

Ion-excited low-energy Auger electron emission from Ti and TiNi

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 5275

(<http://iopscience.iop.org/0953-8984/7/27/012>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 21:37

Please note that [terms and conditions apply](#).

Ion-excited low-energy Auger electron emission from Ti and TiNi

M Polak

Department of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva
84105, Israel

Received 1 November 1994, in final form 4 April 1995

Abstract. Two distinct Auger transition features appear in the spectrum of electrons emitted from titanium surfaces by kiloelectronvolt argon ion bombardment. The main feature, corresponding to the electron-excited $M_{23}VV$ transition and originating with Ti–Ti collisions inside the solid, is accompanied by a very narrow atomic-like line at a slightly lower energy attributed to electron emission from Ti atoms sputter ejected from the surface. Ion bombardment does not stimulate any spectral feature corresponding to the characteristic electron-excited Ti autoionization emission, $3p^53d^23d^* \rightarrow 3p^63d$, which is severely attenuated upon simultaneous ion and electron excitations. The Ar^+ -excited emission from the Ti target is compared to that measured for the intermetallic compound TiNi.

Ion-excited Auger electron emission (IAE, IAES) has been studied extensively both experimentally and theoretically [1], often in comparison to the corresponding electron-excited Auger spectrum (AES). In addition to interest in basic physical aspects of IAE, knowledge of possible ion-induced spectral contributions to AES can be essential when simultaneous inert ion sputtering is used for composition depth profiling. Furthermore, it has been claimed that ion-excited electron spectra can help in interpretation of SIMS depth profiles [2], and recently a highly surface-sensitive version of IAES based on impact of a specularly reflected proton beam has been proposed [3]. Most of the IAES studies using moderate ion energies have been concentrated up to date on magnesium, aluminum and silicon surfaces [4–6], for which collision-induced creation of a 2p vacancy constitutes the initial step in the Auger process. According to a current description, electron promotion occurs under certain conditions via molecular orbital curve crossing, which depends on the internuclear distance of the colliding partners [7]. Often, in addition to a broad bandlike component, somewhat similar to the electron-excited spectrum, sharp atomic-like lines appear in the ion-excited spectra. A common interpretation for these spectral features is that they are due to decays of excited atoms in the collision cascade in the matrix and of excited sputtered atoms leaving the surface, respectively. In the latter case, the specific location of the emitting atoms with respect to the target surface has been somewhat controversial [8]. The complex excitation and de-excitation mechanisms involved in IAES have been investigated in detail, especially in relation to the above light-metal targets [6]. In comparison, perhaps with the exception of chromium, IAES from titanium and other transition metals has been studied less extensively [9–11]. This paper reports a detailed study of the Ar^+/Ti low-energy electron emission as function of ion energy with emphasis on atomic-like features, and a comparison to IAE of the intermetallic compound TiNi, for which a different collision cascade environment can be expected. In addition, the study explored the possibility of ion-excited autoionization

emission from these targets (which is quite strong in the electron-excited spectrum [12, 13]), as well as ion bombardment effects on the electron-excited autoionization emission of Ti.

In the experiments, polycrystalline specimens of pure Ti and $\text{Ti}_{49}\text{Ni}_{51}$ (atomic percent, determined by EDX) containing negligible amounts of foreign phases have been used. Argon-induced spectra in the derivative mode were measured usually under $\sim 6.5 \times 10^{-5}$ Torr Ar pressure in the test chamber (ion beam current, $\sim 2 \mu\text{A}$; diameter, ~ 1 mm) using a PHI 545 SAM spectrometer with a single-pass CMA and a lock-in amplifier. The usual mode of CMA, collecting a wide range of electron take-off angles (angle-integrated spectroscopy), and an $\sim 70^\circ$ ion beam incident angle, have been used. In order to resolve all spectral features, quite a low modulation amplitude (1 V) had to be used. This is demonstrated for pure Ti in figure 1, which shows also the corresponding, well studied electron-excited Ti Auger spectrum. In addition to a broad peak (II) at 28.7 eV (measured at the minimum of the differentiated spectrum), which is similar in energy to the main $M_{2,3}VV$ electron-excited feature, a very narrow component (I) appears at 26.5 eV, with measured width (~ 1 eV) probably limited by the modulation amplitude used. By analogy to assignments made for other elements, this atomic-like line can be attributed to emission from Ti atoms sputter ejected from the surface layer. Since a feature due to the interatomic Ti-O Auger cross transition, $\text{Ti}(M_{2,3}V)\text{TiO}(V)$ [13, 14], appears at only slightly lower energy in the electron-excited spectrum (figure 1, curve c), a similar mechanism involving sputtered TiO clusters, such as those observed in secondary-ion spectra of Ti [15], had to be considered as well. However, this possibility can be ruled out on the basis of further IAES measurements performed for a Ti sample contaminated with various low levels of O. In particular, no correlation between the intensity of the narrow feature (I) and the AES O(KLL) intensity could be noted, indicating that this feature is characteristic of pure Ti. The appreciably wider $M_{23}VV$ -related emission (II) can be assigned (for the low incident energies used) to collisions between Ti atoms inside the matrix of the near-surface region. In both Cr and Ti, within the framework of molecular orbital correlation diagrams [7], target-target symmetric collisions lead to interactions of the $5f\sigma$ molecular orbital (originated from the atomic orbital $3p$) with higher-energy orbitals. Below a certain critical internuclear distance, this results in inner-shell ionization, which initiates these MVV Auger emissions.

