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Cr ATOMS SPUTTERED FROM DIFFERENT MATRICES

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Sputtering of Cr atoms from different Cr compounds under various surface conditions proved to be an interesting playground for investigations of the charge and excitation state of sputtered atoms and molecules. In general we distinguish between a Cr atom leaving a target surface under keV ion bombardment as a neutral atom in the electronic ground state, as a neutral excited atom, as a singly charged ion in the ground state or in an excited state, or as Cr atoms incorporated in a cluster or molecular complex. Particular emphasis was given to the study of sputtered neutral atoms in the electronic ground state and in excited states. Laser induced fluorescence spectroscopy (LIF) and detection of the bombardment induced light emission (BLE) have been used. The composition of the sputtered flux proved to be very sensitive to electronegative adsorbates on the surface. For clean targets the majority of the sputtered particles are neutral atoms in the electronic ground state. Adsorbing gases with electronegative constituents generally result in strongly reduced sputtering yields of ground state atoms. Oxygen compounds show a similar behavior as oxidized metal surfaces. Cr sputtered from alloys or Cr compounds are in general characterized by yields comparable to Cr metal targets. The energy distributions, however, show different maxima corresponding to slightly changed surface binding energies.

1. Introduction

Cr has recently been used in several experiments to study its sputtering behavior [1–4]. It has proven to be an interesting playground for sputtering investigations, because of its extreme sensitivity to adsorbed gases. Most of the experiments we have performed concentrated on measuring sputtered neutral Cr atoms in different excitation levels. LIF and BLE have been used. In the present paper new results will be compared with those published previously. Two perspectives will be emphasized: (1) How is sputtering of Cr particles influenced by surface adsorbates? (2) Are there differences in the sputtering behavior for Cr depending on the target matrix (Cr metal, Cr compound (Cr_2O_3, Cr_3C_2), Cr alloy (stainless steel with 17% Cr))? The sputtering behavior has been investigated on behalf of the sputtering yields of neutral atoms in the ground state and in excited states and the velocity distributions of sputtered neutral ground state atoms.

The influence of oxygen coverages and oxygen incorporated in a metal target on various sputtering parameters has recently been studied extensively [1–8]. In these studies various experimental techniques, like SIMS and laser induced fluorescence or multiphoton resonance ionisation (MPRI), have been used. A common result of all these investigations is the strong decrease of sputtered neutral ground state atoms. The density of sputtered excited atoms and ions generally increases quite considerably with oxygen coverage (increases between 3 and 100 have been experimentally observed [1–4]) but cannot compensate for the strong decrease of the density of sputtered neutral ground state atoms (decreases > 100 have been experimentally observed [1–4,8]). The decrease of the total sputtering yields, experimentally observed on various metals, does not exceed a factor of 5.

The implications of this experimental evidence have many consequences for the understanding of the sputtering process itself, as well as for practical applications of sputtering. In particular, everyone dealing with SIMS, MPRI or other surface analysis methods based on detecting secondary particles has to be concerned with the form in which the particles leave the target surface.

Various models have been proposed to describe the existence of excited and ionized sputtered particles [9–11]. Although there are experimental indications favoring some of these models, at present none of the models can be totally rejected nor taken as the final explanation. Furthermore, it is not yet proven that the excitation process and the ionisation process have the same origin, although many experimental observations would suggest this conclusion.

2. Experimental

Laser induced fluorescence spectroscopy [LIF] and Doppler shift laser fluorescence spectroscopy [DSLFS] have been used to measure the sputtering yield and the energy distributions of sputtered neutral ground state atoms. The sputtering yield of sputtered excited atoms has been recorded via bombardment induced light emission [BLE]. Experimental details concerning the laser

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system, detection optics, ion beam source and data acquisition can be found in previous papers [12,13]. The typical Ar^+ current density at the target surface was about 10 $\mu A/cm^2$ and the ion energy was 15 keV.

