# Sputtering of Atoms in Fine Structure States: A Probe of Excitation and De-excitation Events

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**The electronic mechanisms leading to the formation of excited atoms from ion-bombarded metal surfaces have been examined in light of recent experimental observations. Specifically, populations and kinetic energy distributions are compared for metastable fine structure states of In, Rh, Ni, Co and Ag. The comparison shows that the populations of these depend strongly on the electronic configuration of the departing atom and its correspondence with the metallic band structure. Current hypotheses about fundamental processes are discussed. Missing parts of our understanding of these processes are enumerated, and a number of new experiments aimed toward filling in these gaps are proposed. © 1998 John Wiley & Sons, Ltd.**

Atomic and molecular desorption from ion bombarded surfaces is initiated not only by classical momentum transfer between colliding species but also by various processes. The electronic processes are particularly important in controlling the degree to which the desorbing species leave the surface in excited states or as positive or negative ions. An improved fundamental understanding of the basic mechanisms associated with these electronic events may indeed lead to more effective strategies for enhancing the ionization efficiency of desorbing species and to improve the prospects for mass spectral-based surface analyses.

In general, excited atoms may be classified into two categories. Atoms in short-lived states, on one hand, are easy to detect by their radiative decay and, therefore, a wealth of experimental information on atoms sputtered in such states can be found in the literature.[1] The interpretation of these data, however, is extremely complicated due to the convolution of radiative decay, cascading transitions and emission velocity. Metastable atoms, on the other hand, preserve their excitation state until detection at large distances from the surface, and hence lend themselves to

the study of the physical mechanisms behind the formation of excited atoms in sputtering.

Only a limited number of experiments aimed toward characterizing metastable atomic or molecular excited species formed during ion bombardment have been performed, primarily due to the difficulty in finding sensitive and state-selective methods by which populations and other properties can be probed. Early experiments involving Doppler-shifted, laser-induced fluorescence (LIF) provided the first hint of how electronic energy might be partitioned among various atomic states.[2–7] Some of these results are summarized in Table 1. From this limited set of information, a correlation between the characteristics of the kinetic energy distributions and fundamental properties of the atoms was proposed. Atoms such as Zr and Fe ($^5D_j$ manifold), which are ejected in states with small excitation energies, have the same kinetic energy distributions as the ground state atoms. On the other hand, atoms ejected in states with high excitation energies like Fe ($^5F_5$), Ba and Ca have kinetic energy distributions that peak at a higher energy and are broader than the ground state kinetic energy distributions. These variations in the kinetic energy distributions have been explained using a non-radiative de-excitation model developed originally by Hagstrum to explain ion scattering and ion neutralization experiments.[8]

The application of multiphoton resonance ionization spectroscopy (MPRI) to detection of sputtered atoms made it possible to detect almost any ground or metastable excited state.[9] In LIF there must be an available intermediate state that spontaneously fluoresces, to which the atom in the state to be probed can be excited. On the other hand, in MPRI the atom in the state of interest is excited to an intermediate state, and a second photon is used for ionization as shown schematically in Fig. 1 for Ni. In addition, MPRI provides sufficient sensitivity to permit angular resolution of the energy distributions. As an aside, the possible richness of