Turning the discussion to the broad feature centred around ~ 47 eV in the electron-excited differentiated spectrum of Ti (III, figure 1, curve c), this definitely has no corresponding feature in the ion-excited spectrum. This feature has been previously attributed to autoionization electron emission from a neutral state to a singly ionized final state [12], $3p^5 3d^2 3d^* \rightarrow 3p^6 3d$, that is, direct recombination and emission processes that follow electron excitation from $3p$ to unoccupied states, $3d^*$. In addition to the absence of autoionization emission from the Ti IAE spectrum, simultaneous electron excitation and ion bombardment result in strong attenuation of this emission (figure 1, curve d). This non-additive spectral effect, first reported by us for the case of Ar^+/TiNi [16], becomes stronger with increasing ion beam energy and current. Similar trends regarding autoionization emission have been recently reported for Ar-bombarded Cr [11, 17], and since in an EELS experiment the M_{23} absorption in the Cr loss spectra remained unchanged it was concluded that the basic $3p \rightarrow 3d^*$ excitation mechanism is unaffected by ion bombardment. Hence, in accordance with earlier suggestions for TiNi [16], the effects seem to be due to alternative electron de-excitation processes, which become operative in the presence of incident ions and reduce the probability for the competing direct recombination process. In particular, both phenomena, the autoionization attenuation and the absence of this emission in Ti IAES, are probably related to substantial modifications in the valence electronic states of the target collision cascade environment as compared to the unperturbed solid.

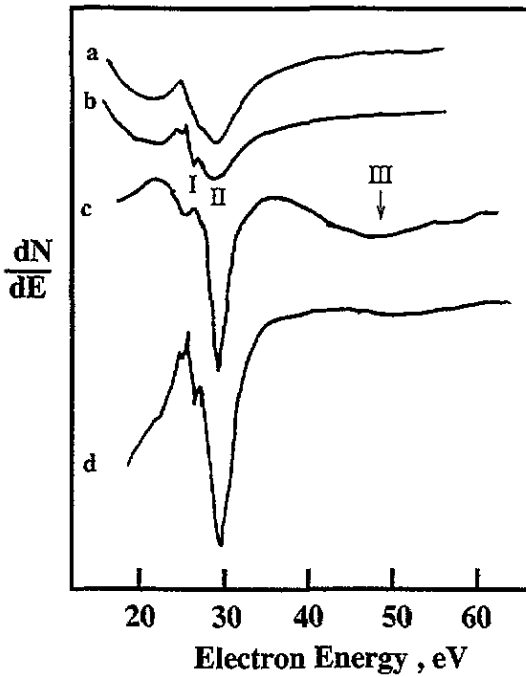


Figure 1. The low-energy range of the ion-induced electron emission (IAE) from Ti compared to the electron-induced spectrum: a, IAE obtained with a 4 kV Ar beam and 3 V modulation amplitude; b, the same spectrum obtained with modulation 1 V; c, AES obtained with a 2 kV electron beam and modulation 1 V; d, combined AES/IAE for the same conditions as c with 4 kV Ar added.