The gas coverage of the Cr target surface was controlled by varying the gas partial pressure in the UHV vacuum chamber. The partial pressure was measured with a quadrupole mass analyzer. The partial pressure and the Ar^+ current density define the ratio N[gasmolecules]/N[Ar^+] between gas molecules and Ar ions reaching the target surface per second and cm^2. This defines the steady state coverage of the surface with the gas. For calculating the exact coverage, the appropriate sticking probabilities and the sputtering yields have to be known exactly.

For some adsorbates (SF_6) it is necessary to cool the target, because the sticking probability at room temperature is negligible. But below 140 K SF_6 physisorbs at the surface [14,15]. Therefore, the target could be cooled by a cooling assembly. A copper container was filled with liquid nitrogen. The container was thermally connected with the target by a copper lace, so that the target could be cooled and rotated. The temperature was measured by a thermocouple. Target temperatures down to approximately 120 K have been achieved.

3. Cr sputtered from different matrices

The sputtering behavior of Cr atoms evolving from Cr compounds and Cr alloys has been investigated by means of LIF, DSLFS and BLE. It is interesting to compare the results with the corresponding values obtained for Cr sputtering from clean Cr metal targets and Cr targets covered with adsorbates. In particular the comparison between oxidized surfaces and compound oxides is of interest.

Yields of neutral Cr ground state atoms sputtered from a Cr_2O_3 target obtained by LIF are lower by a factor of approximately 50 compared to the corresponding yields for Cr sputtered from Cr metal [4]. This low yield is quite reasonable, if one takes into account what has been observed for oxidized Cr metal surfaces.

The yields of neutral Cr ground state atoms and neutral excited atoms sputtered from a Cr_3C_2 compound [4] measured as a function of the $N[O_2]/N[Ar^+]$ ratio show an identical dependence as for Cr atoms sputtered from Cr metal. The velocity spectrum of Cr ground state atoms sputtered from Cr_3C_2 allows us to determine the surface binding energy of Cr atoms in the Cr_3C_2 matrix. Within the experimental error the surface binding energy has been obtained to $E_b = (3 \pm 0.3)$ eV, compared to (4.2 ± 0.2) eV for Cr metal [4].

In addition we have performed corresponding measurements of the yields of Cr atoms sputtered from a stainless steel target containing 17% Cr. For clean targets the observed Cr ground state yield is lower by a factor of 5 compared to sputtering from Cr metal targets. This is in very good agreement with the Cr concentration in the matrix. The yield of sputtered neutral ground state atoms as a function of N[gasmolecules]/N[Ar^+] is shown in fig. 1. The steel target was exposed to an increasing O_2 atmosphere. The results are compared to yields of neutral Cr ground state atoms from a Cr target exposed to O_2 and SF_6.

Assuming the validity of the theoretical collision cascade contribution [16] which has been experimentally verified in many cases for sputtering of clean targets [1,13–15,17], it is possible to obtain the surface binding energy E_b from the velocity distribution of sputtered neutral ground state atoms. Fitting the experimentally obtained values with the theoretical distribution for the velocity distribution of the sputtered Cr atom density

$$\frac{dN(v)}{dv} = \frac{v^2}{\left(v^2 + v_b^2\right)^3}, \qquad (1)$$

values for the surface binding energy E_b can be directly obtained from the maximum in the velocity distribution. By determining the fitting parameter v_b in eq. (1) from the measured DSLFS spectra for Cr sputtered from stainless steel (fig. 2), a surface binding energy of (5.1 ± 0.2) eV is obtained. This value is higher than the surface binding energy of Cr sputtered from Cr metal. In the latter case 4.2 eV has been measured.