**Table 1. Fine structure states measured in keV particle bombardment experiments**

| At. | States | Atomic Config. | E (eV) | Rf. | Energy Distribution[a] | T or % Pop[b] |
|---|---|---|---|---|---|---|
| | **LiF** | | | | | |
| Zr | $^3F_{2,3,4}$ | $4d^2 4s^2$ | <0.15 | 2 | Same | ~800K |
| Fe | $^5D_4, ^5F_5$ | $3d^6 4s^2, 3d^7 4s^1$ | 0.86 | 3 | ExcSt broader than GrndSt | |
| Ba | $^1S, ^3D, ^1D$ | $6s^2, 6s^1 6p^1$ | 1.4 | 4 | ExcSts broader than GrndSt | |
| Ca | $^3P_2$ | $4s^1 4p^1$ | 1.89 | 5 | broader than "assumed" GrndSt ($^1S_0, 4s^2$) | |
| Ti | $^3F_1, ^1D_2$ | $3d^2 4s^2$ | 0.9 | 6 | ExcSt broader than GrndSt | ~300K |
| Fe | $^5D_{4,3,2,1,0}$ | $3d^6 4s^2$ | 0.12 | 7 | Same as GrndSt | ~600K |
| | **MPRI** | | | | | |
| In | $^2P_{1/2,3/2}$ | $5s^2 5p^1$ | 0.30 | 11 | | 0% |
| Rh | $^4F_{9/2,7/2,5/2}$ | $4d^8 5s^1$ | <0.32 | 13,14 | ExcSts broader than GrndSt | 100%,26%,1% |
| Ti | $^3F_{4,3,2}$ | $3d^2 4s^2$ | <0.05 | 29 | Same | |
| Ni | $a^3D_{3,2,1}$ | $3d^9 4s^1$ | <0.21 | 29 | | |
| Ni | $a^3F_{4,3,2}$ | $3d^8 4s^2$ | <0.27 | 29 | | |
| Ni | $a^3D_{3,2,1}$ | $3d^9 4s^1$ | <0.21 | 27 | Same | 810K |
| Ni | $a^3F_{4,3,2}$ | $3d^8 4s^2$ | <0.27 | 27 | Same & Narrower than $^3D$ | 10,500K |
| Ni | $a^1D_2$ | $3d^9 4s^1$ | 0.42 | 27 | Same as $^3D$ | |
| Ni | $a^3F_{4,3,2}$ | $3d^8 4s^2$ | <0.27 | 30,31,32 | $^3F_4$ Narrower than $^3D_3$ | 100%–10% |
| Ni | $a^3D_{3,2,1}$ | $3d^9 4s^1$ | <0.21 | 30,31,32 | | 160%–10% |
| Ni | $a^1D_2$ | $3d^9 4s^1$ | 0.42 | 30,31,32 | | 10% |
| Ni | $b^1D_2, a^3P_{2,1}, a^1G_4$ | $3d^8 4s^2$ | 1.68–2.74 | 30,31,32 | Same as $^3F_4$ | ~10% |
| Ni | $a^1S_0$ | $3d^{10}$ | 1.83 | 42 | Same as $^3F_4$ | ~10% |
| Co | $a^4F_{9/2,7/2,5/2,3/2}$ | $3d^7 4s^2$ | <0.17 | 31,32 | Same as $a^4F_{9/2}$ | 100%–1% |
| Co | $b^4F_{9/2,7/2,5/2,3/2}$ | $3d^8 4s^1$ | <0.58 | 31,32 | Same & broader than $a^4F_{9/2}$ | 10%–1% |
| Co | $a^4P_{5/2,3/2}, a^2G_{7/2}$ | $3d^7 4s^2$ | 1.74–2.14 | 31,32 | Same as $a^4F_{9/2}$ | 1% |
| Co | $b^4P_{5/2,3/2,1/2}, a^2D_{5/2}, a^2P_{3/2,1/2}$ | $3d^8 4s^1$ | <1.95–2.33 | 31,32 | Same as $a^4F_{9/2}$ | 1% |
| Co | $b^2P_{3/2,1/2}$ | $3d^7 4s^2$ | <2.63 | 31,32 | Same as $a^4F_{9/2}$ | 0.1% |
| Ag | $^2S_{1/2}, ^2D_{5/2}$ | $4d^{10} 5s^1, 4d^9 5s^2$ | 3.75 | 33,34,35 | $^2D_{5/2}$ Narrower than $^2S_{1/2}$ | 1.5–5% |

[a] Same means all energy distributions within manifold are the same. GrndSt is ground state and ExcSt is excited state.
[b] % population relative to the ground state. Values give an indication of the order of magnitude only and are not precise values.

fine-structure states as probes of electronic events is exemplified by Ni. A number of states have been identified and are characterized by different atomic configurations (e.g. $3d^8 4s^2$ or $3d^9 4s^1$) and varying excitation energies.

In this paper, we examine the current level of our understanding about the dominant mechanisms that determine the final electronic state of ejected atoms. This analysis is particularly timely in view of the extensive amount of new data that has appeared recently. For example, it is now clear that the original proposals related to Hagstrum's non-radiative de-excitation model are not consistent with the whole of this new information. The electronic character of the excited states and resonant tunneling probabilities must factor into the picture in some fashion. Our discussion points out inconsistencies still to be resolved, and suggests future experiments that might lead to a unified theory of this important phenomenon.

