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OPTICAL EMISSION AND LASER SPECTROSCOPY IN STUDIES OF SPUTTERING:
ACTUAL RESEARCH ACTIVITIES AND RECENT ACHIEVEMENTS

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Abstract

Laser Spectroscopy has been developed into a powerful tool for the detection and energy analysis of neutral particles. Laser Induced Fluorescence Spectroscopy (LIF) has yielded a wealth of information about sputtered neutral particles. In addition, Laser Ionization Spectroscopy has recently offered an increased detection sensitivity. In this paper a summary of recent results is given. By combining LIF with other methods capable of measuring densities and energy distributions of sputtered excited atoms in short lived states, new information about sputtering and excitation mechanisms have been recently obtained and will be summarized here.

Introduction

In the field of particle-solid interaction we are predominantly confronted with the emission of secondary neutral particles mostly in the electronic ground state [3,24]. Even though a whole variety of different excitation states and even ionized secondary particles are observed, the majority is neutral. The physics of the sputtering process can be best characterized by the physical parameters of the emitted neutral particles. If one's major interest lies in using secondary particles as a surface analytical tool, there is some hope, that a considerable enhancement in the detection limit can be achieved as compared to measuring charged particles [41].

Laser-Induced-Fluorescence-Spectroscopy is a powerful diagnostic tool for the detection of neutral particles [3,14,20,22,23,24,26,63]. In spite of the fact that its application in the field of particle-solid interaction for the detection of neutral particles is relatively novel, a variety of new information has been gained in the last few years and has improved our understanding of the physics of the sputtering process. The unique features of Laser-Induced-Fluorescence-Spectroscopy enable us to measure the density and energy distribution of secondary neutrals. Furthermore, they can establish information about the energy level in which the particle leaves the target surface [4,23,63]. If the Doppler Shift of the excitation wavelength is used to measure the velocity (energy) distribution, LIF is usually called Doppler-Shift-Laser-Fluorescence-Spectroscopy (DSLFS) [24]. The principles of the LIF and DSLFS method and its first achievements in the field of particle-solid-interaction have been summarized in a few recent reviews [3,8,24]. In this paper current problems in sputtering treated with Laser-Induced-Fluorescence-Spectroscopy and more recent results by LIF and DSLFS will be summarized. In spite of the high detection sensitivity of LIF, its limits can be reached in many experiments involving particles with extremely low sputtering yields or using very low primary bombarding currents in order to minimize surface damage. The even more powerful method of [Multiphoton-]Resonance-Ionization-Spectroscopy (RIS) has been recently applied to sputtering investigations pushing the detection limits beyond those of LIF [1,20,40,41,46].

KEY WORDS: Sputtering, Desorption, Particle-Solid Interaction, Ion Bombardment, Electron Bombardment, Neutral Particle Detection, Laser-Spectroscopy, Laser-Induced-Fluorescence, Multiphoton-Ionisation, Bombardment Induced Light Emission.

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After LIF had been used for sputtering investigations for the first time in 1977 by Husinsky et al. [20], the method was subsequently used for measuring velocity spectra of sputtered neutral ground state atoms [3,24]. These measurements concentrated on metal targets [9,25,26,61] and alkali halides [20,21]. From the velocity spectra obtained, the validity of the theory [45], which is characterized by an energy distribution of sputtered atoms of the form (1), could be verified in many cases.

$$f(E) = \frac{E}{(E + E_b)^3} \quad (1)$$

In particular, (1) has been verified for many metal targets and the E_b values obtained from the maxima of the velocity distributions, in general, agree with the theoretically predicted heat of sublimation of the metals. As expected, the data obtained with DSLFS have shown, that for light ion sputtering and for low bombarding energies the theory cannot be applied and (1) has to be substituted by a more general expression (2)

$$f(E) = \frac{E \cdot (1 - (E + E_b)/T_m)}{(E + E_b)^{1+n}} \quad (2)$$

[2], where T_m is the energy transfer in a head on collision. Measurements of alkali atoms sputtered from alkali halides have shown the abilities of DSLFS in identifying different contributions to the sputter mechanism [20,21]. In this case strong thermal energy contributions are observed, which indicate that

the alkali atoms are released from the surface by thermal evaporation. New results on this interesting subject will be presented below.

The emphasis in these earlier investigations has shifted from these original questions to more advanced and more complicated situations. The observation, that similar to the situation for sputtered secondary ions and excited particles, the yields and energy distributions of sputtered ground state neutrals are strongly influenced by the presence of oxygen on the surface, has led to extensive investigations of the composition of sputtered fluxes under oxygen exposure of different targets [3,8,10,24,26,28]. These observations on oxidized metal targets will be extended within this summary to other electro negative adsorbates as well as to compound targets with electro negative constituents.

LIF measurements on oxidized metal targets indicate that the majority of sputtered species in this case is due to sputtered molecules [24,8]. The detection of sputtered molecules poses substantial difficulties for LIF, but can be relatively easily achieved with RIS.

Theoretical models and approaches to explain the existence of sputtered excited atoms and ions are still various and controversial [48,51,57,58,60,64,66]. Various experiments have been and are currently performed to solve this puzzle [11,12,13,16,24,26,32,44,54,55,60,63]. LIF and DSLFS are used very successfully to establish a more detailed picture and understanding of these problems.

Experimental approaches

Different schemes for LIF and DSLFS set-ups using c.w. or pulsed dye lasers have been described in the literature. Reviews of the method in general and on different aspects of these techniques and their advantages, as well as of the problems related to interpreting the measured fluorescence signals,

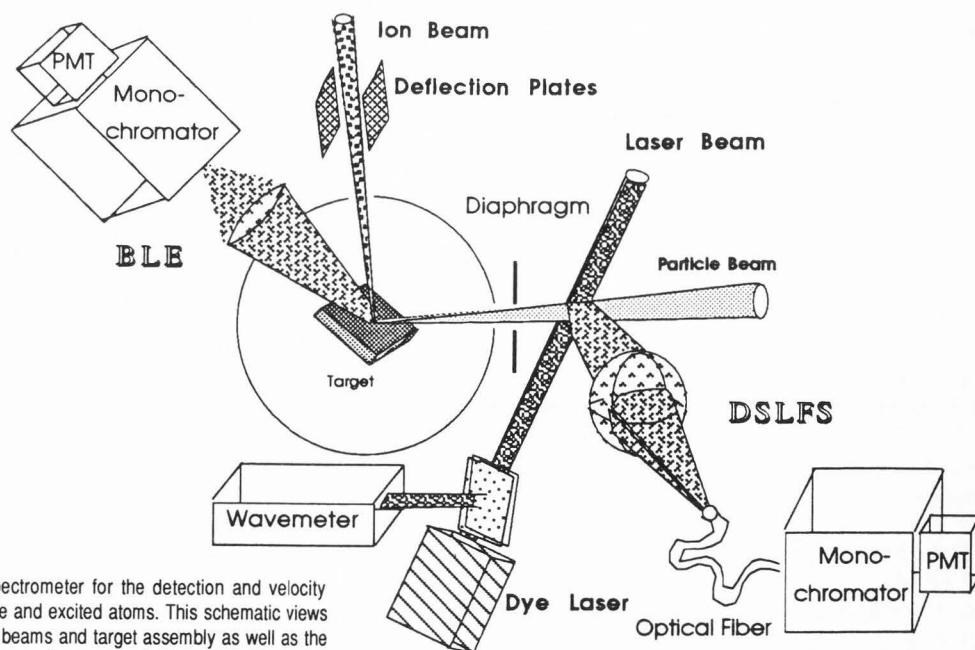


Fig. 1. LIF, DSLFS and BLE Spectrometer for the detection and velocity measurement of neutral ground state and excited atoms. This schematic views the arrangement of ion beam, laser beams and target assembly as well as the observation - detection system used. A continuous wave (cw.) tunable ring dye laser (Coherent 699-21) has been used.

