REFERENCES

1. R.S. Blewer, Solid State Techn., 10, 117 (1986).
2. H.H. Brongersma and P.M. Mul, Chem. Phys. Lett. 14, 380 (1972).
3. H.H. Brongersma, L.C.M. Beirens and G.C.J. van der Ligt in Material Characterization Using Ion Beams, ed. J.P. Thomas and A. Cachard, Plenum Publ. Co. (1978).
4. R.J. Corte, E. Altman, G.R. Corallo, M.R. Davidson, D.A. Asbury and G.B. Hoflund, Surf. Sci. 188, 327 (1987).
5. K. Akitmoto and K. Watanabe, Appl. Phys. Lett. 39, 445 (1981)
6. A.R. Miedema, Z. Metallk. 69, 455 (1978).
7. G.J.A. Hellings, H. Ottevanger, S.W. Boelens, C.L.C.M. Knibbeler and H.H. Brongersma, Surf. Sci. 162, 913 (1985).

The Influence of radiationless deexcitation Processes on the Energy Distribution of sputtered excited Atoms

P. Wurz, G. Betz, E. Wolfrum, B. Strehl and W. Husinsky
Institut für Allgemeine Physik,Technische Universität Wien,
Wiedner Hauptstr. 8-10, A-1040 Wien, Austria

and

P. Nordlander, N. H. Tolk, and R. F. Haglund Jr.,
Center for Atomic and Molecular Physics at Surfaces
Department of Physics and Astronomy,
Vanderbilt University Nashville,Tennessee 37235,USA

1.Introduction

The experimental characterization and theoretical significance of the velocity distribution of ground, metastable and excited state sputtered particles continues to be a subject of active controversy. In particular, the microscopic, electronic mechanism responsible for the velocity dependence of the relative population of these states remains an elusive mystery. In this paper, we describe measurements of the velocity distributions of excited neutral Al, Ca, Cr and Be atoms sputtered from clean and oxygen exposed surfaces which shows radically unexpected behavior.

First direct Laser Induced Fluorescence (LIF) measurements of the energy distribution of sputtered metastable atoms[1-2], in general, showed agreement with sputtered ground state atoms peaking in the range between 1 and 5 eV. Previously, the energies of sputtered excited atoms were believed, on the basis of light intensity versus distance measurements (LvD)[4,5], to be higher by orders of magnitudes. Higher energies have also been deduced from measurements of the broadening of the line-profile of emission lines[6,7]. Theoretical models[8,9] for the excitation process based on these measurements have been proposed. However, LIF measurements of atoms sputtered in a metastable state with electronic configurations different from the ground state and with excitation energies (1-2 eV) comparable to short lived excited states (2-6 eV) yielded average energies in the range of 5-10eV. This is substantially higher than the energies of ground state atoms but also in disagreement with the conclusions from LvD measurements.

2. Experimental

We have studied Doppler-broadened line-profiles of resonance lines of sputtered excited Cr (Cr I 425,4nm), Ca (Ca I, 422,7nm), Al (Al I, 396,2nm) and Be (Be I, 234,9nm; Be I, 332,1nm) atoms. All targets have been bombarded with 15 keV Argon ions with a current density of $5\mu A/cm^2$. Oxygen coverage of the target during ion bombardment was achieved by varying the oxygen partial pressure in the UHV chamber (base pressure $<10^{-9}$ mbar). The ion beam hit the target almost perpendicular (15°) and the observation of the bombardment induced light emission was parallel to the surface. A one meter monochromator with a grating of 3000 lines/mm was used. The resolution for each experimental run was determined with a hollow-cathode lamp and was typically 0.01nm for a slit width of 30µm.