## TECHNIQUE

The MPRI technique as applicable to keV particle bombardment or sputtering has been described earlier[9] and in the primary work summarized here. In addition, there is an article in this issue that relates to the approach used in the Winograd lab.[10] Briefly the MPRI scheme involves resonantly exciting an atom to an intermediate electronic state as shown in Fig. 1 and then using a second photon to ionize the atom. Since a resonance step is involved in the ionization process of the atom, it is fairly straightforward to selectively measure the kinetic energy and angular distributions of atoms ejected in specific fine-structure states. Comparing the relative populations of the different states

involves the efficiency of the overall ionization process, which depends mainly on the cross section for photoionization. This cross section can vary strongly with photon energy. In general, a direct comparison of the photo-ion signals obtained by using simple one-color ionization schemes thus cannot directly be used to determine a quantitative population distribution. Examples of measured kinetic energy, angle and population distributions are given below.

## DE-EXCITATION

The first system[11] investigated by MPRI is In $5s^2 5p^1$. The ground state is a $^2P_{1/2}$ state and the first excited state, $^2P_{3/2}$, lies 0.30 eV above the ground state.[12] The kinetic energy distributions of atoms nominally in each of these fine-structure states were measured along with the energy distribution of $In_2$ dimers. Analysis of the various distributions led the authors to conclude that the supposed $^2P_{3/2}$ signal arose from dissociation of $In_2$ dimers. Consequently, Craig *et al.* suggested that the electronic structure of the fine-structure state is the main factor in determining whether a given state will relax, and that de-excitation is not correlated to the excitation energy.[11] According to the Craig model, in manifolds with a closed outer shell of electrons (e.g. $ns^2$), the de-excitation rate will be negligible and the excited state kinetic energy distribution will be the same as the ground state distribution, provided that the initial excitation probability is weakly dependent on velocity. For a manifold which is partially filled (e.g. $ns^1$) there will be interaction of the departing atom with the metallic band and the kinetic energy distribution will
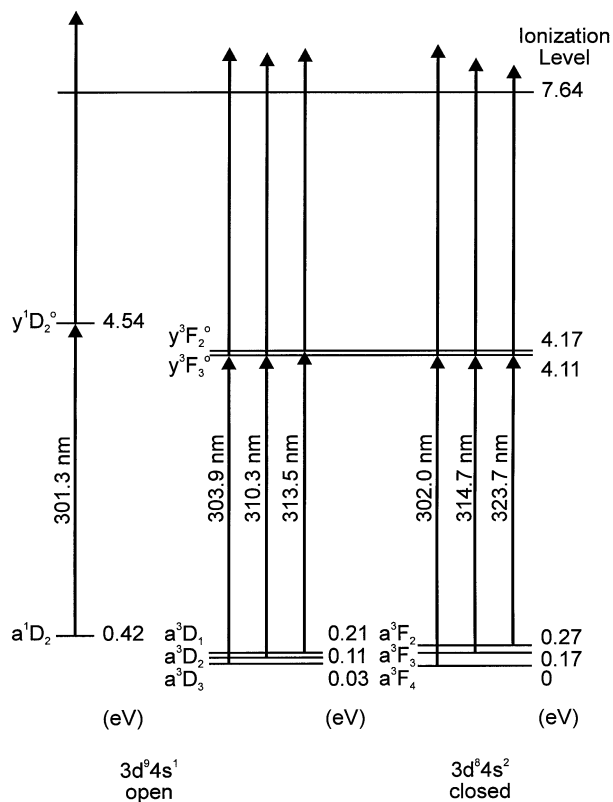
**Figure 1.** Partial electronic structure of atomic Ni showing the ionization schemes used in Ref. 27. The energy of each state above the ground state is noted in units of electron volts.[12]
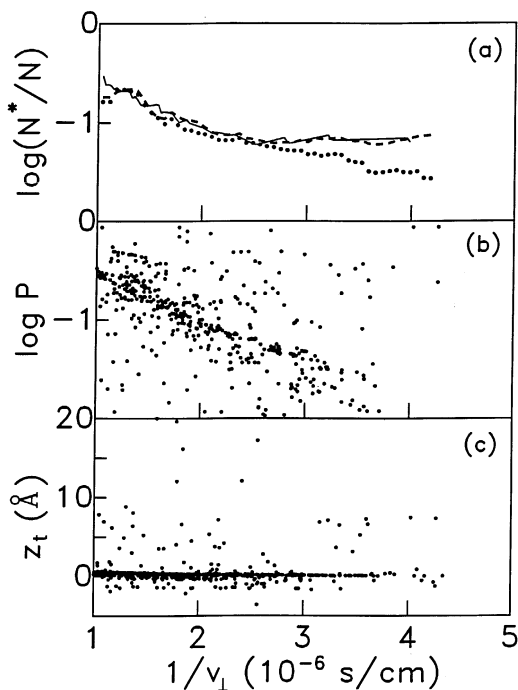