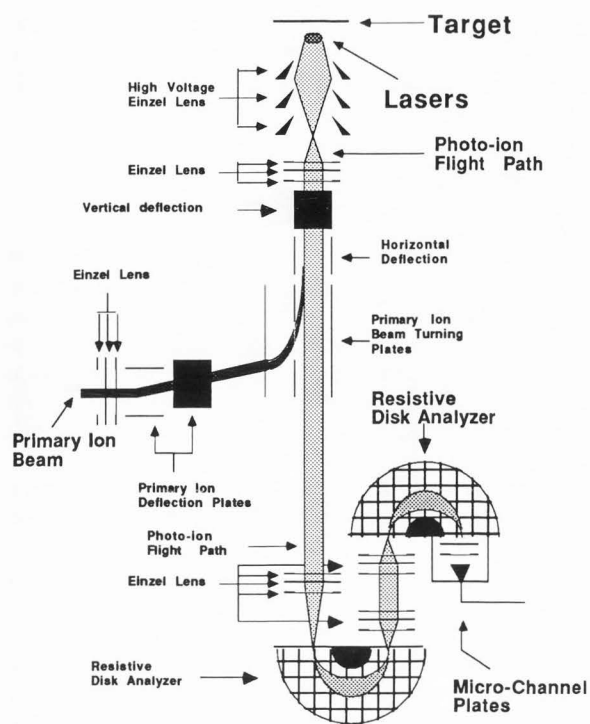


Fig. 2: The SARISA III energy and angle refocusing time-of-flight system for detection of sputtered neutral atoms. The element labels are self-explanatory. (after ref. [41])

have been presented by Husinsky [24] and Bay [3]. The problems, which will be treated in this paper, can be solved by LIF and DSLFS studies combined with Bombardment-Induced-Light-Emission Studies (BLE) [8], covering the analysis of neutral ground state and excited state atoms. LIF Spectroscopy can be easily applied to ground state and metastable atoms, but encounters considerable experimental problems when applied to short lived excited atoms, which one observes near the surface region of ion bombarded targets. In Fig. 1, a schematic of the spectrometer used for most of the results described in this paper is shown. Most of the details have been already described previously [24,26,28].

In this spectrometer a tunable c.w. ring dye laser is used for exciting neutral ground state or metastable atoms. By using Doppler-free 90° excitation the total sputtering or desorption yields can be measured. Doppler-shifted 45° excitation is used for measuring the velocity spectra of sputtered atoms. In the BLE mode of the spectrometer the spectral distribution of the light emitted in front of the bombarded surface can be analyzed. Thus densities of sputtered short lived excited atoms and molecules can be determined. From the Doppler-broadened line profile of particular emission lines the velocity distribution of sputtered short lived excited particles can be obtained (for more details see the corresponding section in this paper).

Depending on the laser type, excitation-observation geometry and resonance line used for the LIF and DSLFS measurements, the measured fluorescence light has to be corrected for saturation and transit time effects in order to obtain particle densities and velocity distributions. A detailed general discus-

sion of this problem can be found in [3,4,5]. In [24] the results obtained in [4,5] have been specialized for the spectrometer shown in Fig. 1.

Another set of results (sputtering of Mo dimers) presented in this paper have been obtained with Laser-Ionization-Spectroscopy [19,31]. The SARISA apparatus [40,41], shown in Fig. 2, has been used to obtain these data. Details of the experimental set-up of SARISA (*Surface Analysis by Resonance Ionization Spectroscopy of Atoms*) and Laser-Ionization-Spectroscopy is given elsewhere [40,41]. For the experiments described here, Resonance-Ionization Spectroscopy (RIS), Nonresonant-Ionization-Spectroscopy and SIMS experiments have been performed in the SARISA apparatus. A Nd:YAG pumped dye laser and an excimer laser have been used to effectively ionize sputtered neutral particles. The elaborate ion detection system of the SARISA apparatus allows effective discrimination of photo ions against background (SIMS) ions.

In all experiments described, mass separated rare gas ion beams have been used with ion beam energies between 5 and 15 keV and ion current densities of a few $\mu\text{A}/\text{cm}^2$. The experiments were performed under UHV conditions with background pressures $<10^{-9}$ mbar.

For electron bombardment an electron gun specially designed for low energies [49] has been used. Electron currents of approximately 300 μA have been obtained at 400 eV. With lower currents, the gun could be operated down to a few eV.

Physical problems of current research activities

At this point it is still a puzzle and widely unknown in which form a sputtered particle initially leaves the target surface. We can detect the different sputtered products only when they are far enough away from the surface. Interestingly, and to a large extent surprisingly, in many cases most of the sputtered products are neutral ground state atoms, even when the atom is released from an ionic crystal [15,20,21]. In general, only a small fraction of the sputtered species are ions or excited ions. In many cases, also molecules contribute to the sputtered flux, but generally only with a small amount. However, the situation is totally different when oxygen is adsorbed on the surface or is present in the matrix of the bulk. Under these conditions, ions and excited atoms can be a substantial contribution [57,58,65,66]. Neutral molecules can even dominate the sputtered flux [7,8,24,25,26].

This has been observed long ago, but relatively little had been known about the behavior of neutral ground state atoms under these conditions. LIF has demonstrated that oxygen strongly reduces the amount of sputtered neutral ground state atoms in many cases investigated [7,8,10,24,26,28]. A summary of some illustrative examples is shown in Fig. 3. It could be further derived from these measurements, that a considerable contribution of the sputtered flux is due to molecules, presumably metal oxides, because neither the enhanced ion nor excited atom yields can compensate for the strong decrease of neutral ground state atoms [8,26]. These measurements opened new questions to be answered: *Is oxygen unique in its strong influence on the form in which particles are sputtered? Do other electro negative adsorbates behave similarly? Are there differ-*

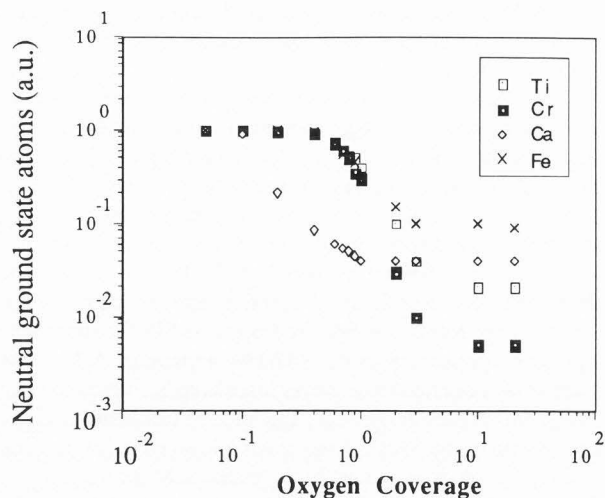


Fig. 3. Dependence of the partial sputtering yield of neutral metal ground state atoms as a function of the surface oxygen coverage as measured by LIF for 15 keV Ar⁺ bombardment of Ca, and Cr, for 1 keV Ar⁺ bombardment of Ti and for 6 keV He⁺ bombardment of Fe. As a measure of the surface coverage with oxygen the ratio between the thermal flux of oxygen molecules onto the surface and the Ar⁺ beam current density $N_{\text{gas}}/N_{\text{ion}}$ (x-axis of the figure) was used. The curves are normalized to the sputtering yield from a clean target to be 1.

ences between oxygen adsorbed and oxygen as a compound constituent? In current research activities detailed measurements of sputtered molecules, in particular their rotational-vibrational population is regarded as a key issue, because different theoretical models predict specific rotational-vibrational distributions. Ionization Spectroscopy is a promising approach to solve problems associated with this subject.