To obtain a velocity distribution from the measured line-profiles, as a first order approximation the sputtered flux of excited neutrals can be interpreted as a superposition of two distinct contributions: i) a collision cascade contribution with low average energies, and ii) an energetic contribution due to recoil sputtering.[6,7] For normal or almost normal ion beam incidence contribution i) will dominate and we have assumed the validity of the Thompson distribution function[2,10] where v^* is linked to the maximum of the energy distribution E^* by $E^* = mv^{*2}/4$. Previous LIF measurements of sputtered excited metastable atoms [1-3] showed that the velocity distribution may be well described by a Thompson like shape. In this work we also assume a cosine angular distribution for sputtered excited atoms. Under these assumptions $v^*(E^*)$ becomes a useful parameter, describing the average velocity (energy) of sputtered excited particles. Furthermore, in this case the theoretical line profile due to Doppler-broadening can be calculated analytically for an arbitrary observation direction.

$$\frac{d^3\Phi}{d\Omega dv} \propto \frac{v^3}{(v^2+v^{*2})^3} \qquad (1)$$

In this study the experimentally obtained resonance line profiles are compared with the Thompson line profiles which have been convoluted with the spectrometer resolution function. A good fit is taken as evidence that the particles originate from a collision cascade. As mentioned above a contribution due to recoil sputtering should be more pronounced for grazing ion beam incidence and this indeed, was experimentally verified for grazing ion beam incidence[11].

3. Results and Discussions

In contrast to the predictions of the standard resonant tunneling model[7,12], we observed that it is possible for the velocity distribution of excited atoms sputtered from the metal to be broadened, narrowed or unchanged relative to sputtering from its oxide. These distinctive changes in velocity distributions can be correlated with the changes in the surface electronic structure due to oxidation.

When atoms are desorbed from a surface by momentum-changing collisions, the final states of the sputtered atoms may evolve from the following: (1) exit-channel states which are adiabatically connected to hybridized states of the particle-surface system; (2) exit-channel states which are populated or depopulated by electron exchange processes in the final-state surface interaction (e.g., tunneling or Auger processes); (3) atomic states deriving from ejected molecules in pre-dissociative states; and (4) atomic states produced by secondary-electron excitation.

In the conventional resonant tunneling model describing the differences of the velocity distributions between sputtering of a metal and its oxide, it is assumed that the higher velocities of atoms sputtered from metals, relative to their oxides, result from loss of slow particles from the excited atomic state due to resonant tunneling of electrons into unoccupied states above the Fermi level.

At the same time, it is assumed that both the enhanced yield of sputtered excited atoms from the oxide and their velocity distribution can be explained by the band structure of the oxide, in particular by the lack of de-excitation channels available in the band gap. However, our results indicate that both the presence of surface states in the oxide and the interaction of the free atom state with metallic electron states influence the velocity distributions significantly. We have found that we can explain all experimental results under the assumption of resonant processes, if we take into account shifts of the excited atomic levels in the near surface region.

Figure 1 shows the relevant electronic level schemes. For Al, the atomic 4s level lies significantly above the Fermi energy E_f. Nearly the same situation applies to the Cr 4p level, and at a first glance we would expect the possibility of resonance ionization. On the other hand the Ca 4p level lies below E_f thus prohibiting tunneling. This also applies to Cr_2O_3. For Al_2O_3 and CaO the atomic levels lie in the bandgap and we do not expect any possibility of de-excitation. For Be both the $2p^1$ level as well as the $3s^3$ level are both above E_f for the metal and are located in the bandgap for the oxide. Thus we would expect deexcitation only for the metal. These simple expectations are based on the assumptions that the relevant atomic states are those of the free atom. However, when an atom is close to a surface its valence electronic levels can shift and broaden substantially[13-16].

To get an estimate of the atomic level shift in the surface region, we used a simple Anderson Hamiltonian and calculated the shifts of the excited atomic levels due to hybridization with the metal states[15]. The calculated shifts are also indicated in Fig. 1.