**Figure 2.** Results of electronic excitation calculations. (a) $\log(N^*/N)$ vs. $1/v_\perp$ for particles ejected within 20° of the surface normal. Solid line represents the experimental data. Dashed line represents prediction of simulations for all particles ejected within 20° of the surface normal. Dotted line represents the atoms which are excited below 1 Å of the surface. (b) Excitation probabilities for individual atoms as predicted by the simulations. (c) Height above the surface ($z_t$) at which an atom was last excited. A value of $1/v_\perp = 2.5 \times 10^{-6}$ s/cm corresponds to a kinetic energy of $\sim$8.5 eV for Rh. Reprinted from *Comput. Phys. Commun.*, Vol. 80, D. N. Bernardo, R. Bhatia and B. J. Garrison, p.259, Copyright 1994, with permission from Elsevier Science.

broaden or, in the case of In, the excited state is completely relaxed. In general, the Craig shielding model[11] works for most cases studied at that time.

This investigation of the In system initiated thinking and experiments to further probe the electronic events that occur during keV particle bombardment. The Craig model, however, only describes the de-excitation process. There is also the excitation process to be considered, which can have some interesting twists.

## EXCITATION — COLLISIONS ABOVE THE SURFACE

As a test case for the Craig model, energy and angular distributions were measured by MPRI for the ground ($^4F_{9/2}$) and first excited ($^4F_{7/2}$) states of Rh sputtered from Rh{001}.[13,14] As suggested by the Craig model, for partially shielded configurations (i.e. $4d^85s^1$) the excited state has a broader kinetic energy distribution than the ground state. A discrepancy appears, however, when one takes the Hagstrum model[8] and plots $\log(N^*/N)$ vs. $(1/v_\perp)$, as shown as a solid line in Fig. 2(a), where $N^*$ is the intensity of atoms sputtered in the excited $^4F_{7/2}$ state, $N$ is the intensity of atoms sputtered in the ground $^4F_{9/2}$ state, and $v_\perp$ is the perpendicular velocity component of the atom leaving the surface. The linear relation predicted by Hagstrum of $\log(N^*/N)$ vs. $(1/v_\perp)$ is observed at high velocities. At low velocities, however, $(N^*/N)$ becomes independent of $(1/v_\perp)$. This abrupt leveling off cannot be attributed to the binding energy effect, which produces a more gentle change in curvature.[15–17]

Based on the success of molecular dynamics (MD) simulations in describing the kinetic energy and angular distributions of ground state atoms ejected due to keV particle bombardment,[18–20] a simple approach was tried for understanding this anomalous velocity dependence of the excited state intensity. Based on the curve-crossing model of Fano and Lichten[21] and similar computational studies,[22,23] Bernardo *et al.* assumed that colliding atoms are excited when the interatomic distance drops below some threshold value.[13,24,25] Each individual atom's excitation is subjected to a time-dependent decay, based on a lifetime that is empirically based but does depend on the local environment of the atomic motion. This parameterization does not involve any assumptions regarding the velocity or angles of ejection.

The individual excitation probabilities predicted by this MD model, including excitation events are shown in Fig. 2(b). Most apparent is the large spread in excitation probabilities. The averages of these values are given as the dashed line in Fig. 2(a), which follows the experimental line. Insight into the low velocity behavior of the excitation probability can be gained by examining Fig. 2(b). Although most particles follow the exponential decay there are a few particles that have quite high excitation probabilities. The excitation history of these atoms can be examined using the MD simulations, and it is thus found that these atoms have been last excited by collision with other atoms at some distance ($z_t \sim$1–20 Å) above the surface (Fig. 2(c)). In other words, the vast majority of the particles are excited in a

collision near the surface, and these relax as would be expected. There are a few collisions, however, involving particles above the surface. Once excited, these particles have relatively little time near the surface to relax. This effect is more important at low velocities as virtually all excited state atoms created near the surface relax to the ground state.

