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~~~~~Outer-Shell Excitation Mechanisms and Static-Mode Laser-
~~~~~Fluorescence Spectroscopy of Sputtered Atoms*~~~~~

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I. Introduction

Photon emission resulting from outer-shell excitation of sputtered atoms, although historically old [1] has been studied intensively only in the last decade [2-4]. The implications of this phenomenon for the larger field of inelastic ion-surface collisions have been delineated in review articles and contributed papers at each of the three previous International Workshops [5,6,7]. Much effort has been devoted to elucidating the mechanisms by means of which a portion of the kinetic energy of a projectile is transformed into internal electronic energy of the sputtered atom. Models have been proposed whose theoretical predictions have been tested in so far as possible against a host of results obtained by patient and ingenious experimentation.

A thoroughgoing discussion of the origin of secondary photon and secondary ion emission resulting from energetic particle interactions with solids shows that these related inelastic processes are very complicated indeed [8]. Their better understanding must depend on further refinement of the theoretical apparatus and on breakthroughs in the experimental approaches. In this paper, we will assume that the reader is familiar with the earlier work in this field which will be discussed in summary fashion only. It will become apparent that certain conclusions, particularly concerning models, arrived at here represent one point of view rather than a firm concensus by workers in the field.

A detailed discussion will be given of "static" mode laser fluorescence spectroscopy (LFS) which allows one to determine for the first time low energy excited state populations and velocity distributions as a function of monolayer oxygen coverages. Furthermore, the development of "static mode" secondary photon emission measurements will be delineated and the effect of monolayer oxygen coverages on excited state fractions will be described.

Finally, it will be shown that the new and unexpected features emerging from the "static mode" LFS and SCANIIR experiments have provided insights into the fundamental mechanism of excited state production which have led us to develop the "causal collision" model of electronic excitation of sputtered atoms.

II. Data Base

A quite extensive data base exists for secondary photon emission from sputtered atoms [9]. Measurements on elemental targets include Li, Be, C, Na, Mg, Al, Sc, S, Sc, Ti, V, Cr, Fe, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ag, In, Sn, Cs, Ta, W, Au, Tl, U. In addition, a number of compound surfaces have been studied including oxides, nitrides, alloys, semiconductors glasses and minerals. Energetic projectiles used for these studies have been Ne, Ar, Kr, Xe, Cs, O, N_2^+ and He.

In part, the extensive experimental information available on secondary photon emission reflects the intense interest in this subject occasioned by possible surface analytical applications [10,11]. Soon after the introduction of SCANIIR,

it was recognized that quantitative surface analysis using this technique was fraught with difficulties traceable persumably to the complexities of the excitation mechanisms and their dependence on "matrix" effects. In the more recent past, practical interest in the details of neutral particle emission has been revived by the problem of high Z impurities in magnetically confined fusion machines [12,13]. Measurements of sputtered impurities in flight before they are incorporated into the plasma usually employ laser excitation of atomic resonance transitions. Quantitative determinations of sputtered atom fluxes clearly presuppose a knowledge of the fraction of atoms sputtered in a particular electronic energy level, usually the ground state, being accessed by the laser [14,15]. Here again, surface composition strongly influences the distribution of atoms sputtered in various excited states introducing serious uncertainties into the interpretation of the measurements unless the composition is well defined.

Despite the strong motivation provided both by the search for solutions to practical problems and the need to understand an important physical phenomenon at the most basic level, the elucidation of excitation and deexcitation mechanisms operative in outer shell excitation of sputtered particles has been a slow process. It is interesting to speculate on the reasons for this state of affairs in the hope that such considerations could guide future experimental and theoretical work into more fruitful channels.

Most secondary photon emission measurements have been done with projectile energies less than 10 Kev where Firsov theory shows [16] inelastic electron energy transfer in binary collisions to result in electronic excitation up to about 10 ev. Cross sections for inner shell electron promotions resulting in Auger electron emission are, generally speaking, below detection limits [17] at these projectile energies. Secondary photon emission therefore involves electronic excitation primarily of outer shell or valence electrons and consequently is very sensitive to changes in the chemical bonding situation of surface atoms. Such considerations make plausible the profound influence of adsorbed gases, of oxidation and of alloying on excited state distributions and photon intensities. The relatively much smaller changes due to chemical effects observed in ion bombardment induced Auger emission are due presumably to the inner-shell nature of the electronic excitation. This fundamental influence of surface chemical composition on the quantitative aspects of secondary photon emission was not fully appreciated in the earlier work and is one of the chief reasons for discordant results reported by different investigators working on similar systems. In a later section of the paper, the effects of submonolayer, multilayer and recoil implanted oxygen on titanium atom excitation coefficients will be delineated. It will be seen that in addition to the oxygen to metal ratio, the detailed structure of the surface oxide layer also influences the excitation

mechanism. A satisfactory theoretical model must be able to account for these subtle but important effects.

It is useful to summarize the current status concerning the most important parameters associated with secondary photon emission so as to put the later sections of the paper in a proper context.

1. Excitation Probability-Dependence of Photon Yield on the Energy of the Bombarding Particle

Excitation functions, a measure of the dependence of the photon yield on the energy of the incident ion, are among the most basic quantities needed for an understanding of outer-shell excitation mechanisms [4,18,19,20]. There has only been one attempt to measure absolute photon yields [21].

Because of the extreme sensitivity of the photon yield on surface composition, particularly on oxygen contamination, recent measurements have been made under UHV conditions [22, 23,24]. In this work, the secondary photon emission due to ion bombardment of Be metal foil by 200-3000 eV Kr^+ , Ar^+ , Ne^+ , O_2^+ , and N_2^+ was studied and the emission yield from four Be(I) and one Be(II) transitions as a function of incident ion energy was interpreted in terms of relevant excitation processes. A model based on a velocity dependent excitation process, the random linear collision cascade theory of sputtering which made allowance for non-radiative de-excitation of the excited sputtered atoms accounted for the observed energy dependent emission yields. The results of

this model indicate that the secondary photon emission yield, $Y_i^{\text{ex}}(v_m)$, of a given emission line, i , can be expressed as $Y_i^{\text{ex}}(v_m) = J(\mu\text{amp}/\text{cm}^2) S(\text{no.}/\text{ion}) \exp[-(A/a)_i/v_m]$, where J is the incident ion current density; S the sputtering yield; v_m is the velocity corresponding to the maximum transferred energy between the incident ion of energy E_1 , mass M_1 , and the target atom of mass M_2 , i.e., $v_m = [8M_1E_1/(M_1 + M_2)^2]^{1/2}$; $(A/a)_i$ is the effective non-radiative de-excitation parameter for state i . Values for the $(A/a)_i$ parameters were found to be $1-3 \times 10^7$ cm/sec for the Be(I) and Be(II) states; a decrease to $5-7 \times 10^6$ cm/sec upon O_2^+ bombardment was observed for the Be(I) states, while the value for the Be(II) state did not change.