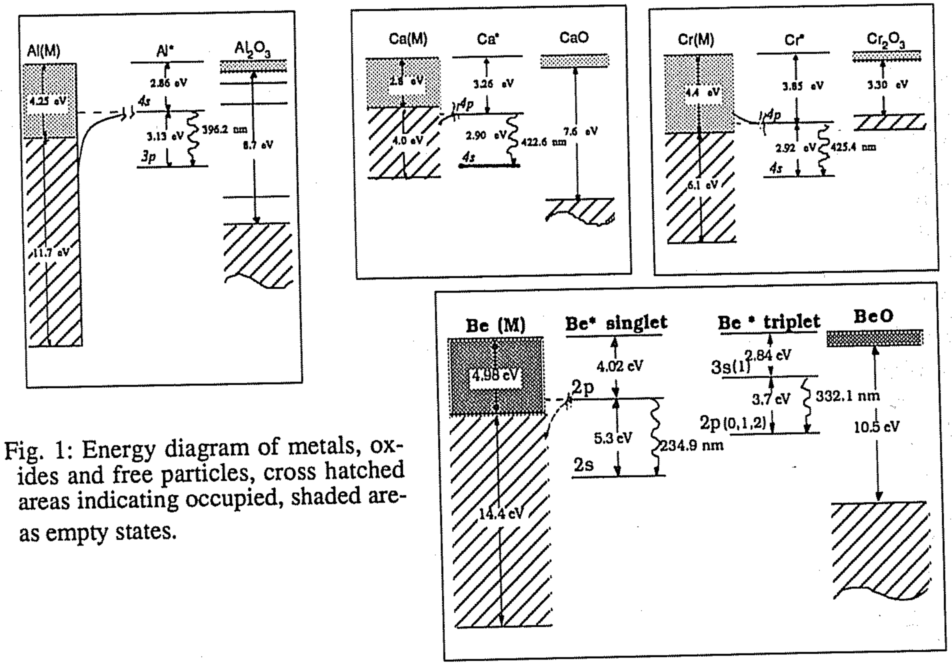

Fig. 1: Energy diagram of metals, oxides and free particles, cross hatched areas indicating occupied, shaded areas empty states.

In case of the Ca I line (Ca I 422.7nm), the line shape does not change at all when the Ca target is gradually oxidized (Fig. 2). The intensity, however, of the line increases by a factor 10 from the metal to the oxidized surface. Assuming a collision cascade, the experimental results can be fitted very well with a value for E* in eq. 1 of 6 eV in agreement with previous LIF measurements[2] of the velocity distribution of sputtered metastable Ca atoms. The fact that E* does not change from the clean metal to the oxide indicates that the deexcitation probabilities do not change during oxidation. This behavior is entirely consistent with the proposed model, since no de-excitation channels are present in either case (Fig. 1).

For Cr (Cr I 425.4nm) the velocity distribution for the clean metal exhibits, besides the collision cascade contribution, high energy tails due to recoil sputtering, that were not present in the Ca data. A comparison of the clean metal and Cr_2O_3 results reveals that the low velocity contribution is suppressed in the metal. The high energy tails remain the same, because atoms with high velocities are much less affected by the de-excitation process. This behavior is again consistent with a resonant deexcitation model, since there is a de-excitation channel for the metal which does not exist for the oxide (fig. 1).

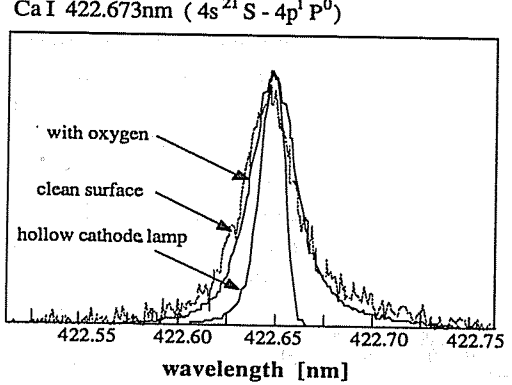

Fig.2: Doppler broadened line profile of the Ca I (422.673nm) resonance line. The resolution of the spectrometer was FWHM = 0.0088nm. The curves shown are normalized to their maxima. The absolute intensity of for the oxygen covered surface (2.10^{-6} mbar oxygen pressure) was larger by a factor of 10 as compared to the clean surface.