The energy distribution of sputtered particles is representative of the mechanisms which lead to particle ejection. As mentioned earlier, measurements of the energy distribution of sputtered ground state atoms by DSLFS have confirmed the Sigmund theory for clean metals. The situation for the energy distribution of sputtered excited atoms is much more difficult. In most practical cases, DSLFS is only easily applicable for sputtered metastable atoms, because other excited atoms decay in the near surface region. Experimental difficulties arise from background light and from the excitation and detection geometry in this case. This leaves us with the question of how far metastable excited states and their respective population found in sputtering are representative of the population and energy distributions of short lived excited states in general. Even though no physical reason seems to exist which would reasonably well explain such differences, this question had to be asked regarding discrepancies encountered in comparing BLE Light-vs.-Distance measurements with DSLFS measurements [23,24,63].

A detailed knowledge of the energy distribution of sputtered excited atoms, metastable as well as short lived excited, is essential for a better understanding of the ejection and excitation mechanism in the sputtering process. The knowledge of the behavior of the yields of excited atoms and their energy dis-

tribution with increasing coverage with electronegative adsorbates has the potential of a further step forward in making the right choice among existing theories for the formation of excited and ionized sputtered species.

Electronegative Adsorbates and matrix constituents - Influence on Sputtering.

The exceptional influence of electronegative adsorbates on ion and excited atom fractions in sputtering has various important consequences. Its explicit features seem to indicate, that electronegative atoms play an important role in the excitation process or in the survival probability of excited particles at the surface. But this is not only important from the standpoint of fundamental physics, but is of important relevance for many practical applications, as there is, e.g., SIMS. The strong enhancement of the ion or excited particle yield is used in many surface analysis methods based on secondary particle emission [37,40,41].

The influence of oxygen (see Fig. 3) on sputtering of neutrals has been investigated quite extensively by LIF. Relatively little has been done in this regard to investigate the influence of other electro negative adsorbates. But it is known that electro negative adsorbates in general enhance the ion yield and the yield of excited atoms. We have recently performed measurements on the influence of adsorbed fluorine on the sputtering yields of sputtered neutral Cr ground state atoms [29]. Fluorine has been adsorbed onto the surface by enhancing the SF₆ background pressure in the target chamber. A

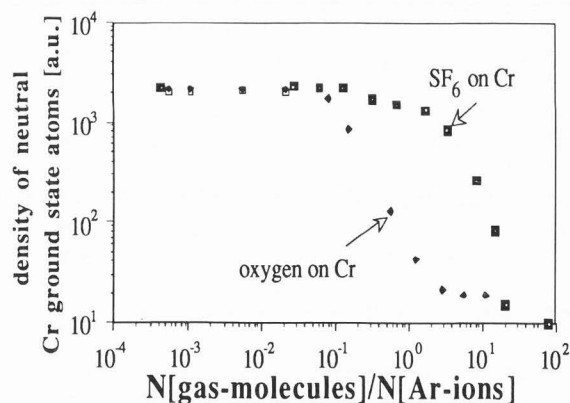


Fig. 4. Dependence of the density of neutral Cr ground state atoms sputtered from a Cr target at 120 K on the ratio $N[\text{SF}_6]/N[\text{Ar}^+]$ of SF₆ molecules to argon ions striking the target surface per sec and cm². For comparison the corresponding yields of Cr ground state atom sputtered from a Cr at room temperature are plotted as a function of the ratio oxygen molecules to argon ions.

complication arises from the fact that SF₆ does not stick to the surface at room temperature. But it is known from using SF₆ for chemical sputtering of silicon that sticking occurs around liquid nitrogen temperature [38,39,59,67]. A comparison of the influence of SF₆ and of O₂ adsorbed on a Cr target, as far as the resulting Cr ground state sputtering yield is concerned, is shown in Fig. 4. The data for SF₆ shown in Fig. 4 have been measured at a target temperature of 110 K. With respect

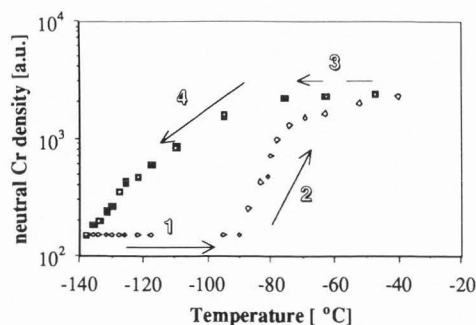


Fig. 5. Dependence of the density of neutral Cr ground state atoms sputtered from a Cr target and exposed to a ratio $N[\text{SF}_6]/N[\text{Ar}^+]=100$ on the target temperature.

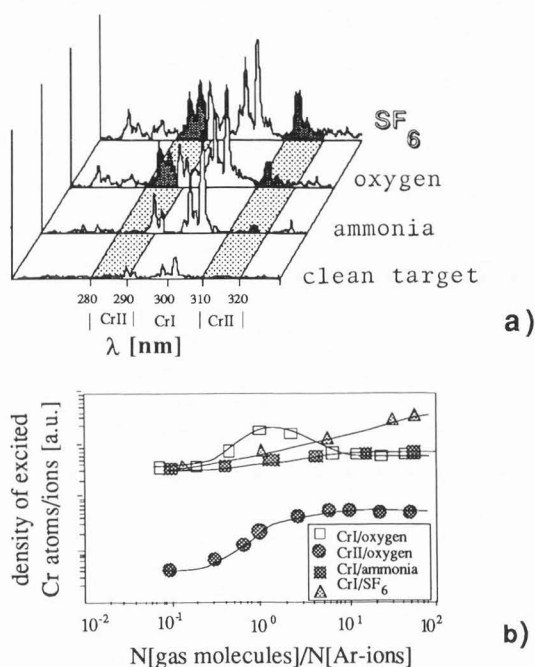


Fig. 6. (a) Part of the BLE spectrum obtained by bombarding clean Cr targets and Cr targets exposed to different gases. The spectra shown for the different gases have been recorded at ratios $N[\text{gas molecules}]/N[\text{Ar}^+]$ which correspond to a maximal yield of excited Cr atoms or ions. (b) Dependence of the density of excited Cr atoms and ions sputtered from a Cr target at 120 K on the ratio $N[\text{SF}_6]/N[\text{Ar}^+]$ of SF_6 molecules to argon ions striking the target surface per sec and cm^2 . For comparison the corresponding yields of excited Cr atoms and ions sputtered from a Cr target at room temperature are plotted as a function of the ratio of oxygen molecules to argon ions. For determining the yields of neutral excited Cr atoms the fluorescence intensity of the 425.4 nm transition line, for determining the yields of excited Cr ions the fluorescence intensity of the 283.5 nm transition line have been measured.

to the neutral ground state yield, the influence of oxygen and sulfur-hexafluoride is nearly identical, both resulting in a strong reduction of sputtered neutral ground state atoms. It is assumed that the changes in the sputtering parameters are due

to the influence of fluorine, which forms, similar to oxygen, molecules with the metal atoms. The temperature dependence of the neutral Cr yield at high SF_6 partial pressures, shown in Fig. 5, clearly demonstrates the increasing sticking coefficient of SF_6 for low target temperatures.