A similar functional dependence of the secondary photon emission yield on the incident ion energy was found by Heiland, *et al.* [19] employing a different interpretation of the origin of the excited sputtered particles in their studies of Mg, Cu, Fe, and Mo targets when bombarded by 400 eV to 8 keV He^+ , Ne^+ , and Ar^+ . Only "direct knock-off" and the "reflected-ion" contributions to the sputtering process were considered [25]. Bhattacharya, *et al.* [20] used a similar relation with S being the "direct knock-off" (25) contribution only. They obtained values of 1.7×10^7 to 2.6×10^7 cm/sec for $A_i^{\dagger}$ by studying various excited states of sputtered Si(I), Si(II), and Si(III) produced using 50-500 keV Ar^+ incident ions. Van der Weg and Bierman, [3] and White and Tolk [4] have reported values of approximately 2×10^6 cm/sec

for A_i' for sputtered Cu(I) (324.75 nm emission line). These authors assumed that the binary collision between the impinging ion and atoms in the first layer of the target was simultaneously the liberating and exciting event. A similar approach was taken by Hippler, *et al.* [26] who used line shape measurements of the Doppler shifted secondary photon emission lines to determine A_i' values for selected excited states of Al, Cu, and Zn. They observed a value of $A_i' = 5 \times 10^5$ cm/sec for the 307.95 nm line of Zn(I) which has the excited level below the Fermi level of Zn; for the 481.05 nm Zn(I) line which has its excited level lying above the Fermi level a value of $A_i' = 5 \times 10^6$ cm/sec was determined. Presumably, the possibility that the latter level can undergo a resonance ionization de-excitation process in addition to the Auger deexcitation process accounts for the increase in the effective A_i' value. This observation supports the idea that the total probability for the non-radiative de-excitation of a sputtered excited atom or ion is the product of the survival probabilities [i.e., the sum of the $(A/a)_i$ values] of all of the allowed de-excitation channels for a given excited state.

2. Excited State Distributions as a Function of Excitation Energy.

Studies of excited state populations as a function of excitation energy have in general shown a Maxwell-Boltzmann distribution [27,28] which had been taken as evidence in support of the Anderson and Hinthorne LTE model [29]. A

current view, which appears to be gaining wider acceptance is that the Maxwell-Boltzmann-like distribution could result from excitation cross sections which themselves vary as the exponential in the excited state energy. The energy range accessible for measurements of distributions over excited states has traditionally been rather restricted (2-4 ev) and therefore the observed distribution could result from any energy dependence for which an exponential form is a reasonable approximation over a limited energy range [7]. It is for this reason that measurements of distribution functions over low-lying energy states (.01-1 ev) accessible to laser fluorescence measurements take on a special significance since they provide data for more stringent tests of alternative models.

A comparison of the population distributions of excited atomic states in equilibrium plasma, single collision gas phase, beam foil and sputtering excitation showed remarkable similarities in spite of the different physical mechanisms responsible for the excitation [30]. Though suggestive, the reasons for the similarities of excited state distributions must be closely examined. In the gas phase, electronic excitation in low energy collisions (10-1,000 ev) has a low probability. The reason is that such collisions have large impact parameters and are therefore largely elastic. In the solid however, collisions by and large have lower impact parameters with a significant fraction of the moving atom's momentum being directed along the internuclear axis formed with its collision partner. As the two colliding atom's

internuclear distance decreases, they move up the repulsive portion of a potential energy curve and because their relative velocities are small compared to the orbital electron velocities, the electrons can in principle relax adiabatically into two center molecular orbitals [32,33]. If one calculates the inelastic electronic energy transfer processes "statistically" using Firsov theory [16] as has been done by Kelly [34] one arrives at the equivalent of a Maxwell-Boltzmann distribution over excited states.

For low enough kinetic energies the inelastic energy transfer was found to be proportional to the kinetic energy given to the sputtered atom. This results in an expression which reproduces experimental measurements of the relative yields of sputtered excited atoms, and gives reasonable agreement with experiment regarding many aspects of their kinetic energies and absolute yields. Kelly's expression equates the yield of the i th state to $2g_i U K \sum_{k=i}^{\infty} G_k^{-1} (\epsilon_k^{-1} - \epsilon_{k+1}^{-1})$, where g_i is the degeneracy, U is the surface binding energy, K is the cumulative degeneracy (namely, $G_i = g_0 + g_1 + g_2 + \dots + g_i$), and ϵ_1 is the excitation energy.

The model does not treat "chemical" effects such as enhancements due to surface oxygen or the well known matrix effects due to differences in electronegativities of components in an alloy system. A distinction is drawn between excitation mechanisms involving low lying as compared to higher energy excited states in order to rationalize the observed low kinetic energies of atoms sputtered in low

lying electronic states. The statistical model appears not to be able to account for the bi-modal velocity distribution of excited sputtered neutrals observed by some investigators [35].

3. Velocity Distributions of Excited Atoms

Velocity distributions of excited atoms have been determined and the results used in modeling excitation mechanisms. Van der Weg, *et al.* [2,3] measured the Doppler shift and line shape of the CuI 3247 Å emission which they fit to a model based on binary collisions at the surface combined with non-radiative de-excitation processes by electron tunneling [36]. A peak shift of 0.6 Å was observed indicating a mean energy of ~1 Kev for excited Cu atoms. The Doppler line shape measurements of Hippler, *et al.* [26] on a variety of ion-bombarded surfaces were interpreted taking into account contributions due to collision cascades as well.

A second method of determining velocity distributions is by observing the decay of the photon yield as a function of the perpendicular distance away from the solid surface undergoing bombardment. Such "defining slits" experiments performed by different groups of investigators [35,37] can in principle suffer from repopulation of initial states of the transition under study by cascades from upper levels [38]. However, recent studies tend to show comparable kinetic energies from "defining slits" and Doppler broadening experiments although the latter are essentially free of the cascade feeding problem [39,40].

Much evidence has been adduced to show that the kinetic energies of sputtered excited neutrals are in the hundreds of electron volts rather than of the order of 10 electron volts characteristic of the energies of ground state neutrals. A role for recoil sputtering has been advocated both to explain the high kinetic energies of sputtered excited neutrals [41] and the increase in kinetic energy with incident ion energy [42].