He *et al.* subsequently measured the next state, $^4F_{5/2}$, of Rh, and found that the ratio of the intensity in the $^4F_{5/2}$ state to the ground $^4F_{9/2}$ state is independent of velocity for nearly all velocities.[14] Based on input from both experiment and the MD simulations, a simple model was developed to predict the kinetic energy and angular distributions of atoms in those excited states that were created in collisions above the surface.[26] These collisions above the surface are relatively rare, accounting for <3% of the total sputtering yield. They are, however, the dominant mechanism in this system for creation of particles in excited fine structure states. Thus there is more to predicting final populations than simply using a relaxation model. This conclusion becomes even more apparent in the next section.

## INITIAL STATE EFFECTS, HIGH LYING STATES AND ANOMALOUS ENERGY DISTRIBUTIONS

Since 1995 there have been a series of very interesting published observations[27–35] on systems that have atomic configurations comprising either a shielding outer shell, i.e. $ns^2$, or a partially shielding outer shell, i.e. $ns^1$. Such a system is shown in Fig. 1 for Ni. There is one configuration with a shielding outer shell, $3d^84s^2$, of which the lowest manifold is $a^3F$, although there are many more states with the same atomic configuration as denoted in the Table. The related configuration with a partially shielding outer shell, $3d^94s^1$, has two low lying manifolds, $a^3D$ and $a^1D$. Although the $^3F_4$ state is the ground state of atomic Ni, it is the $3d^94s^1$ configuration (D states) that primarily participates in bonding of diatomic $Ni_2$[36,37] and metallic Ni.[38,39] In fact, the interaction between two Ni atoms both in $^3F$ states is repulsive.[40]

He *et al.* measured kinetic energy distributions of the $a^3F_{4,3,2}$, $a^3D_{3,2,1}$ and $a^1D_2$ states of Ni produced by 5 keV $Ar^+$ bombardment of Ni{001}.[27] All kinetic energy distributions of D state atoms were found to be alike and all energy distributions of the F state atoms are more narrow than the D state distributions and peak at a lower energy. The kinetic energy distributions for the lowest level of each configuration are shown in Fig. 3. Also shown in Fig. 3 is the energy distribution predicted by molecular dynamics simulations.[41] The calculated distribution fits the distribution for the D states. Thus it appears that the energy distributions from the $a^3F_4$ ground state peak at an anomalously low energy. He *et al.* also had found indications that the D states might actually be more heavily populated than the F states.[27,28]

Vandeweert *et al.* designed MPRI ionization schemes using two laser wavelengths such that for different initial states of interest, there are common intermediate states and the same final autoionizing states. In this manner they could measure relative intensities of Ni atoms ejected in each state by canceling out cross-sections.[30,31,32] As shown in the top frame of Fig. 4 the population distribution of Ni atoms sputtered in different fine structure states by 12 keV $Ar^+$ bombardment of a pure polycrystalline foil is not even close to a Boltzmann distribution.[30] On the other hand, the
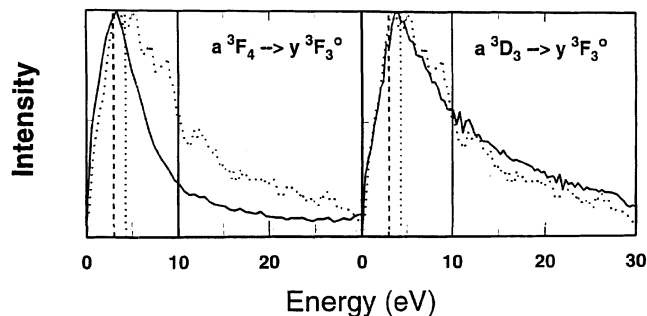


**Figure 3.** State-selected angle-integrated kinetic energy distributions of Ni atoms ejected from Ni {001} bombarded with 5 keV $Ar^+$ ions. The peak energy of the F states is $\sim 3 \pm 0.5$ eV (dashed vertical line) and of the D states is $\sim 4.3 \pm 0.5$ eV (dotted vertical line). The energy distributions denoted by dotted curves are from molecular dynamics simulations.[41] Figure was adapted from *Phys. Rev. Lett.*, Vol. 75, C. He, Z. Postawa, S. W. Rosencrance, R. Chatterjee, B. J. Garrison and N. Winograd, p.3950. Copyright 1995, with permission from the American Physical Society .