It is important to investigate the yields of sputtered excited atoms under the same conditions under which we have obtained the results in Fig. 4. Only then a valid correlation between oxygen and SF_6 adsorption can be established. Otherwise, one might argue, that the Cr surface is covered with an increasing amount of SF_6 and one actually sputters a SF_6 target. In contradiction to this assumption, the yield of excited Cr atoms increases with increasing SF_6 coverage, in good accordance with the results for oxygen coverage. Fig. 6 shows a characteristic part of the light spectrum emitted from sputtered excited particles in front of a Cr target under 15 keV Ar^+ bombardment for a clean, an oxygen, an ammonia and a SF_6 covered surface.

From these results we can conclude, that electronegative adsorbates play a key role in the formation of different types of sputtered particles. In particular, they reduce the yield of sputtered neutral atoms in the ground state and enhance the ion and excited yields. We further know that a substantial amount of molecules is sputtered from surfaces with electro negative adsorbates. The question of the influence of electro negative adsorbates is, therefore, directly connected with the search for the origin of the excitation and ionization process (or the survival probability of ions and excited particles at the surface) in sputtering.

In many cases, particularly for oxidized surfaces, the bond breaking mechanism [64,66] can be regarded as a good basis for describing excitation and ionization in sputtering. In the picture of the bond breaking model the sputtering of an atom M from an oxidized surface breaks the surface oxide bond and creates a vacancy X on the surface. If this cation vacancy can retain an electron during the sputtering event, a finite chance for the electron exists to form (M^+, X^-) or $(\text{Mo}^*, \text{X}^0)$ via nonradiative electron transfer between M and X.

The bond breaking model has been recently applied by Yu for sputtering of ions and excited atoms [64,66]. The mechanism is visualized in Fig. 7, which shows the sputtering channels of a) a neutral atom Mo, b) a positive ion M^+ and c) an excited neutral metal atom Mo^* from a surface leaving a vacancy X. Charge exchange can happen at the appropriate crossings of the diabatic potential energy curves at distances R_c and R_{ex} from the surface. In this model the excitation probability P^* can be expressed as a function of the velocity of the ejected particle $v(R_{ex})$ at the crossing distance, the matrix element H_{13} , the degeneracies of the levels g^* , g^+ and $l_a(R_{ex}) = (I - A - E_{ex})^2$ and can be written in the form of equation (3).

$$P_i^*(R_{ex}) \approx 2\pi \frac{g_*}{g_+} \frac{H_{13}^2}{v(R_{ex})} l_a(R_{ex}) \quad (3)$$

The extraordinary influence of electronegative atoms is also clearly demonstrated by comparing the sputtering behavior of metal with that of compound targets with at least one electro-

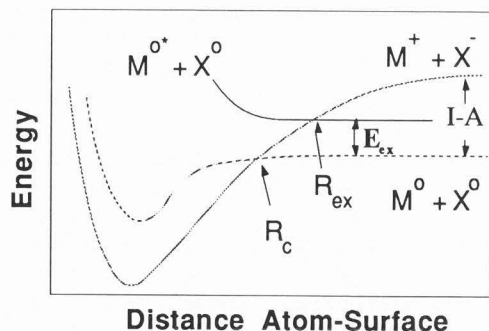


Fig. 7. Schematic energy diagram of the diabatic potential energy curves of $Mo^{0+}X^0$, $M^{++}X^{-}$ and $Mo^{+}X^{-}$. R is the distance between the sputtered atom M and the vacancy X . E_{ex} is the excitation energy of the excited level, A the electron affinity and I the ionization energy. (after ref. [65,67]).

negative constituent. We have compared the sputtering yields of neutral Cr atoms from Cr_2O_3 and Cr_3C_2 targets with the previously described results from Cr metal targets [27]. A direct comparison between the yields from Cr metal and Cr_2O_3 shows values by approximately a factor 50 lower for Cr_2O_3 targets. This is about a factor 2 higher than the reduction achieved by exposing the Cr metal targets to an oxygen partial pressure of about $1 \cdot 10^{-6}$ mbar. On the other hand, the Cr ground state yield from Cr_3C_2 targets is only between 5 to 10 times lower than for the metal. This reduction can be explained by the lower Cr concentration on the Cr_3C_2 surface and by a reduced sputtering yield of carbides. For Cr_3C_2 the yield can be further reduced by exposing the target to oxygen.

For oxides, however, the strong influence of electronegative atoms comes into play causing the strong reduction of sputtered neutral ground state atoms. The difference for the yields between oxidized Cr and Cr_2O_3 targets is noteworthy. Detailed studies of the time dependence of the Cr ground state yield for Cr targets exposed to an oxygen atmosphere and simultaneous ion bombardment show characteristic transient behavior (Fig. 8). This can be attributed to different accumulating contributions from oxygen adsorbed and implanted in the near surface region of the bulk.

A lot of information, as far as the influence of electronegative adsorbates is concerned, has been obtained from the velocity spectra of sputtered neutral ground state atoms. For

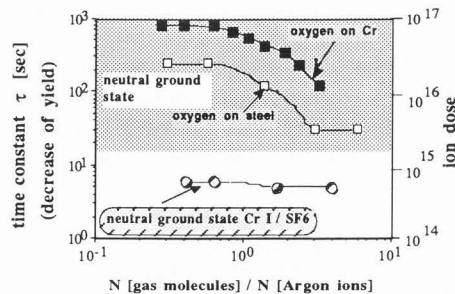


Fig. 8. Time constants (ion doses) for reaching the steady state condition (yield decreases) after increase of the O_2 and SF_6 partial pressure for neutral Cr atoms in the ground state as a function of the ratio $N[\text{gas molecules}]/N[\text{Ar}^+]$. Measured with LIF.

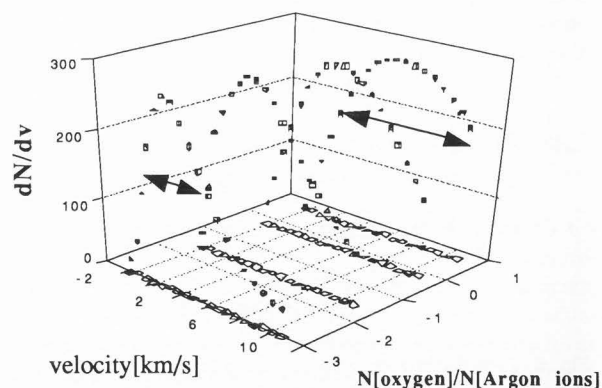


Fig. 9. Velocity distributions of neutral Cr ground state atoms sputtered from a stainless steel target as a function of the $N[O_2]/N[Ar^+]$ ratio. The spectra are normalized in their maxima. For high oxygen coverage the signal is lower by a factor of approximately 100.

clean surfaces and isotropic well developed sputtering cascades in general eq. (1) describes the energy distribution quite well. Furthermore, the parameter E_b in (1) is very close to the value of the heat of sublimation and can be understood as the surface binding energy for clean metals. Small, but observable deviations from the value of the heat of sublimation of E_b might be attributed to a slightly modified picture of the surface binding energy, as proposed by Kelly [30]. Oxygen strongly influences the energy distribution, generally shifting the maxima to higher values (by factors 3-5) and broadening the spectra. This has been observed in many cases, e.g., for Cr sputtered from Cr metal but also for Cr sputtered from stainless steel (see Fig. 9) [28]. However, this has not been observed for SF_6 coverage of Cr, in spite of all the similarities as far as other features are concerned.