A suggestive series of experiments was reported at the Third International Workshop by Tsong [35] in "defining slits" experiments. The decay in photon intensity with distance away from the surface shows a smooth velocity distribution. However, following the curve-fitting practice of other workers in the field [43-45], each curve was broken up into two straight line segments to which average velocity values were assigned. From this work and that of other investigators [43,44], it is readily apparent that there are two populations of excited sputtered atoms. The first is characterized by fast velocities, v_f , and high kinetic energies, E_f , and the second by slow velocities, v_s and low kinetic energies E_s . Here, v_f , E_f and v_s , E_s refer only to the component of velocity or energy normal to the surface. The salient results taken from the paper of Tsong [35] are brought together in Table I. It could be argued that the inherently poor spatial resolution (≥ 150 nm) of the defining slits experiment tends to discriminate against measuring excited atoms with low energies in the range 10-eV and that a more careful search for the slow velocity

group of atoms should therefore be instituted. In any event, the bimodal velocity distributions emerging from the work of Tsong and others are extremely interesting particularly in view of the results obtained in laser fluorescence measurements on the velocity distributions of atoms sputtered in low lying electronic states.

4. Effects of Surface Chemical Composition on Excitation Coefficients.

The enhancement of secondary photon (and ion) yields as a result of adsorption of gases (O_2 , CO) on a surface is by now a well known phenomenon. The effect is important for increasing the sensitivity of surface analysis using SCANIIR or SIMS techniques. Most of the quantitative measurements on secondary photon enhancement due to adsorbed oxygen have been done using the "dynamic" technique in which the oxygen/metal ratio is kept constant by balancing the arrival rate and sticking coefficient of oxygen molecules at a surface against the sputtering rate or desorption coefficient due to the impinging ion beam [46,47]. Numerical values for the enhancement factor vary from element to element and often there are discrepancies between different sets of experiments. Nonetheless there appears to be agreement that the "oxygen" effect can lead to an order of magnitude enhancement of photon yields; that it appears to reach saturation at a certain oxygen coverage; and that further "oxidation" can in

fact lead to a decrease in photon yield, due presumably to a lower overall sputtering yield for the oxide.

Chemical effects clearly play an important role both in secondary photon and ion emission leading to the conclusion that the nature of the surface chemical bond is intimately involved in both surface excitation and ionization mechanisms. In view of this situation, it is somewhat surprising that studies aimed at a more detailed understanding of these effects have only recently begun insofar as secondary photon emission is concerned. Taglauer, *et al.* [48-50] initiated a series of "static" exposure studies on which ion desorption yields could be determined. Subsequently, in similar experiments, changes in secondary photon signals were monitored as a function of ion fluence on a nickel surface covered with CO [50]. These data were interpreted in terms of a maximum signal enhancement at the monolayer level. In a "dynamic" experiment involving dosing a molybdenum surface with CO and sputtering with He^+ , Ne^+ and Ar^+ , the fraction of atoms sputtered in excited states was found to be the same and independent of the incident ion [51]. This result was interpreted in terms of excitation caused by collision cascades rather than due to recoils from incident ion-surface atom collisions. Furthermore enhancement could be related linearly to surface coverage with localization occurring in the vicinity of the adsorbed atom [51].

III. "Static Mode" Laser Fluorescence Spectroscopy of Sputtered Atoms

The previous discussion underscore the perception that one of the most intriguing problems in the field of inelastic ion-surface collisions remains the detailed mechanism by means of which kinetic energy is transformed into internal electronic energy of sputtered atoms. The lifetimes of electronic transitions are long (10^{-9} sec) compared to the collision events (10^{-13} sec) and therefore a study of the electronic states of sputtered atoms can in principle provide information about the sputtering process itself. The data base presently available is restricted to secondary photon emission which covers the excitation region from ~ 4 ev to ~ 2 ev [35]. If one assumes, with Kelly [34], the validity of random inelastic energy transfer ΔE_e , such as is observed [52,53] to occur for collisions at low kinetic energies, then one calculates using Firsov theory [16] for example that in a binary $K \rightarrow K$ collision, 4 ev can be transferred inelastically for a kinetic energy of ~ 600 ev while 2 ev is transferred in a ~ 400 ev collision. However, one can test such a theory based on random inelastic energy transfer only over the narrow range of collision energies responsible for the secondary photon emission lines that are currently being observed (2-4 ev).

The development of laser fluorescence spectroscopy (LFS) has vastly extended the range of excited energy levels accessible to measurement so as to include low energy excitations due presumably to the less energetic collision regime (0-400 ev). It will be shown in this section that LFS provides

information on excitation probabilities, excited state distributions, velocity distributions and very importantly, the effect of surface chemistry on low-lying excited state fractions. It will be seen that data becoming available with this technique provides a base against which rigorous tests of current excitation models can be carried out.

1. Principles of Laser Fluorescence Spectroscopy of Sputtered Atoms

Tunable radiation from dye lasers is available to access most of the resonance transitions of atoms in the periodic table of elements. Narrow-bandwidth laser radiation intersects a sputtered particle beam and excites resonance transitions of the atoms under investigation. Details of the experimental procedures are described in the literature [54-59].

The spontaneously emitted fluorescence radiation can be proportional to the particle flux or number density depending on experimental conditions [60]. If the intersecting angle between laser beam and sputtered particle beam is different from 90° , the laser excitation frequency is Doppler-shifted proportional to the particle velocity. By detuning the laser from the unshifted resonance frequency, the spectrum of the velocity component of the atoms in the laser beam direction can be obtained. The velocity resolution that can be achieved with LFS making use of Doppler-shifted excitation depends on two factors. The first concerns the collimation of the beam of sputtered particles and the

second has to do with the bandwidth of the laser radiation. By using etalons, the linewidth of CW lasers can be reduced to a few MHz and that of pulsed systems to the GHz range. Velocity resolutions of a few times 10 m/s can be achieved with CW lasers and a few times 10^3 m/s with pulsed systems. One can thus measure energy distributions of sputtered particles with much higher accuracy than has been possible up to now.

Detection sensitivities achieved with LFS in laboratory experiments are in the range $10^3 - 10^8$ particles/cm³ with the higher sensitivities attainable with CW excitation.