However, for sputtered excited Al atoms (Al I, 396.2nm) we observe a behavior contrary to the conventional resonant de-excitation model, namely, a pronounced broadening of the line profile for an oxidized surface as compared to the clean metal surface (Fig. 3). For the clean Al metal surface an excellent collision cascade fit with E*≈ 2eV in eq. 1 can be achieved and for the oxygen covered surface a fit results in E* ≈ 10eV. The fact that the clean metal spectrum is narrow shows that the tunneling deexcitation mechanism is absent for the 4s level, which is consistent with our calculation of a downshifted Al 4s level. The broadening of the spectrum for the oxide is strong evidence that there are empty states available in the surface. This is an opposite behavior to what we would expect from the level scheme in fig. 1. There is however experimental[17] and theoretical[18,19] evidence for surface states in the bandgap of Al_2O_3; also defects arising from vacancies in the bulk structure create states that are located in the bandgap[18]. Such states provide a deexcitation channel, and hence provide a plausible explanation for the observed line broadening.

In the case of Be we investigated the excited singlet $2p^1$ and triplet $3s^3$ states. Considering no hybridization resonance ionization would be

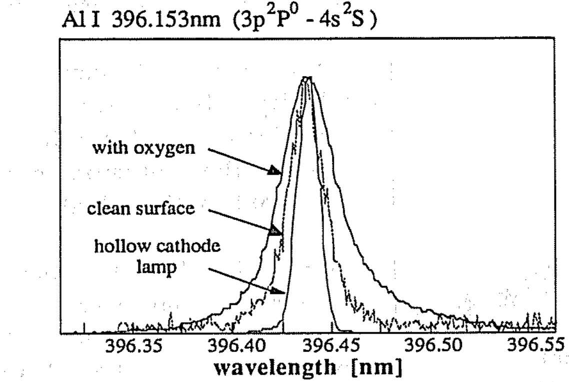

Fig.3: Doppler broadened line profile of the Al I (396.2 nm) resonance line. The curves shown are normalized to their maxima. The absolute intensity of for the oxidized surface (1.10^{-5} mbar oxygen) was larger by a factor of 10 as compared to the clean surface.

possible for both levels in the case of the pure metal. The calculations however show that both levels will be downshifted and the downshift is more pronounced for the $2p^1$ level (approx. 2.5-3 eV). This together with the fact that the unshifted $2p^1$level lies close to E_f, the $3s^3$ level more than 2 eV above E_f and both lie opposite the bandgap for the oxide we would expect no de-excitation processes occuring for the $2p^1$ level both for the metal and the oxide and in the case of the $3s^3$ level resonance processes to occur for the metal and not for the oxide. This is indeed what we observe (Fig. 4). For the $2p^1$ level a collision cascade fit with $E^* \approx 6$eV in eq. 1 can be achieved both for the clean and the oxidized surface. On the other hand for the $3s^3$ level the collsion cascade fit yields an E* value of appr. 220 eV for the clean surface, which decreases dramatically with oxidation to $E^* \approx 6$eV the identical value as for the $2p^1$ level. Thus the observed behaviour can again be explained by resonance ionization if we take into account hybridization.