One attempt to explain this behavior is to assume an increased surface binding energy for oxidized surfaces. This explanation seems to be at hand, because the shape of the energy spectra still resembles (1) with E_b now becoming a fitting parameter, otherwise without physical meaning. However, the surface binding energies obtained in this way would be in the range of 15 eV or more and no convincing explanation for such high surface binding energies has been found so far.

In another attempt one might explain the broadening due to an increasing contribution to the ground state yield from originally excited atoms in an intermediate regime where the neutral ground state yield becomes low and comparable to the excited yield [24,25].

Yet another explanation is based on the assumption that the increasing amount of sputtered metal oxide molecules leads to a preferential depletion of slow sputtered metal atoms, because these slow atoms will more preferably form molecules when ejected together with oxygen atoms [6].

Energies of excited sputtered particles

The energy distribution of sputtered excited particles (atoms, ions and molecules) has been a much debated issue in

the last few years. Measurements of the energy distribution of excited species have been motivated by the hope of finding an explanation for the mechanism of excited particle ejection. The mechanism of ion ejection is believed to have the same or at least a similar physical origin. A better understanding of these processes has been sought for many years, motivated by the relevance of sputtered ions and, to some extent also excited atoms, for surface analytical applications [34,35].

For the measurement of the energy distribution of excited particles three different methods have been reported in the literature:

a) The intensity of the light emitted from excited particles has been measured as a function of the distance from the target (often called Light-versus-Distance Measurements) [11,12,13,32]. This method has been used quite extensively by several authors and has yielded energies considerably higher than is known for ground state atoms. Values up to the keV range have been reported. Results obtained with this method are very sensitive to the population of higher excited levels, which can feed the lower levels by cascading. This cascading increases the fluorescence of the particular line in front of the target, causing problems in the interpretation of the fluorescence decay. We have shown, that depending on relevance of cascading, the obtained energies can be shifted over a wide range [6,24].

b) The Doppler Broadening of the light emitted from excited particles can be analyzed [17]. From the Doppler Broadening one can obtain information about the velocity of the sputtered excited particles. The main difficulty in relating the Doppler Broadening to a velocity distribution is caused by the complicated observation geometry. We have recently performed Doppler line profile studies for several different targets. Under the assumption of an energy distribution of the form (1), a cosine angular distribution for the sputtered particles and an observation geometry as shown in Fig. 10 the line profile can be written in an analytical form [42]:

$$Y(z) = \frac{2z \cos \alpha \sqrt{z^2 + \sin^2 \alpha} + z^2 \sin^2 \alpha + 2z^2 \cos^2 \alpha + \sin^2 \alpha}{2(z^2 + 1)^2 \sqrt{z^2 + \sin^2 \alpha}} \quad (4)$$

Eq. (4) has been obtained using the MACSYMA Program (developed at MIT). In (4) z is given by $z = \Delta \lambda \cdot c / (\lambda_0 v^*)$, v^* is linked to the maximum of the energy distribution (1) E_b by $E_b = mv^{*2}/2$ and α is the angle between target normal and direction to the monochromator. λ_0 is the unshifted wavelength of the observed resonance line and $\Delta \lambda$ is the wavelength shift. The advantage of the analytical form (4) is the possibility to directly compare (4) with the measured line profiles. Thus we can find out whether an energy distribution of the form (1) is also valid for excited particles and if it is the case, we can obtain the corresponding E_b values, representing thus an average energy of the sputtered excited atoms.

c) LIF and DSLFS are, in principle, the most precise ways of measuring the energy distribution of sputtered excited particles. However, due to the fast decay very close to the target of most of the short lived excited particles, only metastable

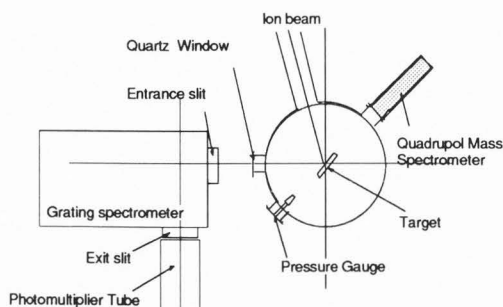


Fig. 10. Experimental details of the spectrometer shown in Fig. 1 for measurements of the Doppler-broadening of resonance lines of sputtered excited particles.

excited particles have been measured so far [23,44,63]. The still limited number of measurements of this kind show very good agreement among themselves. The maxima of the energy distributions of sputtered metastable atoms are clearly higher (10-30eV) than for ground state atoms (1-8eV). But, astonishingly, a fit with (1) can be achieved in most cases. For that reason it makes sense to try to fit the Doppler Broadening of the resonance line, as described in b) with (4), which itself is based on (1). It is remarkable, that the energy distributions found with DSLFS for sputtered metastables differ quite considerably from the results obtained with method a). Furthermore, DSLFS measurements brought another unexpected result: the intensity of metastable atoms increases with oxygen

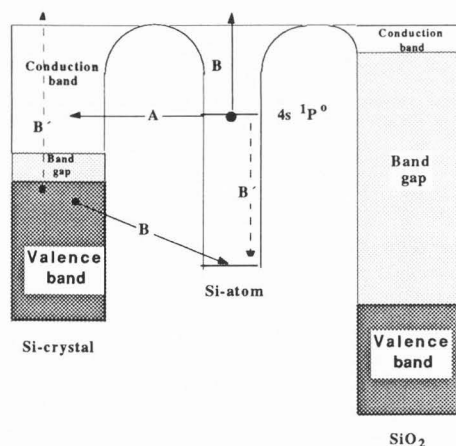


Fig. 11. Energy level diagram of an excited Si atom ($4s^1 P_0$) near a Si and a SiO_2 surface. For Si resonance ionization (A) or Auger deexcitation (B,B') is possible, but not for SiO_2 .

coverage of the target but the shape of the velocity spectra is unchanged. This is somewhat astonishing, because a commonly used explanation of the oxygen enhancement effect is based on the decreasing possibility of ions and excited atoms to relax via Auger deexcitation or neutralization as visualized in Fig. 11 for Si and SiO_2 . (It should be mentioned that the DSLFS results have been obtained for metastable Ba and Ca atoms, which are close in the periodic system). In this model one

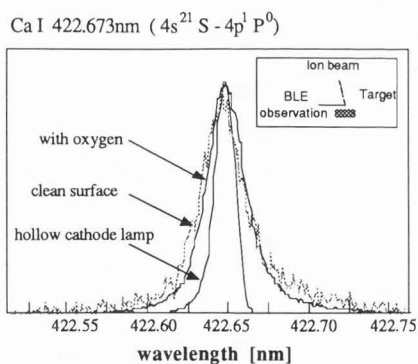


Fig. 12. Doppler broadened line profile of the Ca resonance line at 422.6nm of sputtered excited Ca atoms. Within the experimental accuracy the line profile is identical for clean and oxidized surfaces. The intensity, however, increases for oxidized surfaces by a factor 10. The bombarding-observation geometry is indicated in the figure. The line profiles are compared with the line profile of a reference Ca hollow cathode lamp.

would expect a shift of the velocity spectrum to higher velocities for clean surfaces, contrary to what has been observed.

The oxygen enhancement effect itself can be explained and understood on the basis of the bond breaking model, as described earlier. However, a detailed study of the behavior of the velocity distribution of the sputtered excited atoms under different surface conditions reveals additional features, the reason being the complicated nature of the processes involved. When we observe a sputtered atom in a particular excited state,

duced by secondary-electron excitation.

Due to the restriction of the different methods a)-c), it is necessary to perform measurements with more than one method in order to obtain sufficient information to draw valid conclusions.