2. Velocity Distributions of Sputtered Excited Atoms Determined by Doppler Shift LFS

We will now describe how LFS has been used to determine the number density velocity distributions of neutral zirconium atoms sputtered from a zirconium metal surface in the a^3F_2 ground state and in two excited electronic states ($a^3F_{3,4}$) which lie 570 and 1241 cm⁻¹, respectively, above the ground state [59,60]. These number density velocity distributions have been determined for both Ar⁺ and Kr⁺ primary ions at a variety of primary ion energies (1.5-3 keV).

The interpretation of LFS data has been discussed both in the context of molecular beams [61] and of sputtering (see 58-60 and the references listed there). Quantitative evaluation of the LFS results requires an understanding of three effects which have only recently begun to be properly

taken into account: power broadening, transit-time broadening, and velocity-dependent fluorescence detection efficiencies. A detailed theoretical treatment of LFS data including these three effects has been given in the above-cited references; we will make use of the results of these considerations in the following discussion of the data.

Consider an isolated atom with the energy-level diagram of Fig. 1 and traveling with a velocity relative to a laser beam propagating along the $\hat{z}$ axis. The Doppler-shifted transition frequency from level 1 to level 2 can be expressed as

$$\nu_o = \nu_o \left(1 + \frac{v \cos \theta}{c} \right) = \nu_o \left(1 + \frac{v_1}{c} \right), \quad (1)$$

where v_1 is the perpendicular velocity component of the sputtered atom's velocity v , and θ is the emission angle of the atom defined with respect to the target surface normal (i.e., with respect to the laser direction in the present case). One can therefore convert the number density distribution $n(v)$ into $n(v_1)$ resulting in

$$n(v_1) dv_1 \propto \frac{2^n}{M_2^{n-1}} \frac{2\pi}{2n+1} \frac{v_1 dv_1}{v_1^2 + v_b^2}^{n+1/2} \quad (2)$$

This equation was used to compare the Thompson-Sigmund model for linear collision cascade sputtering with the measured LFS velocity distributions.

Linear collision cascade theory yields velocity distributions which can therefore be characterized by two parameters n and v_b . Here, n is a variable which is generally measured to be $1 \leq n \leq 2$, though theory would place it closer to 2; and v_b is the velocity corresponding to the surface binding energy E_b , i.e., $v_b = [2E_b/M_{Z_r}]^{1/2}$, due to the assumed planar potential barrier encountered by the sputtered atom in the near-surface region.

The LFS data on sputtered Zr atoms can now be compared with linear collision cascade theory. A partial energy-level diagram shown in Fig. 2 for zirconium displays the transitions used in the LFS measurements. The sputtering properties of ground-state zirconium atoms were probed using the a^3F_2 (0 cm^{-1}) $\rightarrow$ $z^5F_1^0$ ($16\,787 \text{ cm}^{-1}$) transition. This transition, although weak ($gA = 8.8 \times 10^5 \text{ s}^{-1}$) produced sufficient excited zirconium atoms for detection. Fluorescence involving the $z^5F_1^0 \rightarrow a^5F_1$ (4871 cm^{-1}) transition was monitored. This transition with its relatively large branching ratio ($gA = 1.6 \times 10^6 \text{ s}^{-1}$) was spectrally far removed from the excitation source, thus minimizing scattered light problems. Alternate transitions from the $z^5F_1^0$ state are also significant giving $g \sum_{i=3} A_{2i} = 1.08 \times 10^6 \text{ s}^{-1}$.

The sputtering properties of the a^3F_3 metastable level which lies 570 cm^{-1} above the ground state were determined using the a^3F_3 (570 cm^{-1}) $\rightarrow$ $z^3F_4^0$ ($17\,556 \text{ cm}^{-1}$) $\rightarrow$ 3F_4 (1241 cm^{-1}) excitation-monitor scheme. Transition strengths were $gA = 8.7 \times 10^5$ and $7.1 \times 10^6 \text{ s}^{-1}$, respectively. The total

decay rate from $z^3F_4^0$ was $g\Sigma_i A_i = 8.24 \times 10^6 \text{ s}^{-1}$, and the energies of excitation and emission were 16 986 and 16,315 cm^{-1} , respectively.

Similarly, measurements of the a^3F_4 level which lies 1241 cm^{-1} above the ground state utilized a a^3F_4 (1241 cm^{-1}) $\rightarrow z^4D_3^0$ (18 244 cm^{-1}) $\rightarrow a^3P_2$ (4186 cm^{-1}) excitation-emission scheme. This had $gA = 4.1 \times 10^6$ and $3.5 \times 10^6 \text{ s}^{-1}$, respectively, with a total decay rate from $z^3D_3^0$ of $g\Sigma_i A_i = 9.02 \times 10^6 \text{ s}^{-1}$. The energies of excitation and emission were 17003 and 14058 cm^{-1} , respectively.

The velocity distribution of ground-state neutral zirconium atoms sputtered by normally incident 3-keV Kr^+ ions is displayed in Fig. 3. The points are the result of averaging several measurements after each had been deconvoluted from an appropriate power and transit-time-broadened Lorentzian. It was possible additionally to deconvolute the excitation laser linewidth from the data. However, the spectral narrowness of the Nd/YAG pumped dye laser source was sufficient to make this unnecessary. All frequencies higher than 50 Hz were suppressed in the Fourier transform. Further it was necessary to account for the velocity-dependent photon yields [59]. The solid curve of Fig. 2 was constructed using Eqn. 2 with $n = 2$ or 1.75 and $v_b = 3.652 \times 10^5 \text{ cm/s}$.

Velocity distributions taken for primary Kr^+ energies in the range 1.5-3 keV showed, within experimental error, no dependence on primary ion energy. This fundamental prediction of linear collision cascade theory was verified by the LFS

data. Again $n = 1.75$ or 2 were used as parameters with $v_b = 3.652 \times 10^5$ cm/s.

Figures 4 and 5 represent number density velocity distributions of zirconium atoms sputtered by normally incident 3-keV Kr^+ in the a^3F_3 and a^3F_4 metastable levels. Again the velocity distributions appear to be well fit by linear collision cascade theory. This result is remarkable since, as already discussed atoms which are sputtered in 2-4 eV excited states have velocity distributions shifted to substantially higher velocities than those expected for ground-state atoms. An indication of the magnitude of this effect in zirconium was seen by monitoring the $z^5F_1^0 \rightarrow a^3F_2$ SCANIIR transition in zirconium. The fluorescence profile of atoms sputtered in the $z^5F_1^0$ state showed a FWHM of $4.5 + 0.6 \text{ cm}^{-1}$, about a factor of 10 larger than the Doppler width profiles of atoms sputtered either in the ground state or the 3F_3 and 3F_4 lowlying states. Velocity distributions of atoms in low lying levels therefore are much closer to those of atoms sputtered in ground states than to those sputtered either in high-energy excited states or as ions.