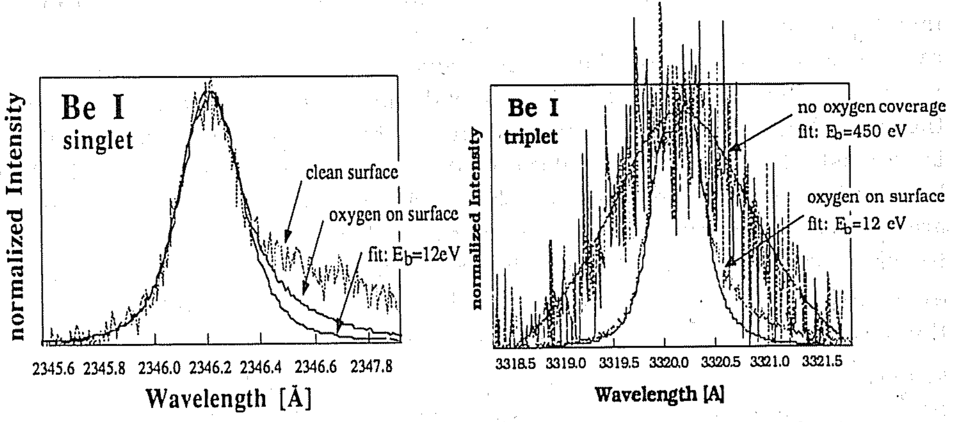

Fig.4a,b: Doppler broadened line profiles of Be I (234.86nm) and Be I (332.10nm) resonance lines. The spectrometer resolution was FWHM = 0.017nm. The curves are shown are normalized to their maxima. The absolute intensity for the oxygen coverd surface ($1.5\ 10^{-5}$ mbar oxygen partial pressure) was larger by a factor of 40 as compared to the clean surface. Fits with equation 1 are given. (Note $E_b = 2.E^*$)

We have demonstrated that the relative velocity distributions of excited atoms upon sputtering of metal and oxide surfaces are especially sensitive to the electronic structure of the substrate. We have also shown that these velocity distributions can be explained qualitatively by a simple picture of level hybridization with realistic parameters for the band structure.

The support of the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (Project Nos. 5577 and 5833) and of the National Science Foundation (N00014-86-C-2546), Air Force Office of Scientific Research (proj.nos.AFOSR-86-0150 and F49620-86-C-0125DEF) and Martin Marietta Corporation (A71052) is greatfully acknowledged.

References

1 M.L. Yu, D. Grischkowski, A.C. Balant, Phys. Rev.Lett. 48 (1982)472
2 W. Husinsky, G. Betz, I. Girgis, Phys. Rev. Lett. 50 (1983) 1689
3 E. Dullni, Appl. Phys. A38 (1985) 131
4 C.M. Loxton and R.J. MacDonald, Surf. Sci. 110 (1981) 339
5 S. Dzioba and R. Kelly, Surf. Sci. 100 (1980) 119 and Nucl. Instr. Meth. 182/ 183 (1981) 207
6 R. Hippler, W. Krüger, A. Scharmann and K.H. Schartner, Nucl. Instr. Meth.132 (1976) 439
7 W.F. van der Weg, D.J. Bierman, Physica 44 (1969) 206
8 R. Kelly, Phys. Rev. B25 (1982) 700
9 R.B. Wright and D.M. Gruen, J. Chem. Phys., 72 (1980) 147
10 P. Sigmund, Phys. Rev. 184 (1969) 383
11 G. Betz, Nucl. Instr. Meth. B27 (1987) 104
12 C.W. White, D.L. Simms, N.H. Tolk and D.V. McCaughan, Surf. Sci. 49 (1975) 657
13 B.I. Lundqvist in "Many-Body Phenomena at Surfaces", Eds. H. Suhl and H. Suhl, Academic Press(1983)93
14 D.Brust, Phys. Rev. B, 2(1970)818
15 P. Nordlander and Ph. Avouris, Surf. Sci, 177 (1986) L1004
16 G. Betz, P. Wurz, W. Husinsky, B. Strehl, H. Störi, N.H. Tolk, P. Nordlander and R. F. Haglund Jr., to be published
17 V. Mazacurattti and G.Signorelli, Lett. Nuovo Cimento 12(1975)347
18 S. Ciraci and I.P. Batra, Phys. Rev. B28(1983)982
19 A.L. Pushkarchuk, P.P. Mardilovich, A.I. Trokhimets, G.M. Zhidomirov and S.G. Gagarin, Phys. stat. sol. (b) 124 (1984)699

SYMPOSIUM ON ATOMIC AND SURFACE PHYSICS

'88

Contributions

EDITORS :

A. Pesnelle
F. Gounand
M. Cheret
F. Fabre

Institut de Recherche Fondamentale
du Commissariat à l'Energie Atomique
Département de Physique Générale
Service de Physique des Atomes et des Surfaces

La Plagne - France - January 17-23