Although a possible explanation for the discrepancies between DSLFS and LvD (*Light versus Distance*) measurements has been proposed by the influence of cascading in LvD measurements, basic physical differences in the excitation mechanisms for metastable and short lived excited atoms cannot be totally excluded from these measurements. For this reason we have recently performed detailed investigations of the Doppler Broadening of sputtered short lived excited atoms from various clean and oxidized targets. In particular, we have investigated those systems, where DSLFS results for metastable and ground state atoms exist for clean and oxidized targets.

We have chosen two different bombarding-observation geometries (shown schematically in the Figures with the results) in order to investigate different mechanisms for the ejection of excited particles, which we will discuss on behalf of the results.

The first important result is shown in Fig. 12. The Doppler broadened line profile of the Ca resonance line of sputtered excited Ca atoms is independent of the oxygen coverage of the Ca target (The intensity, however, increases for oxidized targets). The spectra shown in Fig. 12 can be fitted with (4), from which the E_b fitting parameter can be obtained, which is a measure for the average energy of the sputtered excited atoms. In this case a value of 6 eV is obtained. Both results are in-

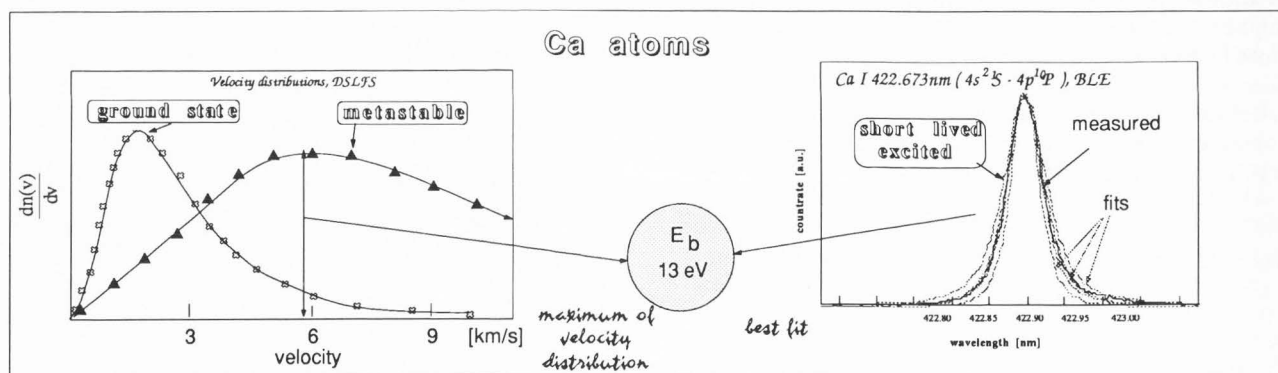


Fig. 13. Determination of the fitting parameter E_b in eq. (1) for neutral Ca ground state atoms and metastable atoms from the maxima of their velocity distribution (right) and for the short lived excited Ca atoms from the Doppler broadened line profile (left). For neutral ground state atoms an E_b value of 1.3eV is obtained and this value can be identified with surface binding energy of Ca. For sputtered excited Ca atoms, in both cases an E_b value of 13eV is obtained, representing a measure for the average energy of the sputtered excited atoms. For metastable atoms this value is directly obtained from the maximum of the velocity distribution and fitting with (1), while the best fit of the broadened line profile with (4) also results in a value of 13 eV.

this final state is a consequence of various excitation and deexcitation steps (possibilities). To mention a few of them: (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 pro-

cellent agreement with results obtained with DSLFS (Fig. 13), which have been described above. From this we can conclude, that for Ca metastable and short lived excited sputtered atoms behave in the same way.

A more complex situation exists in the following examples. Whereas the sputtering of excited Ca atoms can be explained by basically one mechanism, for Cr at least two different mechanisms seem to be involved. The first mechanism is

the one we already know from Ca and which involves a *cascade-like* energy distribution. A second mechanism can be attributed to ejected excited atoms with considerable higher energies and a *non-cascade-like* distribution.

This second contribution is particularly pronounced for oblique ion beam incidence as can be seen for the example presented here, i.e., Cr targets (Fig. 14). For clean surfaces the high energy contribution is dominant, because cascade like particles are very few from clean surfaces. For increasing oxygen coverage the intensity of cascade like particles steadily decreases and high energy particles become dominant. But the shape of the cascade like distribution itself stays unchanged under oxidation, as we have already seen for Ca. This becomes even more evident, if one uses a normal beam incidence geometry, where the intensity of high energy particles is very low.

A very surprising result has been obtained for Al (Fig. 15). Increasing the oxygen coverage on an Al target results in a broadening of the measured line profiles. It is noteworthy, that the profiles can be fitted with (4) with increasing E_D parameters.

These results can be explained to a large extent by a significant, velocity dependent contribution to the final state the sputtered atom is found in by nonradiative electron transfer. In order to understand the different behavior for different targets and atoms sputtered in different electronic states, we have to know, how the atomic levels behave close to the surface. This allows us, at least qualitatively, to estimate the influence of resonance deexcitation processes and their influence on the velocity distribution (Fig. 16). On Al, the atomic 4s level lies signif-

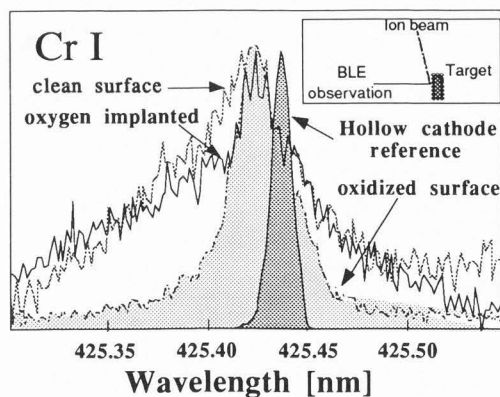


Fig. 14. Doppler broadened line profile of the Cr resonance line at 425.4nm of sputtered excited Cr atoms. The line profile shows a high energy contribution for clean and slightly oxidized surfaces, which cannot be fitted with (4). The intensity of the low energy contribution increases for oxidized surfaces by a factor 5. The bombarding-observation geometry is indicated in the figure. The oblique ion beam incidence enhances the high energy part of the profile. The line profiles are compared with the line profile of a reference Cr hollow cathode lamp.

icantly 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 deexcitation.

Na I 588.995nm ($3p^2P^0 - 3s^2S$)

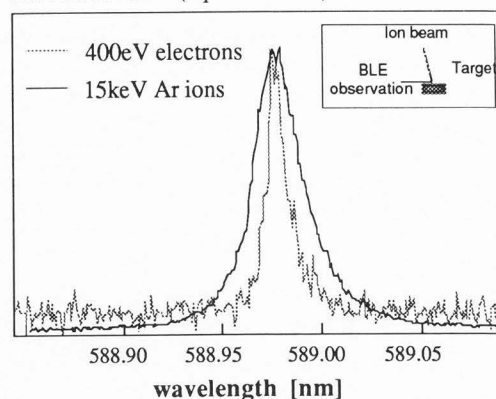


Fig. 15. Doppler broadened line profile of the Al resonance line at 396.1nm of sputtered excited Al atoms. The line profile broadens considerably for oxidized surfaces and can be fitted with (4). The intensity increases for oxidized surfaces by a factor 10. The bombarding-observation geometry is indicated in the figure. The line profiles are compared with the line profile of a reference Al hollow cathode lamp.

tation. These simple expectations are based on the assumptions that 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 [33].