This important result as will be seen, has far-reaching consequences for the development of the theory of excitation mechanisms at surfaces and would have been difficult to obtain by a technique other than LFS. Because the a^3F_3 and a^3F_4 states of Zr differ from the a^3F_2 ground state only in the relative orientations of the S and L angular momenta, it has been argued [34] that these two states are not excited

in the usual sense and that atoms sputtered in these states would therefore be expected to have kinetic energies similar to those sputtered in ground states. However, low kinetic energies for atoms sputtered in relatively low-lying electronic states appears to be a more general phenomenon extending to atoms sputtered in states with electronic configurations completely different from that of the ground state. Recent work by Yu, *et al.* [62a] showed that the velocity distributions of Ba atoms sputtered in the 1D (1.4 ev) and 3D (1.2 ev) states were quite similar to those of 1S ground state atoms. Using Doppler shift LFS, these investigators were able to show that $v_b = 2.23 \times 10^5$ cm/sec for 1S atoms while the most probable velocities for the 1D and 3D states were 3.8×10^5 and 3.2×10^5 cm/sec respectively. The corresponding energies of 10.1 and 7.4 ev respectively remain comparable to the surface binding energy of 3.6 ev. No evidence for a kinetic energy threshold was found in these measurements. Recently, measurements have become available on velocity distributions of Fe atoms in the a^5F_5 level at 0.86 ev [62b] and of Ca atoms in a state ~ 2 ev above ground [62c]. In these cases also, the kinetic energies of the sputtered atoms are more comparable to ground state energies than to the energies of atoms sputtered in SCANIIR levels.

3. Excited State Distributions Among Low-lying Levels.

The "Causal Collision" Model of Electronic Excitation in Sputtering

Measurements on the velocity distributions of low-lying excited states of Zr, Fe, Cu and Ba described in the previous section showed these to be not too strongly shifted to higher energies compared to ground state sputtered atoms. In addition to velocity distributions, a number of measurements have been made on population distributions among low-lying states of sputtered atoms. The available information all of which has been obtained by Doppler shift LFS is brought together in Table II. All the data have been normalized to unity for ground state occupations.

As can be seen by inspecting Table II and contrary to the traditional view of atoms sputtered in electronically excited states, the fractions of atoms sputtered in low-lying levels can be quite large. The picture that emerges is of a *continuum* both in the fractional occupation of energy levels and in the most probable kinetic energy with which a given atom is sputtered: the higher the degree of electronic excitation, the higher the kinetic energy and the lower the fractional occupation.

We now show that detailed considerations of electronic energy transfer in the binary collision approximation can rationalize the observations on atoms sputtered in low (0-2 eV) as well as high-lying states without making additional assumptions concerning energy partitioning.

It would seem reasonable to suppose that a sputtered neutral atom in a ground or excited state originates from the very surface layer or next to outermost layer of atoms after suffering a collision with a (target) atom having kinetic energy sufficient to overcome the binding energy of the sputtered atom. Computer simulations of sputtering [63,75] which mimic the salient results of standard sputtering theory [76,77] lend strong support to this supposition. We will now briefly describe calculations of electronic energy transfer, using the TRIM Monte Carlo code [78,79] for the "causal" collision leading to sputtering.

The TRIM code uses the binary collision approximation to follow the projectile and target atom trajectories collision by collision. The target is assumed to be amorphous and has an associated planar surface potential. Sputtered target atoms must overcome a surface binding energy.

Bulk atoms undergoing cascade (recoil) events are assumed to have binding energies equal to the monovacancy formation energy, ΔH_v . The Miedema model for ΔH_v has been invoked.

Nuclear scattering and energy loss is prescribed using the Molière interatomic potential modified by a constant to approach the Biersack-Ziegler potential. [S. A. Cruc, *et al.*, Nucl. Instr. & Methods 194 (1982) 659]. The constant, $C(r)$, is a function of the turning point. For Ar $\rightarrow$ Ti $C(r) \approx .9$ for Ar-Ti and Ti-Ti interactions. Electronic energy loss makes use of a combination of Linhard-Scharff and Oen-Robinson prescriptions.

Calculations of electronic energy loss in the "causal" collisions involving Ti atoms and resulting in sputtering are shown as a function of collision energy in Fig. 6. On the assumption that the model used here can be applied over the range 8-400 ev, the electronic energy loss is seen to be essentially linearly dependent on the energy of the "causal" collision. The energy distribution of the atoms involved in "causal" collisions was found to be a function of E^{-2} as expected [21,22]

The data in Table II are plotted in Fig. 7. For comparison, the TRIM calculations (for Ti) of fractional populations as a function of electronic excitation energy imparted in the "causal" collision is shown as a dashed line. Effects due to degeneracy or to very closely spaced energy levels are not considered in this treatment. There is qualitative agreement between experiment and theory even though the experiments include a variety of different atomic systems while the calculations are for Ti sputtering only. The fractional populations fall off more rapidly at low energies of excitation than predicted by TRIM indicating that electronic energy loss is a stronger than linear function of the kinetic energy of the "causal" collision in the range 8-100 ev.

TRIM calculations are currently being done by us of the effects of oxygen adsorption on excited state fractions and of velocity distributions of atoms sputtered in excited states of different energies. Comparisons of these calculations

with available experimental data will provide further tests of the validity of the "causal collision" model for outer shell excitation in sputtering.

IV. "Static Mode" Laser Fluorescence and Secondary Photon Emission Measurements: Effects of Surface Oxygen on Excited State Fractions

The profound influence of surface oxygen on excited state fractions is fully documented in the literature. Secondary photon emission studies have been done up to now only in the "dynamic" mode [46,47], in which recoil implanted oxygen can modify the surface oxide structure in unknown ways [71]. A systematic characterization of surface oxygen-metal reactions [67] have shown that oxide-like sorption layers and "two-dimensional" oxides can form at room temperature on many metal surfaces. The kinetics, mechanisms and structures of such layers can take many varied forms and the energetics for the formation of such layers appear to vary from metal to metal. Clearly, the details of the oxygen-metal bond influence many of the surface dependent properties. Simultaneous Auger and energy analyzed SIMS, for example was able to show a dramatic increase in the secondary ion yield of Ti as a result of submonolayer oxygen adsorption [68,69,70].