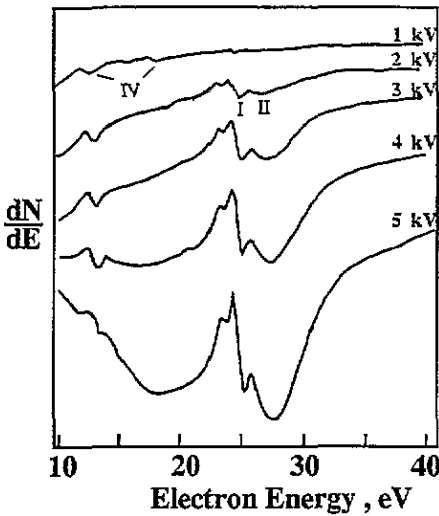


Figure 2. IAE of Ti measured with different Ar⁺ ion excitation energies (modulation, 1 V).

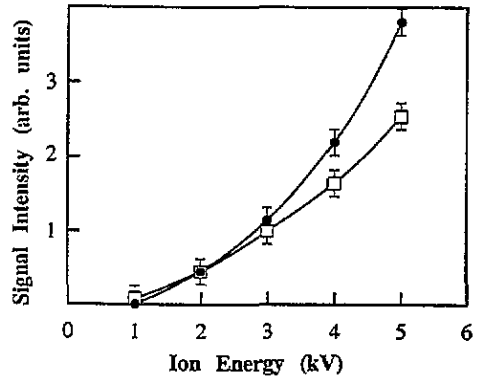


Figure 3. The ion energy dependence of the Ti IAE signal intensity plotted for the narrow (I) and broad (II) components (squares and circles, respectively; the lines are best fits to the experimental data).

Variations in the spectra induced by ions with energies between 1 and 5 kV are displayed in figure 2. To obtain line intensities, 'peak to peak' amplitudes of component I were corrected for the steeply sloping background, and for component II the vertical separation between the derivative minimum and the extrapolated high-energy background was used.

As can be seen in figure 3, both intensities vary quadratically with ion excitation energy, but feature II increases more efficiently with ion energy compared to feature I, which, on the other hand, is characterized by a lower threshold energy. A quadratic dependence of IAE yields on ion energy was reported earlier for Ar^+/Si [18], as well as in He^+ , Ne^+ , Ar^+ and Kr^+/Al experiments, and was confirmed by simulation of collision cascades for symmetrical (Al-Al) collisions [5]. Furthermore, a relatively stronger enhancement of the 'bulk' emission yield with increasing Ar^+ energy (up to 7 kV) has been observed also in IAES of Si [19]. The low-energy fine structure (IV), with dominant features around 14 and 20 eV, exhibits a significantly different energy dependence (e.g., the 20 eV peak completely disappears at 2–3 kV Ar, figures 2 and 4) and these are the only peaks clearly visible in the spectra recorded under 0.5 kV Ar^+ excitation of both Ti and TiNi (figure 4, curve a). These emission features originate with impinging Ar ions that are neutralized on approaching the surface, with excited autoionizing states involving 4s and 4p levels. The peak energies are partially consistent with argon spectra recorded in Ar^+/Al and Ar^+/Si experiments, which agree with theoretical predictions [20].

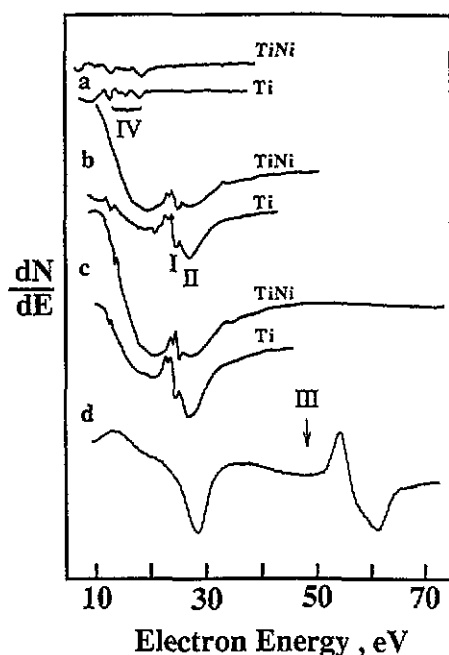


Figure 4. IAE of TiNi against pure Ti (modulation, 1 V): a, 0.5 kV Ar^+ ; b, 3 kV Ar^+ ; c, 4 kV Ar^+ ; d, AES of TiNi recorded after 4 kV Ar sputtering (modulation, 3 V).