populations of Ni atoms evaporated from a wire heated to $1550 \pm 100$ K exhibit a well-behaved Boltzmann distribution, as shown in the bottom frame of Fig. 4. There are two points of note. First, these results confirm the suggestion of He *et al.*[27] that the $^3D_3$ (and $^3D_2$) states are more populated
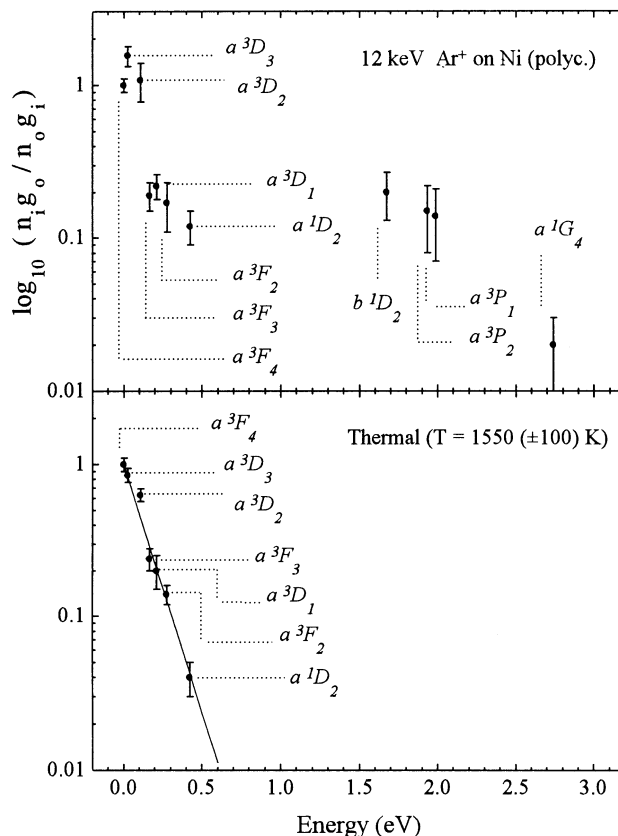


**Figure 4.** Population distribution of Ni atoms produced by thermal sublimation of a wire (lower frame) and by 12 keV $Ar^+$ bombardment of a polycrystalline foil (upper frame). The populations ($n_i$) are given relative to the ground state and corrected for the degeneracy of each state ($g_i$). Reprinted from *Phys. Rev. Lett.*, Vol. 78, E. Vandeweert, V. Philipsen, W. Bouwen, P. Thoen, H. Weidele, R. E. Silverans and P. Lievens, p.138. Copyright 1997, with permission from the American Physical Society.

than the ground $^3F_4$ state. Second, significant intensity ($\sim$10% of the ground state) was observed in metastable states that lie 1.5–2 eV above the ground state!

Similar measurements have been performed on polycrystalline Co which has two atomic configurations, $3d^74s^2$ and $3d^84s^1$, similar to those of Ni.[31,32] In this case the $a^4F$ ($3d^74s^2$) manifold lies completely below the $b^4F$ ($3d^84s^1$) manifold, and the states are not intertwined as in Ni. The populations of the $a^4F$ and $b^4F$ subsets of states, with the same electronic configuration, both exhibit an exponential decrease with excitation energy but the populations of the $b^4F$ ($3d^84s^1$) states are clearly shifted to higher values with respect to the population of the $a^4F$ ($3d^74s^2$) states. Again metastable states that lie 1.7–2.2 eV above the ground state were observed, at populations at the $\sim$1–0.1% level.