In order to study the effect of monolayer and submonolayer coverages of oxygen on excited state fractions both for low-lying and SCANIIR levels, we have developed the techniques of "static mode" laser fluorescence and secondary

photon emission spectroscopy coupled with Auger spectroscopy and have applied the method to a study Ti-metal surfaces interacting with oxygen. Details of the "static mode" laser fluorescence method have been described in the literature [63]. The "static mode" secondary photon emission measurements will be described in a forthcoming publication [83]. Suffice it to say here that the principal innovation in the "static mode" LFS technique involves operating the ion source in a pulsed mode by application of a brief flat topped pulse (4 μ s duration), producing a 600 V potential difference across the deflection plate system of the ion gun. This caused a deflection of about 6 mm at the Ti-target, for 3 keV ions. The target was aligned so that the deflected beam reached the target center. During most of the 100 ms interval between laser pulses the undeflected ion beam impacted the outer edge of the Ti target. This mode of operation minimizes sputtering during LFS data collection and has been shown to result in virtually unchanged O/Ti ratios during a single run. After measurements at a given O/Ti ratio have been completed, the ion beam is allowed to bombard the central region of the target continuously until the next desired O/Ti ratio is established using the Auger monitoring system.

A dye laser (Molelectron MY34-DL16) was synchronized to fire 3 μ s after pulsing the ion beam. Broadband operation (~ 1 cm⁻¹ linewidth) was employed, with sufficient power to ensure high saturation condition of the transitions being

excited. Details of the laser system and LFS techniques have been published elsewhere [58,66].

The Ti-target was oxygen-coated in a position facing an AES system, after sputter-cleaning. The oxygen partial pressure ($\sim 10^{-6}$ Pa) was monitored with a quadrupole gas analyzer. In accordance with the high sticking coefficient, for oxygen on titanium [67], one monolayer coverage was achieved at exposures of 1-2 L, while 5L was sufficient to produce an AES signal corresponding to about 3 monolayers. Desorption of oxygen by the AES electron beam could be easily observed at coverages higher than two monolayers but could be kept to an acceptable rate by minimizing the electron beam current.

1. Nature of Surface Oxide Layers-Sputtering Kinetics

In order to clarify the nature of oxygen bonding to titanium, which effects both the sputtering yield and the excitation coefficients, the kinetics of oxygen sputtering were investigated. The erosion of the oxygen near-surface layer by a steady beam of ions of current density J ions/cm² can be described in terms of a cross section σ for the desorption process:

$$\sigma = \frac{d \ln y}{dt} / J = S/n_o \quad (3)$$

where S atoms/ion is the sputtering yield at one monolayer coverage, n_o atoms/cm² the area density for one monolayer, and y is any quantity proportional to actual surface coverage $n(t)$ atoms/cm². Here we take for y the AES O/Ti signal

ratio from the peak heights of the 510 eV oxygen and the 418 eV titanium lines in the differential Auger spectrum. While the sputtering process is not strictly describable by a cross section for independent ejection events, the approximation appears valid for low coverage [45,48]. In Fig. 8 where the O/Ti Auger ratio is plotted against time (for a beam current density of 2×10^{14} ions $\text{cm}^{-2}\text{s}^{-1}$ at the monitoring position), four distinct regions, labelled A-D can be identified. The assignment of oxygen coverage values, given in Table III is deduced from a model of the expected O/Ti Auger peak ratio as a function of coverage. As is discussed below, this is strongly supported by experimental evidence from other studies. Also given in Table VI are the σ and S values calculated from Eq. 3 for a value of $n_o = 1.474 \times 10^{15}$ atoms/ cm^2 .

A tightly bound layer corresponding to the D region of Fig. 8 has the lowest sputtering yield and has a transition to the C region at O/Ti (AES) of ~ 1 . A change in slope at this O/Ti ratio had been observed by Shih and Jona [72] and identified by them on the basis of LEED data as due to the formation of a $1/4$ monolayer of oxygen. Later studies [73] confirm that the characteristic $p(2 \times 2)$ pattern seen in LEED is due to the presence of $1/4$ monolayer of oxygen. The LEED results could not be used to differentiate between formation of an over or underlayer. It has been shown that such information is obtainable from the sputtering results [63].

The noteworthy features of the oxygen sputtering yield data shown in Table III are (i) the dependence of titanium

sputtering yield on oxygen coverage and (ii) the small yield for desorption of O atoms at coverages up to two monolayers. In order to understand the physical basis for these results, model calculations were performed with the TRIM code of Haggmark and Biersack [78,79], modified to include multiple layers and components for sputtering calculations. The best agreement between the data in Table III and the TRIM code calculations were obtained using a model in which at least the first and possibly the first 1.5 oxygen monolayers form an underlayer. Interestingly, this situation was found to be the case for N_2 on Ti [80]. The two dimensional TiN structure bears a remarkable structural similarity to bulk TiN. It is tempting to speculate that oxygen monolayers on Ti form a two dimensional oxide whose structure and bonding properties resemble bulk TiO.

2. Effect of Oxygen on Ti Sputtering Yield and on Excited State Fractions

Experiments with LFS detection were now performed on the sputtering of Ti atoms as a function of oxygen coverage. First, successive members of the a^3F_J , $J = 2,3,4$ ground state multiplet, were accessed and fluorescence detected at wavelengths selected from the $a^3F \rightarrow z^3F^0$ system at ~ 520 nm. The LFS signal was followed through diminishing oxygen coverage until essentially clean metal was indicated by Auger measurements. The relative normalization of the curves shown in Fig. 9 for the different fine-structure states was obtained in separate experiments on the clean metal target for each of the $J = 2,3$ and 4 levels. Corrections for the different

degeneracies, radiative lifetimes and branching ratios at the detection wavelength were applied. The sum of the three ordinates at zero oxygen coverage was taken to be the total sputtering yield of Ti metal for 3 keV Ar^+ ($S=1.1$) [71,76,78]. Assumptions made in interpreting the data of Fig. 9 as Ti^0 yields are that the velocity of the ejected Ti atom does not vary substantially with oxygen coverage or the state of the ejected species and that atoms sputtered in more highly excited electronic states or as ions constitute a negligible fraction of the total sputtered flux. Large errors are not expected but additional work is clearly required so as to be able fully to assess the effects of changing velocity, excited state and ion distributions.

The salient result is that the Ti^0 sputtering yield is a strongly decreasing function of oxygen coverage. It is lower by a factor of about four in the case of three monolayer oxygen coverage compared to a clean Ti metal surface.

