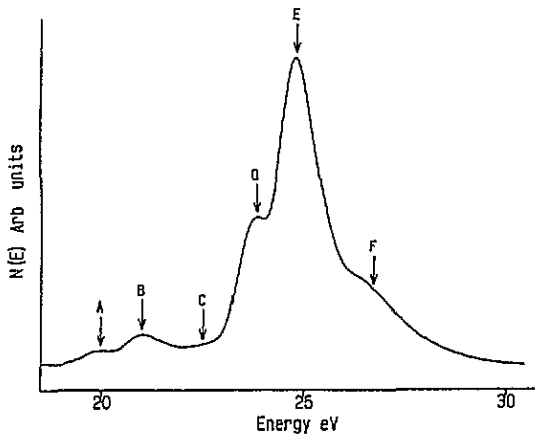

Figure 3. The electron spectrum of clean Ti excited with a 3 keV beam of krypton ions after subtraction of a smooth background.

D and E compared with the spectrum of Meyer *et al*. The estimated FWHM for the most intense peak E is 1.4 eV which compares with a spectrometer half-width of 0.4 eV.

The difference in energy of ~ 1.4 eV seems too large for a calibration error, although this cannot be completely eliminated. One possible explanation for the higher values reported here could be that the excited species decay close to the surface of the titanium and the induced image charges will reduce the final state energy. This could also explain the broadening we observe since atoms emitting at different heights above the surface will experience different final state screening. The sharp spectral features of figure 3 confirm that the electron emission is distinctly different from the electron excited metal spectrum in figure 1.

The $M_{23}N_1N_1$ interpretation of the features in table 1 assumes the complete absence of autoionization peaks in the ion-excited emission from Ti in sharp contrast to Mg, Al and Si [17] where the highest and most intense feature (and some others) are associated with emission from an excited atom which had left the surface with the core hole neutralized by a 'screening' valence electron. It would be very surprising if such an autoionization

Table 1. Measured values of the peaks shown in figure 3 compared with the $M_{23}N_1N_1$ spectral data of Meyer *et al* [10] for titanium vapour.

Peak label This work	A	B	C	D	E	F
Energy (eV)	19.8	20.9	21.9	23.6	24.8	26.8
±	0.1	0.1	0.2	0.1	0.1	0.2

Peak label Meyer *et al*	2,3	4	5,6	7,8	9	10
Energy (eV)	18.1	19.2	19.8	22.1	23.5	24.5
	18.7		20.9	22.6		

Line	Initial state	Final state [10]
2	$3p^5 3d^2 4s^2 (^3F)\,^4G,\,(^3P)\,^4P$	$3p^6 3s^2\,^3P$
3	$3p^5 3d^2 4s^2 (^3F)\,^4D$	$3p^6 3d^2\,^3F$
4	$3p^5 3d^2 4s^2 (^3F)\,^4G$	$3p^6 3d^2\,^3F$
5	$3p^5 3d^2 4s^2 (^3F)\,^4F$	$3p^6 3d^2\,^3F$
6	$3p^5 3d^2 4s^2 (^3F)\,^2G$	$3p^6 3d^2\,^3P$
7	$3p^5 3d^2 4s^2 (^3P)\,^2D$	$3p^6 3d^2\,^3P$
8	$3p^5 3d^2 4s^2 (^3P)\,^4D$	$3p^6 3d^2\,^3F$
9	$3p^5 3d^2 4s^2 (^3P)\,^2D$	$3p^6 3d^2\,^3F$
10		