For both Co and Ni, the Leuven group found that the kinetic energy distributions of atoms sputtered into low-lying metastable states depend on the electronic configuration of the state. Co and Ni atoms with a partially filled outer shell configuration ($3d^x4s^1$ with $x = 8$ for Co and 9 for Ni) tend to have kinetic energy distributions which peak at a higher energy,[32,42] similar to the energy distribution shown on the right side of Fig. 3. Kinetic energy distributions for low lying metastable states with a closed outer shell configuration ($3d^{x-1}4s^2$), on the other hand, tend to peak at lower energies, similar to the distribution shown on the left side of Fig. 3. For atoms sputtered into metastable states with excitation energies at least 1.5 eV above the ground state, the kinetic energies of the Ni states (only the $3d^{x-1}4s^2$ states are present) seem to be either intermediate between the above distributions, or to be similar to the ground state ($3d^{x-1}4s^2$) distribution. The kinetic energy distributions of the high-lying Co states look similar to the ground state distribution, irrespective of their atomic configuration.[42]

To add further insight or confusion, Berthold and Wucher have measured the population and energy and angular distributions for the excited $^2D_{5/2}$ ($4d^95s^2$) state of Ag.[33–35] The population in the $^2D_{5/2}$ state ranges from $\sim$1.5–5% of the ground $^2S_{1/2}$ ($4d^{10}5s^1$) state, depending on the bombarding particle, even though it is 3.75 eV above the ground state in energy![34,35] The energy distribution of the excited state peaks at a lower energy than that of the ground state.[33,35]

## CURRENT STATUS

There are several questions which have been brought to the fore by these new studies.

1. Why are there anomalously high populations for the low lying states with a $3d^x4s^1$ atomic configuration in Ni and Co vs those with a $3d^{x-1}4s^2$ configuration?

2. Why are there relatively high populations observed for states (1.5 to 2 eV) above the ground state in Ni and Co? Is the formation mechanism the same as for the 3.75 eV state of Ag?

3. Why are the energy distributions for all the $^{3,1}D$ ($3d^94s^1$) states of Ni alike even though there is an open s shell, whereas the Rh ($4d^85s^1$) states exhibit broadening of the energy distributions? Why do the highly excited open shell states ($3d^84s^1$) of Co even survive at all with significant populations? According to the Craig model[11] they should relax. Of note is the fact that the Rh data and one set of the Ni data were obtained by the same workers using the same experimental apparatus, and similarly one set each

of the Ni data and of the Co data were obtained by the same workers and the same apparatus. Thus, variations in experimental procedures are unlikely to be suspect.

4. Why do the kinetic energy distributions of the low lying $3d^{x-1}4s^2$ states of Ni, Co, and the $4d^95s^2$ state of Ag, peak at 'low' values, and why are the kinetic energy distributions of Ni and Co atoms sputtered into highly excited metastable states only weakly (or not at all) dependent on their atomic configuration? For atoms sputtered into metastable states with excitation energies at least 1.5 eV above the ground state, why do the kinetic energy distributions bear close resemblance to the distributions obtained for the closed shell ($3d^x4s^2$) atoms, irrespective of their atomic configuration?

As long as the data about excited state populations and kinetic energy distributions were limited, one could use simple phrases and concepts to explain qualitatively what is occurring. As the richness of the data has increased, however, the simple concepts become inadequate. Some of the questions asked above have been at least partially settled, but others are left to future investigations, both experimental and theoretical.

Both the significant population of high-lying states, and the enhanced populations of the low-lying $3d^x4s^1$ states over the $3d^{x-1}4s^2$ states in Ni and Co, have been interpreted by the Leuven group as evidence for the important role of resonant electron tunneling during the emission process, and its dependence on the correspondence of the electronic atomic configuration with the bulk band structure.[30,31,32] One essential element of the resonant tunneling model is that all states lying within the energy window of the valence band will have a substantial probability of being populated.[43,44,45] This requirement is fulfilled for all populated states, but the populations depend on the energy-level broadenings and shifts which are functions of the distance to the surface.[32,42] Furthermore, atomic states with electronic wave functions having good overlap with those of the valence electrons in the metal will be preferentially populated. Indeed, the probability that an electron tunnels from the metal to the departing ion depends on the coupling matrix element between the final state of the atom and the metal.[43–45] The fact that the valence band electronic structure of Ni,[39] and to a lesser extent Co,[38] is predominantly $4s^1$ in character, explains the enhanced population of the states with $3d^x4s^1$ configuration. It should be remarked that the concept of resonant tunneling was already used by Veje years ago to explain large populations of excited state atoms ejected due to bombardment with 80 keV Ar$^+$ ions, observed in photon emission studies.[46]

The significant population of the $4d^95s^2$ configuration of Ag cannot be explained solely by a simple tunneling process, since this state lies at a higher energy than the top of the conduction band. Wucher and Sroubek therefore invoked the creation by the incoming ion of a d-band hole which stays localized sufficiently long such that an Ag$^+$ ion with the configuration $4d^95s^1$ starts to sputter.[47] The ion is then resonantly neutralized by an electron preferentially entering the s orbital, thus, accounting for the occurrence of $4d^95s^2$ excited states. It has to be determined, however, whether a similar mechanism of excitation of valence band electrons can contribute to the population of the Ni and Co excited states.