Of interest for the present work is the dependence of the excitation probability, R^* , on oxygen coverage. To extract this information from the data shown in Fig. 9, the assumption was made that the total Ti sputtering yield is the sum of the yields into the ground state multiplet $^3F_{2,3,4}$ levels only. In Fig. 10, the R^* curves were calculated by dividing the fractional population in a given state as a function of coverage, θ , by the total sputtering yield, $S_T(\theta)$. The behavior of R^* is quite revealing. For the ground state, there appears actually to be a small decrease with oxygen coverage. The R^* of 3F_3 stays essentially constant while

that of the 3F_4 level shows a small increase. An increase by a factor of two in R^* with increasing oxygen coverage is seen for the 5F_5 level at ~ 0.8 ev.

In order to determine the relation between $R^*(\theta)$ and higher excitation energies, "static mode" secondary photon emission measurements were undertaken. The apparatus for the secondary photon emission work consisted of four parts: (1) vacuum system and target holder, (2) ion bombardment system, (3) light collection and detection, and (4) data manipulation and storage. In order to achieve static mode sensitivity, improvements and modifications over standard methodology were necessary in each of the four areas. The ion pumped vacuum system in which the polycrystalline Ti target was held routinely maintained a 6×10^{-11} torr base pressure. Residual gas analysis of this background gas demonstrated that He was the major contaminant. In this environment a clean Ti surface oxidized no faster than 2% of a monolayer/hr. An Auger spectrometer was used to calibrate surface coverages for these experiments.

The ion bombardment system was a Varian 3 keV ion gun producing 20 μ amps of beam current. The raster system of the gun was modified to give a gate signal when the ion beam x and y deflection plate voltages were within present values. Thus, the SCANIIR signal was examined only during a portion of the sputtering time corresponding to erosion occurring from the central portion (usually 25% of total area) of the rastered area. In this manner signal was observed from an area which had no more than an 8% of a monolayer coverage

variation (as determined by Auger spectroscopy).

The light collection and detection system used all supracyl optics which imaged on a McPhearson 1/3 m monochrometer. Light was detected by an RCA C31034 photomultiplier tube interfaced to gated (by the raster gate) Ortec photon counting system. This unit is a sensitive system for monitoring signals even from clean Ti surfaces. Data manipulation and storage including simultaneous monitoring of ion current and SCANIIR data was accomplished with an LST 11/23 computer system.

Data was first collected on a clean surface by scanning the spectrometer over the full spectral range $2000 \text{ \AA} - 8800 \text{ \AA}$. During this measurement careful Auger spectroscopy demonstrated that the oxygen level never reached more than 0.005 of a monolayer. Interesting SCANIIR lines were then chosen for detailed study. Subsequently the surface was dosed to about 3 monolayers of oxygen and the light intensity as a function of ion dose was measured. Ion dose was related to surface coverage by taking many Auger spectra during a run, and interpolating between fiducial Auger spectra using the known Ti-O erosion kinetics discussed earlier.

Secondary photon emission measurements as a function of oxygen coverage were made on four transitions between the ground state of Ti^0 and the z^3F_4 ($19,574 \text{ cm}^{-1}$), z^3D_3 ($20,126 \text{ cm}^{-1}$), z^3G_5 ($21,740 \text{ cm}^{-1}$), 5D_4 ($25,927 \text{ cm}^{-1}$) levels. The data were evaluated in terms of R^* (excitation probability) values and are displayed in Fig. 11. The enhancement in excited state fractions ranges from a factor of 8.8

to 10.5 depending on the particular excited state in going from the clean surfaces to the two monolayer coverage condition. The limited data available on the Ti system indicates that excitation probabilities increase with increasing energy of the excited state in response to oxygen coverage.

Calculations are currently underway to see if this effect can be understood in the binary collision approximation involving now also collisions between oxygen and titanium atoms.

V. Summary

A review of the literature on atoms sputtered in electronically excited states is given together with a discussion of various mechanisms that have been proposed to account for the observations. The major observational features that have emerged from the older studies may be summarized as follows: (1) the kinetic energies of neutral atoms in highly excited electronic states are 1-2 orders of magnitude greater than E_p , the surface binding energy; (2) relative yields show approximately exponential dependence on excitation energy with characteristic "temperatures" measured in thousands of degrees; (3) absolute yields are lower by 2-3 orders of magnitude than secondary ion yields which themselves are usually very small compared to total sputtering yields. (4) In many cases, excited state yields increase 1-2 orders of magnitude as a result of surface oxidation.

Until recently, information concerning excited state sputtering has been based entirely on secondary photon emission data in the 2-4 eV energy region. The reason for this situation is that spin and parity allowed transitions, the ones which are in fact observed in secondary photon measurements, only rarely occur at energies less than 2 eV. However, the electronic density of states for many atomic systems is comparable in the 0-2 eV region to that in the 2-4 eV region. The low energy regime (0-2 eV) is beginning to be opened to study by the new technique of laser fluorescence spectroscopy (LFS). These measurements, although still in their infancy, are beginning to have a major impact on our view of electronic excitation mechanisms in sputtering.

One recent finding is that large fractions of sputtered flux goes into low-lying excited state channels. Another major result is that the velocity distributions of atoms sputtered in low-lying states is not as dramatically shifted to higher energies as claimed for more highly excited states. Thirdly, the development of "static" mode LFS and SCANIIR techniques has shown that the enhancement of excitation probabilities due to oxygen begins to saturate, at least for Ti-surfaces, at the two monolayer level.

The new results have led us to develop the "causal collision" model based on the TRIM code. Using Linhard-Scharff and Oen-Robinson prescriptions for electronic energy loss in solids, one can, assuming atoms in excited states to

originate at the surface, rationalize the observed functional dependence on energy of the fractions of atoms sputtered in excited states in a quite satisfactory way.

Further tests of this model await the results of calculations currently in progress for comparison with observed velocity distributions of atoms in excited states and excitation probabilities as functions of oxygen coverage.