To get an estimate of the atomic levels shift in the surface region, a simple Anderson Hamiltonian can be used to cal-

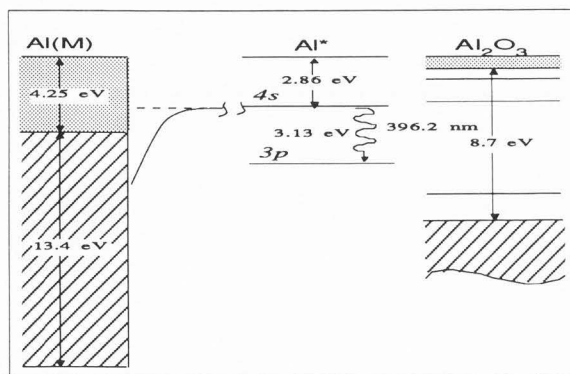


Fig. 16. Energy levels of Al metal, Al oxide and a free Al atom. Near the Al metal surface the 4s level of Al is shifted downwards due to hybridization. Thus the level lies opposite filled states, prohibiting radiationless deexcitation by electron tunneling into the metal. On the other hand, surface states in the band gap of Al_2O_3 enhance electron tunneling of an excited Al atom near an Al_2O_3 surface.

culate the shifts of the atomic levels due to hybridization with the metal states. Aluminium is characterized by a free-electron-like elliptical density of states (DOS). The hybridization between the 4s level and the metal states is dominated by the interaction between the 4s level and the unoccupied part of the metal band, which pushes down the 4s level [36]. Simple estimate using a hopping matrix element of $(|V_{2k}|^2 = 1.10\text{eV}^2, \lambda^2 = 0.02)$ [36] gives a down shift of 3.3 eV. That means that

close to the surface the 4s levels effectively lies below E_f (see Fig. 16) and that resonant deexcitation cannot occur. For the same reason we also obtain a downshift of the Ca 4p level. Since the Ca 4p level already lies below E_f the deexcitation channel remains closed. Cr is a transition metal and its DOS is characterized by a d-band that is centered around E_f . The 4p level lies above E_f and the interaction between the Cr 4p level and the metal DOS results in a slight upshift of the atomic level, which may enhance the possibility of resonant ionization.

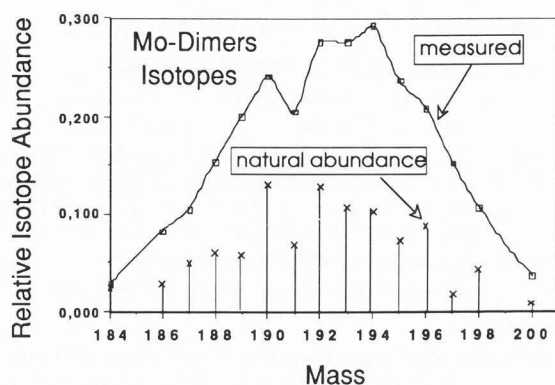


Fig. 17. Measured (photo-ions from laser ionized neutral Mo_2 dimers) and natural abundances of sputtered Mo_2 isotopes (Ar^+ bombardment, $1\mu\text{s}$ pulses). The signal was averaged over 100 ion pulses. The pulses were counted at the channel plates of the SARISA apparatus.

Table 1. Relative yields of different neutral and ionized particles emitted from a Mo surface under 4 keV Ar^+ ion bombardment. All data are given in respect to the number for neutral Mo atoms, arbitrarily set to 100 in this table. The data are valid for clean, oxygen free surfaces. Absolute yields of each species can be drawn using the measured sputtering yield of Mo atoms (≈ 1.4) and an ion transmission measurement using the known Cu^+ sputtering yield.

	Mo	Mo_2	Mo_3	Mo_4
Neutral	100.	0.22	4×10^{-4}	—
Ionized	0.89	0.89	0.02	2×10^{-3}
P^+	0.0089	4.05	50	—

Sputtering of Metal Dimers

The ejection of polyatomic particles has been a challenge among scientists interested in sputtering for a long time, both theoretically as well as experimentally [53]. However, due to the complexity and insufficient detection tools, particularly for neutral polyatomic particles, only a limited number of results is available [18,43,47,56,62]. From experiments described at an earlier stage of this review we know, that for oxidized targets neutral molecules represent the dominant species of sputtered products. This knowledge should stimulate more detailed in-

vestigations of sputtered molecules in the near future.

As an example for the advanced possibilities which are possible nowadays with Laser Spectroscopy, in this context recent measurements of sputtered Mo dimers should be mentioned which we have performed recently. Interest in the physics of dimers has increased dramatically over the last few years due to the finding, that even relatively small size clusters can exhibit metal characteristics.

The experiments described here have been performed in the SARISA system and the sputtered dimers have been detected via Laser Ionization Spectroscopy (LIS). Using this extremely sensitive method and taking advantage of the excellent features of SARISA, absolute sputtering yields for Mo atoms and Mo dimers have been determined (Table 1). Furthermore, ion fractions for both the monoatomic and polyatomic species could be obtained from these measurements. In Fig. 17 the distribution of sputtered Mo_2 dimer-isotopes is shown, as it was obtained with Ionization spectroscopy.

The application of LIS to the study of sputtering of molecules is in its infancy and a lot of new information can be expected from future investigations of this phenomenon.

Sputtering of insulators

Sputtering or desorption mechanisms of insulators are even more complex than those for metals. The complexity arises from the fact that inelastic (electronic) processes play an important role in the release process of particles from insulators. Alkali halides represent a much investigated group of insulators, because self-trapped excitons and the migration of permanent defects play a dominant role in the sputtering process [50,52]. In this case the release of particles can be initiated by ion, electron or photon bombardment.

Ion Stimulated Desorption (ISD), Electron Stimulated Desorption (ESD) and Photon Stimulated Desorption (PSD) of alkali halides have been investigated by several groups [15,20,21]. In all cases neutral ground state and excited atoms are desorbed from the target surface. Interesting and sometimes controversial results have been obtained, indicating a variety of DIET (Desorption Induced by Electronic Transition) processes involved [15,42]. Laser Induced Fluorescence Spectroscopy, again, is a very important tool for these investigations, because the majority of desorbed particles are neutral ground state atoms. A further important source of information is the energy distribution of the desorbed atoms.

NaCl is a very good example and has been studied by many groups [15,21,42]. DIET processes are very pronounced for NaCl and Na is easily accessible for LIF studies. Another ideal candidate is LiF . For LiF an interesting time behavior of the neutral ground state yield and the excited state yield has been observed [43]. When the electron or photon beam is turned off, desorption of neutral ground state atoms continues for a considerable amount of time (10^{-3} sec for ESD and several seconds for PSD), whereas the emission of excited atoms stops immediately after the beam is turned off. This indicates that the origin of the excited atoms is a surface process, whereas bulk and surface processes are responsible for the release of ground state atoms [15].

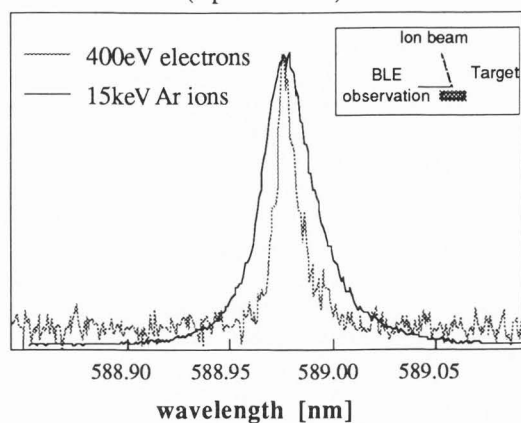
Na I 588.995nm ($3p^2P^0 - 3s^2S$)

Fig. 18. Doppler broadened line profile of the Na D_2 resonance line at 588.9 nm emitted from sputtered excited Na atoms under 400 eV electron and 15 keV Ar⁺ bombardment of a NaCl target. For Ar⁺ bombardment a fit with (4) results in a best fit assuming a E_b value of 6eV, while for electron bombardment the line profile is identical with the broadening of the reference hollow cathode lamp, indicating the thermal nature of the desorbed excited Na atoms.