A natural question then is, why do the populations from the evaporation experiments (Fig. 4) not exhibit a high $^3D_3$

population? One could assume that the observed population distribution in the sputtering experiments reflects the true initial population in the solid. Since the removal of particles by evaporation is very slow compared with removal by sputtering, the atoms and electrons reach thermal equilibrium and the atoms desorb according to a Boltzmann distribution. On the other hand, energetic processes in the collision cascade could produce anomalous populations even though the initial populations might be Boltzmann-like. In this case the observed population distribution in the sputtering experiment reflects the excitation process and not the initial population. There is, of course, an intermediate situation where both the initial population is not Boltzmann-like and the collision cascade is preferentially populating some fine structure states.

In addition to explaining the anomalously large populations of highly excited states, kinetic energy distributions of excited states that peak at low energies need to be understood. If one assumes that the non-radiative de-excitation model is appropriate, then the survival probability of an atom emitted in an excited metastable state relative to one in the ground state is generally given by an expression of the form:[8]

$$P \propto \exp(-a/v_\perp)$$

where $a$ is a constant. It is this velocity dependence, in fact, that was assumed to account for the observation that atoms formed in excited states which exit with low velocities tend to relax to the ground state more readily than those with higher velocities. Thus atoms ejected in excited states should have kinetic energy distributions which peak at higher energies than atoms ejected in the ground state. This has been the conventional wisdom for ions since the work of Hagstrum,[8] and certainly is the language that many use.[11] How, then, does one explain the kinetic energy distributions of atoms in excited states that appear to peak at lower energies than those of ground state atoms?

The resonant electron transfer model in the wide band limit gives, if the energy difference between the departing ionic state and the final atomic state is much larger than the work function of the metal, a neutralization probability which at high velocities decreases with increasing velocity.[43] Wucher and Sroubek derived, for the neutralization probability of the departing Ag ions containing a d-hole, a dependence of the form $P_{\text{neutr.}} \sim 1 - \exp(-b/v)$, which was used to explain the narrowing of the excited state kinetic energy distribution compared to the ground state distribution.[47] It provides no explanation, however, for the observed angular distributions.[35] On the other hand, the fact that the neutralization transition rate depends on the coupling strength has been used as a possible explanation for the systematic differences in kinetic energy distributions of the low-lying Ni and Co states with different electronic configuration; that is, the shorter the interaction time, the less probable is electron transfer to states with weak coupling.[32,42]

## PROSPECTS

Even with the recent spate of data describing the detailed behavior of a variety of excited states in sputtering atoms, a unified picture of how these states form is still elusive. It is clear, however, that the magnitude of the excitation energy, the character of the electronic state, the character of the band-structure of the substrate, the excitation mechanisms, and the de-excitation mechanisms are essential components of the overall events. The development of MPRI to assess the roles of these various components over a range of species and states has certainly opened new research avenues.

A number of obvious future experiments present themselves. Rh has states of atomic configuration $4d^7 5s^2$ about $\sim 1.5$ eV above the ground state. Will these be highly populated with kinetic energy distributions that peak at a low energy? Other elements with intertwined energy levels in two fine structure manifolds are W, Os and Ir.[12] Do these elements exhibit similar population and energy distribution characteristics? Do the angular distributions for the Ni and Co systems follow the same trends as for the Ag system? Some of the proposed models predict that there should be some dependence on work function. Yu and Lang have performed elegant experiments measuring ion intensities as a function of work function by varying the surface coverage of alkali metals.[48] Would similar experiments on any of these systems yield further insight into the excitation and de-excitation mechanisms? In addition, could alloy systems, where the d character of the band structure can be changed systematically, provide guidance as to the role of electronic structure? Will it be possible to observe excited states from desorbing molecular adsorbates and will it be possible to make a connection to ionization probability? Clearly, there are many complex implications associated with these questions, and their answers will continue to provide pieces, which hopefully form a simple yet predictive picture.

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