Table I Results from the defining-slits experiment

| Line
°
(Å) | E_i
(eV) | Transition | v_s
($\times 10^4 \text{ ms}^{-1}$) | E_s
(eV) | v_f
($\times 10^4 \text{ ms}^{-1}$) | E_f
(eV) | τ
($\times 10^{-8}$) | E^*
(eV) |
|------------------|---------------|-----------------|--|---------------|--|------------------|--------------------------------|----------------|
| Si I 2882 | 5.08 | $3p^1D-4s^1P^o$ | 4.34 ± 0.59 | 272 ± 40 | 31.28 ± 5.35 | 14258 ± 2440 | 0.52 | 684 ± 140 |
| Ba I 5535 | 2.24 | $6s^1S-6p^1P^o$ | 1.90 ± 0.44 | 256 ± 30 | 15.91 ± 3.03 | 18038 ± 3430 | 0.83 | 1150 ± 130 |
| BaII 4934 | 2.51 | $6s^2S-6p^3P^o$ | 2.46 ± 0.28 | 432 ± 50 | 7.32 ± 1.19 | 3805 ± 620 | 0.78 | 830 ± 150 |
| Na I 5890 | 2.11 | $3s^2S-p^2P^o$ | 1.49 ± 0.19 | 26 ± 5 | 8.84 ± 1.76 | 932 ± 190 | 1.59 | 31 ± 7 |
| Ni I 3461 | 3.60 | $4s^3D-4p^5P^o$ | 1.10 ± 0.15 | 36 ± 5 | 2.78 ± 0.44 | 236 ± 40 | 2.81 | 101 ± 20 |
| Cr I 4254 | 2.91 | $4s^7S-4p^7P^o$ | 0.97 ± 0.10 | 21 ± 3 | 2.64 ± 0.46 | 189 ± 30 | 4.50 | 40 ± 8 |

E_i = energy of the upper level

v_s = velocity component normal to the target
surface of the 'slow' group of excited atoms

E_s = kinetic energy associate with v_s

E^* = threshold kinetic energy of excited atoms

v_f = velocity component normal to the
target surface of the 'fast' group
of excited atoms

E_f = kinetic energy associate with v_f

τ = life-time of the excited states =
 $1/\sum_i A_{fi}$

Table II. Fractional Occupation of Low-Lying Electronic States of Sputtered Atoms with Ground State Population = 1.

| Energy above
Ground State
(ev) | Fractional
Occupation | Atomic
Species | Spectroscopic
State | Bombarding Particle
and Energy (Kev) | Ref. |
|--------------------------------------|--------------------------|-------------------|------------------------|---|--------|
| 0 | 1.00 | -- | -- | -- | -- |
| .021 | .60 | Ti | 3F_3 | Ar ⁺ , 3 | 63 |
| .048 | .40 | Ti | 3F_4 | Ar ⁺ , 3 | 63 |
| .052 | .43 | Fe | 5D_3 | Ar ⁺ , 10 | 82 |
| .071 | .39 | Zr | 3F_3 | Kr ⁺ , 3 | 59 |
| .077 | .21 | U | 5K_5 | Ar ⁺ , 3 | 58, 66 |
| .087 | .21 | Fe | 5D_2 | Ar ⁺ , 10 | 82 |
| .11 | .097 | Fe | 5D_1 | Ar ⁺ , 10 | 82 |
| .12 | .029 | Fe | 5D_0 | Ar ⁺ , 10 | 82 |
| .15 | .24 | Zr | 3F_4 | Kr ⁺ , 3 | 59 |
| .47 | .005 | U | 5L_7 | Ar ⁺ , 3 | 58, 66 |
| .48 | .008 | U | 5H_3 | Ar ⁺ , 3 | 58, 66 |
| .84 | .015 | Ti | 5F_5 | Ar ⁺ , 3 | 58, 66 |
| .86 | .011 | Fe | 5F_5 | Ar ⁺ , 10 | 82 |
| .90 | .008 | Ti | 1D | Ar ⁺ , 3 | 63 |
| .91 | .007 | Fe | 5F_4 | Ar ⁺ , 10 | 82 |
| .95 | .004 | Fe | 5F_3 | Ar ⁺ , 10 | 82 |
| .99 | .002 | Fe | 5F_2 | Ar ⁺ , 10 | 82 |
| 1.01 | .001 | Fe | 5F_1 | Ar ⁺ , 10 | 82 |
| 1.46 | .002 | Ti | 5F_4 | Ar ⁺ , 3 | 63 |

Table III. Sputtering yield data from erosion kinetics of O/Ti Auger signal.

| region
(Fig. 2) | O/Ti (Auger)
at slope change | coverage
(monolayers) | S
(atoms/ion) | σ
(10^{-16} cm^2) |
|--------------------|---------------------------------|--------------------------|------------------|---|
| A | A-B = 0.92 | > 2 | 1.9 | 13 |
| B | B-C = 0.39 | 1 - 2 | 0.35 | 2.4 |
| C | C-D = 0.15 | .25 - 1 | 0.20 | 1.4 |
| D | | 0 - .25 | 0.11 | 0.7 |

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Figure Legends

- Figure 1. Energy-level model diagram with state 2 having an optically allowed transition to the ground state and another (3), but with no transition between states 1 and 3. Levels 1 and 2 are coupled by laser radiation.
- Figure 2. Diagram of the energy levels of neutral zirconium atoms which were investigated here. Vacuum level energies in cm^{-1} are displayed on the left-hand side, transition strength on the right-hand side.
- Figure 3. Number density velocity distribution of neutral ground-state zirconium atoms sputtered by normally incident 3-keV Kr^+ . (o) represent deconvoluted data averaged over several runs. The solid curves were generated using linear collision cascade theory.
- Figure 4. Number density velocity distribution of zirconium atoms sputtered in the a^3F_3 level, 570 cm^{-1} above the ground state. The primary ion was normally incident 3-keV Kr^+ . The solid curves are identical to those in Fig. 3.

- Figure 5. a 3F_4 zirconium atom number density velocity distribution. The primary ion was normally incident 3-keV Kr^+ . The solid curves are identical to those in Fig. 3.
- Figure 6. TRIM calculations of electronic energy loss versus the kinetic energy of the "causal collision" leading to sputtering.
- Figure 7. Data given in Table II (X) and TRIM code calculations for Ti^O (---).
- Figure 8. The kinetics of oxygen removal as monitored by AES at a position on the target receiving a current density of 5×10^{13} ions/cm². See (3 keV Ar^+). Four distinct erosion rates are identified A-D.
- Figure 9. Ti^O LFS signal as a function of O/Ti AES signal for the lowest multiplet.
- Figure 10. Excitation probability R^* from LFS data for several low-lying levels of Ti^O , as a function of oxygen coverage.
- Figure 11. Excitation probability R^* (arbitrary units) from secondary photon emission measurements for several higher-lying excited states of Ti^O as a function of oxygen coverage.

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Fig. 1

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Fig. 6. TRIM calculations of electronic energy loss versus the kinetic energy of the "causal" collision leading to sputtering.

Fig. 2. Data given in Table I (x) and TRIM code calculations for Ti^0 (---).

Fig. 10

Fig. 10