path were not present in the case of Ti. Yet there is no observed emission around 29 and 31 eV where the most prominent autoionization emission is observed in the electron-excited spectrum of Ti vapour. These features are consistent with dipolar excitation to the $3p^5\,3d^3\,4s^2\,^3G$ and ^3F (the most intense features observed in x-ray absorption spectrum) followed by decay to $3p^6 3d^1 4s^2\,^2D$. Why are such processes absent in the ion-excited spectrum? The basic difference between the case of Ti and the second row elements Mg, Al and Si is the presence here of strong Coulomb and exchange coupling between the core hole and the excited electron. Dirac–Fock calculations [18] of the $3p^5 3d^3 4s^2$ configuration reveal a wide range of multiplets between 30 and 52 eV with many lying below the ^3G and ^3F states emphasized in dipole excitation. Figure 4 shows the states with excitation energies in the range 30–38 eV; given that the $3p^6 3d^1 4s^2$ final state is 9.9 eV above the ground state these multiplets could decay with auto-ionizing emission between 20 and 28 eV. In the ion-excited spectra we are not dealing with a dipole excitation followed by auto-ionizing decay. As noted by Xu *et al* [4], 3p ionization will occur in metal–metal collisions through excitation into $5f\sigma$ molecular orbitals with no possibility of direct transfer into a 3d excited state. When the atom leaves the surface in a neutral $3p^5 3d^3 4s^2$ configuration the screening electron will have been incorporated into one of the lower $3p^5 3d^3$ multiplets well below the 3p ionization thresholds. The highest energy auto-ionizing state possible for screening to be possible will have energy

$$E_{AUTO} = I - \phi$$

where I is the ionization energy and ϕ is the work function (around 4.5 eV); in Ti I has no unique value but the $3p^5 3d^2 4s^2$ multiplets imply an ionization range between 39 and 44 eV (see Meyer *et al* [10]). This gives a maximum possible $3p^5 3d^3 4s^2$ neutral state level of 39.5 eV (auto-ionizing energy $\sim$ 29.5 eV) with greater emphasis on states below that energy.

The large electron–hole coupling accompanied by the preference for low-lying multiplets not related to the initial state by dipole selection rules, would then lead to a wholly different autoionization spectrum from that produced by electron excitation. Figure 4 outlines some
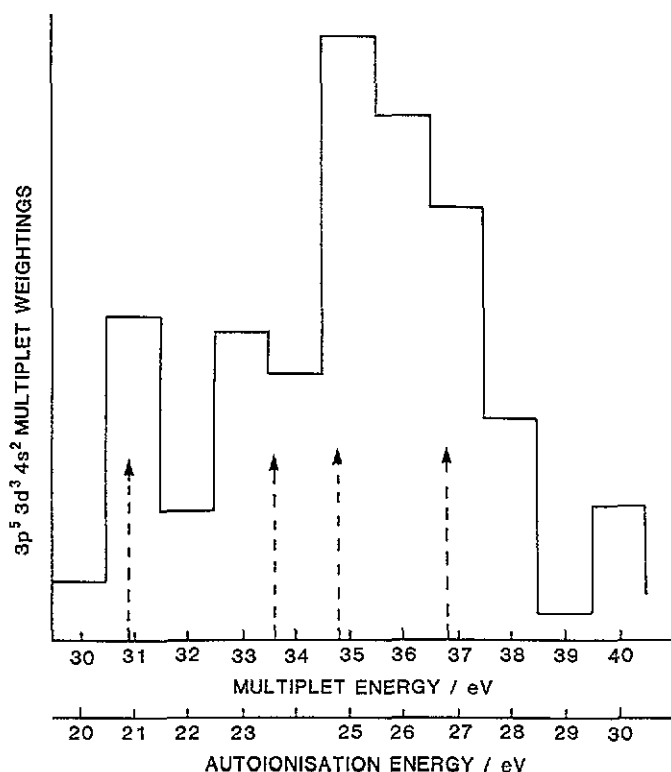
Figure 4. The energy distribution of $3p^5 3d^2 4s^2$ multiplets of Ti with $2J + 1$ statistical weighting for energies below the ionization limit. Corresponding auto-ionization energies are indicated with arrows showing the more prominent ion-excited emission features.

possible transitions from multiplets below the ionization threshold calculated with the Dirac–Fock programme of Grant [18]. The calculations correctly reproduce the main dipole allowed ^3G, ^3F and ^3D transitions within 1 eV, so should give a reasonably reliable guide: the histogram represents the number of available multiplets weighted by $2J + 1$ in various energy ranges. This is compared with the energies of the main emission features. On this interpretation any emission well below 20 eV would be due to Auger emission but the observed peaks could well be associated with auto-ionization, and the rapid fall off of intensity above 27 eV is consistent with such an interpretation.