As for the TiNi target spectrum, only emission from Ti is induced (figure 4). Ion-excited electron emission from Ni atoms in the alloy is relatively inefficient for several reasons. First, for a certain ion energy the probability of collision-induced M_{23} ionization is expected to decrease for a higher-atomic-number transition metal, as the electron binding energy increases and its orbital radius decreases. Secondly, a much lower efficiency for M_{23} ionization in the higher-mass Ni atoms is expected during asymmetric Ni-Ti collisions. Furthermore, symmetric Ni-Ni encounters are apparently quite rare or relatively inefficient due to the particular atomic packing in TiNi (CsCl crystal structure). Both Ti IAE features I and II appear in the TiNi spectrum at nearly the same energies as for pure Ti, but feature II is somewhat broader in TiNi. Moreover, its relative intensity is greater than anticipated on

the basis of nominal composition and structure, i.e., the reduced Ti atomic density in TiNi. In particular, the Ti IAE intensity from TiNi is about 60% of the intensity measured under identical ion dose and spectrometer parameters for the more closely packed pure Ti (figure 4, curves b and c), whereas a quantitative analysis, based on the AES intensities (figure 4, curve d) relative to those measured for an *in situ* scribed TiNi sample, indicates a mean Ti composition of only ~40% in the first two or three surface layers of the sputtered sample (this deviation from the 49% bulk composition is attributed to Ti preferential sputtering). Hence, it can be concluded that Ti–Ni asymmetric collisions are more efficient in creating Ti 3p holes than Ti–Ti collisions. Likewise, significant yield enhancements reported for Cr IAE from Cr silicides, relative to pure Cr, were attributed to emission initiated by Cr–Si collisions [11]. Finally, the characteristic electron-excited autoionization emission (III in figure 4, curve d) does not appear in the ion-excited TiNi spectrum, just as in the cases of pure Ti and Cr. These observations, together with the attenuation of autoionization emission under ion excitation, appear to be general phenomena of similar origin, at least as far as 3d transition metals are concerned

References

- [1] Valeri S 1993 *Surf. Sci. Rep.* **17** 85
- [2] Milne R H, Maydell E A and Fabian D J 1991 *Appl. Phys. A* **52** 197
- [3] Pfandzelter R and Landskron J 1993 *Phys. Rev. Lett.* **70** 1279
- [4] Hennequin J F and Viaris De Lesegno P 1974 *Surf. Sci.* **42** 50
- [5] Vrakking J J and Kroes A 1979 *Surf. Sci.* **84** 153
- [6] Xu F and Bonanno A 1992 *Surf. Sci.* **273** L414
- Whaley R and Thomas E W 1984 *J. Appl. Phys.* **56** 1505
- [7] Fano U and Lichten W 1965 *Phys. Rev. Lett.* **14** 627
- [8] Matthew J A D 1983 *Phys. Scr.* **T 6** 79
- [9] Viaris De Lesegno P and Hennequin J F 1974 *J. Physique* **35** 759
- [10] Viel L, Benazeth C and Benazeth N 1976 *Surf. Sci.* **54** 635
- [11] Valeri S and Verucchi R 1992 *Phys. Scr.* **T 41** 246
- [12] Bertel E, Stockbauer R and Madey T E 1983 *Phys. Rev. B* **27** 1939
- [13] McBreen P H and Polak M 1985 *Surf. Sci.* **163** L666
- [14] Shih H D and Jona F 1977 *Appl. Phys.* **12** 311
- [15] Kraus A R and Gruen D M 1978 *Nucl. Instrum. Methods* **149** 547
- [16] Polak M and McBreen P 1985 *Solid State Commun.* **56** 407
- [17] Verucchi R and Valeri S 1993 *Solid State Commun.* **86** 695
- [18] Iwami M, Kim S C, Kataoka Y, Imura T, Hiraki A and Fujimoto F 1980 *Japan. J. Appl. Phys.* **19** 1627
- [19] Valeri S and Verucchi R 1991 *Nucl. Instrum. Methods B* **59/60** 37
- [20] Nixon A P, Gallon T E, Yousif F and Matthew J A D 1994 *J. Phys.: Condens. Matter* **6** 2681