We have recently started a research program on comparative studies of ISD and ESD from NaCl and CaF₂. In the context of this review paper we will concentrate on one important aspect of these investigations: What information can we obtain from the comparison of the energy distribution of sputtered ground state and excited Na atoms for different ion and electron bombardment? The energy distribution of Na ground state atoms has been measured by DSLFS and that of excited atoms via the Doppler broadened line profile, as previously described. The energy spectrum of neutral ground state atoms is thermal for electron as well as for ion bombardment. We have used H, He, Ar and Xe ions (15 keV) and in all cases the spectrum is predominantly thermal. In all cases, the contribution of collisional sputtering is very weak, indicating the dominant role of DIET processes even for heavy ions. Although this has been known for some time, the strong dominance even for Xe ions is somewhat surprising. On the other hand, the energy distribution of sputtered excited Na atoms is purely thermal for 400 eV electron bombardment, but average energies of excited sputtered Na atoms under 15 keV Ar ion bombardment are in the range of 3 eV as concluded from the Doppler broadened line profiles shown in Fig. 18. The line profile under 400 eV bombardment is identical with the line profile of a Na hollow cathode lamp used for calibration.

From this we can conclude, that the origin of excited Na atoms desorbed from NaCl under electron and Ar ion bombardment is different. Under ion bombardment excited atoms seem to originate from the collision cascade, however very weak it may be, whereas under electron bombardment a different mechanism applies. Excitation by the electron beam or, by contrast, excitation at the surface from decaying excitons has been proposed. More detailed investigations on this subject are under way and promise a deeper insight into the physics of DIET processes.

Conclusions

Laser Spectroscopy and conventional spectroscopy can be effectively combined to study complex problems related to the physics of particle-surface interaction. The extremely high sensitivity of Ionization Spectroscopy and the high state selectivity and velocity resolution obtained with LIF and DSLFS are suitable to tackle many problems in sputtering concerned with neutral particles. When short lived excited atoms and molecules are of interest, BLE Spectroscopy and Doppler broadening studies can be used to solve the problem.

In this review some representative examples of sputtering related problems and their treatment with conventional spectroscopic methods and Laser spectroscopy have been presented. Referring to current research activities, the power and possibilities of Laser Spectroscopy in Studies of Sputtering have been demonstrated.

Acknowledgements

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Discussion with Reviewers

O. Auciello: In looking at Fig. 1, one realizes that only a limited section of the total flux of sputtered particles is probed by the LIF and DSLFS techniques. Extrapolations apparently are made with respect to the uniformity in density and velocity distributions of the sputtered particles measured in all directions around the direction normal to the target surface. Although this can be a reasonable assumption in the case of perpendicular bombardment, it may not be accurate for oblique bombardment as it occurs in many experiments. The question is then, have the density and velocity distributions been measured for different emission directions, and if not, why not? and could we expect to obtain relevant mechanistic information on the sputtering phenomenon from such measurements?

Authors: For the bombarding angles used throughout our experiments the influence is negligible. To measure the entire angular distribution poses experimental problems and has not been done. However, we plan to do this in future experiments, using optical fibers for feeding the laser beams and the detected fluorescence light into or out the vacuum.

O. Auciello: In relation to the Doppler broadening method to measure velocity distributions of excited sputtered particles, a mathematical expression for the line profile has been derived on the assumption that (a) the energy distribution of the sputtered particles is given by $f(E) \propto E/(E+E_0)^3$ and (b) the spatial distribution of the sputtered particles follows a cosine law; the observation geometry being that of the Fig. 10. It appears from the geometry represented in Fig. 10 that the ion beam impacts on the target at an oblique angle. It is well known that depending on the angle of incidence and the energy of the beam, the distribution of sputtered particles may depart substantially from the cosine distribution towards a reflection direction-like distribution; this, in turn, may affect the velocity distribution on the

* See page 1616.

excited sputtered species. Has this problem been taken into account when analyzing Doppler broadening? Do the values obtained from (4) compare always favorably with experimental results?

Authors: The experiments mentioned here have been performed, as outlined in the text, for two different bombarding geometries. The bombarding geometry for each particular result is indicated in the figures. Indeed, under oblique in beam incidence we can clearly distinguish two velocity distributions (see Fig. 14 and discussion there), one cascade-like (which can be reasonably fitted with (4)) and a second contribution with velocities considerably higher (several 100 eV) which we attribute to direct knock-ons.

N. Winograd: O₂ and SF₆ exposure experiments are discussed. Is the Cr signal a function of time during an exposure? Upon shutting-off the gas, does the signal stay the same or does it change to its original values?

Authors: In general, the Cr signal (ground state as well as excited) is a function of time during an exposure. After some time an equilibrium state is reached. This time can vary quite substantially depending on the gas as well as the target. See the example in Fig. 8. Upon shutting off the gas changes to its original value, again after a time interval characterized by the time constants shown in Fig. 8.

N. Winograd: A theory of metastable yield enhancement by oxygen is discussed. It is predicted that velocities should be higher for clean surfaces. Could the author state clearly why this is predicted?

Authors: Assuming that the radiationless deexcitation at the surface is responsible for the existence of excited atoms, one would expect that near a metal surface deexcitation is very probable and assumed to be inversely proportional to the particle velocity.

N. Winograd: Sputtering is a surface phenomenon. What can you tell us about the actual state of the surface either before or during ion bombardment? Isn't this state crucial to making realistic comparisons to proposed theories?

Authors: As everyone concerned with sputtering knows, the state of the surface is changed during ion bombardment. Of course, an influence of the changing surface might cause problems in some cases. However, the effects which can be expected as far as the properties are concerned which we investigated and compared to theories (E_b), no substantial influence is expected.

N. Winograd: Your comments about the Sigmund theory are intriguing. In reference 26, you suggest that E_b values do not yield correct velocity distributions. Also, recent RIS results from our group show that the velocity distributions as a function of desorption angle are incorrectly predicted by Eq. 1. The prediction of the angular distributions as a function of velocity are also wrong. Do you think these data indicate there are some fundamental problems with these older theories?

Authors: It is true that we have reported deviations from the tabulated E_b values. As mentioned there, we believe that these

deviations are mainly due to surface impurities (for example carbon in the Cr surface). In the context of this review, in our opinion, it is, however, remarkable to mention that despite all the slight deviations (some tens of an eV) found experimentally the measured velocity maxima (from many experiments by various groups) result in E_b values which generally agree with equation (1).

N. Winograd: The SARISA experiments on Mo₂ are of interest. First, we have found that for high laser powers on In₂, for example, that photodissociation is the main channel to produce In*, In and In⁺. This means that the photoionization cross sections are power dependent and a complicated item to get at. How did you obtain the Mo₂ sputtering yields? Also, since the name SARISA refers specifically to atoms, you will have to call your method SARISM.

Authors: The details of the Mo-dimer experiments are described in a paper which we have submitted for publication (J. of Vac. Sci. Technol. B).

*Editor: How may a reader obtain the IBM report in reference 64?

Authors: Copies of the report may be requested from: IBM, Thomas J. Watson Research Center, Distribution Service 73-F11, Post Office Box 218, Yorktown Heights, New York 10598, USA