The electron excited spectrum of Meyer *et al* [10] is remarkable for the dominance of the $M_{23}N_1N_1$ channel over the Coster–Kronig $M_{23}M_{45}N_1$ transition in Ti, in contrast to the case of Sc and Cr. This suggests that the Coster–Kronig transition rate of Yin *et al* [19] is too high, and that the lifetime of 3p hole states in Ti is larger than their result would suggest. It is probably for this reason that excited/ionized Ti atoms have time to emerge from the surface before decaying in the vapour phase.

4. Conclusions

The ion-excited Auger spectrum of Ti has a shape which is considerably different from that of the electron-excited spectrum. The IAES contains detailed structure which is consistent with electron emission occurring in a free atom, although possibly from an atom still close

to the surface. No systematic variation in either peak energy or peak width with incident ion energy was observed for the range of ion energies, 2 keV to 5 keV, used in these measurements and it is concluded that emission occurs in excited atoms sputtered from the surface with low kinetic energy. The electron spectra were essentially the same for Ar and Kr incident ions and it is likely that excitation occurs through target–target atom interaction rather than projectile–target interaction.

Overall it is not possible to make an unambiguous interpretation of the ion-excited Ti electron emission spectrum. The observed emission is clearly different from both the electron-excited solid and electron-excited vapour spectra. Compared to the former the emission is sharper, at distinctly different energies and contains more structure. Compared to the latter there is no counterpart of emission following dipole-excited 3p → 3d excitation. The observed emission falls in the energy range of $M_{23}N_1N_1$ Auger emission but there are significant energy discrepancies. An alternative interpretation is of auto-ionizing emission from $3p^5 3d^3 4s^2$ multiplets not normally emphasized in photon or electron excitation. Experiments on adjacent transition metal systems may resolve the controversy, but, if the autoionization mechanism suggested here were to be confirmed, it would give new insights into ion excitation/ionization mechanisms in solids.

Acknowledgments

References

[1]   Valeri S 1993 *Surf. Sci. Rep.* **17** 85
[2]   Barat M and Lichten W 1972 *Phys. Rev.* A **6** 211
[3]   Viel L, Benezath C and Benezath N 1974 *Surf. Sci.* **54** 635
[4]   Xu F, Riccardi P, Oliva A and Bonanno A 1993 *Nucl. Instrum. Methods* B **78** 251
[5]   Polak J 1995 *J. Phys.: Condens. Matter* **7** 5275
[6]   Bertel E, Stockbauer R and Madey T E 1983 *Phys. Rev.* B **27** 1939
[7]   Bader S D, Zajac G and Zak J 1983 *Phys. Rev. Lett.* **50** 1211
[8]   Zajac G, Bader S D, Arko A J and Zak J 1984 *Phys. Rev.* B **29** 5491
[9]   Valeri S and Verucchi R 1992 *Phys. Scr.* T **41** 246
[10] Meyer M, Prescher Th, von Raven E, Richter M, Schmidt E, Sonntag B and Wetzel H-E 1986 *Z. Phys.* D **2** 347
[11] Bassett P J and Gallon T E 1973 *J. Electron Spectrosc.* **2** 101
[12] Seah M P, Smith G C and Anthony M T 1990 *Surf. Interface Anal.* **15** 293
[13] Olsen J O and Andersen N J 1977 *J. Phys. B: At. Mol. Phys.* **10** 101
[14] 1981 Data in *AIP Physics Vade Mecum* (New York: AIP)
[15] Gallon T E and Nixon A P 1992 *J. Phys.: Condens. Matter* **4** 9761
[16] Nixon A P, Gallon T E, Yousif F and Matthew J A D 1994 *J. Phys.: Condens. Matter* **6** 2681
[17] Whaley R and Thomas E W 1984 *J. Appl. Phys.* **56** 1505
[18] Grant I P 1972 *Comput. Phys. Commun.* **9** 377
[19] Yin L I, Adler I, Tsang T, Chen M H, Ringers D A and Craseman B 1974 *Phys. Rev.* A **9** 1070