The similarity of the results under O_2 exposure in fig. 2 for stainless steel targets and Cr targets has also been confirmed by the changes of the velocity spectrum of sputtered neutral Cr atoms for increasing O_2 coverage. A substantial broadening of the velocity distributions of sputtered neutral ground state atoms has been

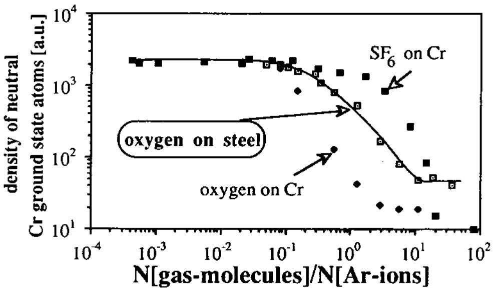

Fig. 1. Yield of neutral Cr ground state atoms sputtered from a stainless steel target containing 17% Cr bombarded with 15 keV argon ions. The target was exposed to an increasing partial pressure of O_2. The yield of neutral ground state Cr atoms has been recorded by LIF for increasing $N[O_2]/N[Ar^+]$ ratios. For comparison corresponding curves for Cr atoms sputtered from a Cr metal target under O_2 and SF_6 exposure are given. The yields are normalized for clean targets.

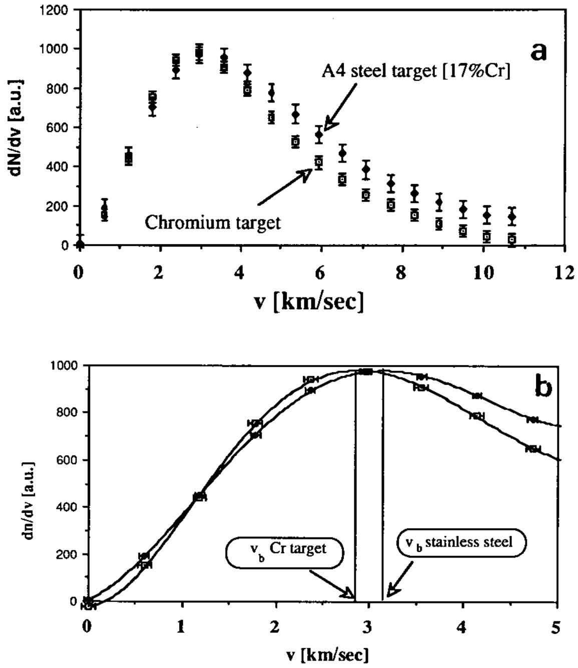

Fig. 2. (a) Velocity spectrum of sputtered Cr ground state atoms obtained by DSLFS. A Cr metal and a stainless steel target have been bombarded by 15 keV argon ions. The spectra have been measured at an O_2 background partial pressure below 1×10^{-10} mbar (total background pressure 1×10^{-8} mbar, predominantly Ar). (b) Low energy part of the spectrum in (a). The shift of the maximum is clearly seen and outside the experimental error.

observed for Cr targets covered with an increasing amount of O_2. In fig. 3 velocity spectra of neutral Cr ground state atoms sputtered from stainless steel are plotted as a function of the $N[O_2]/N[Ar^+]$ ratio. The curves in fig. 3 have been normalized for visual reasons (in order to obtain the actual values the curves have to be divided by the corresponding factors, which can be obtained from fig. 1).

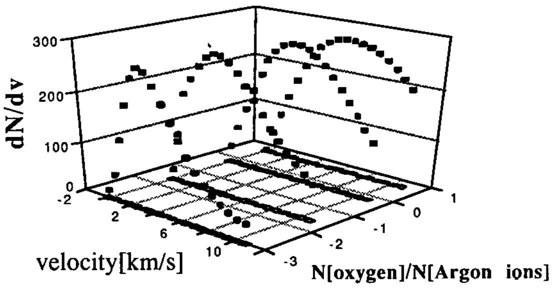

Fig. 3. Velocity distributions of neutral Cr ground state atoms sputtered from a stainless steel target as a function of the $N[O_2]/N[Ar^+]$ ratio. The spectra are normalized in their maxima.

The broadening of the spectra at increasing O_2 coverage is quite substantial and in good agreement with results for Cr sputtered from Cr metal. Fitting the broadened spectra with eq. (1) would yield values for the surface binding energy up to (15 ± 3) eV at high O_2 coverages. We would, however, like to point out, that the validity of the collision cascade theory as expressed in eq. (1) is doubtful in this case.

4. Cr atoms sputtered from Cr targets with electronegative adsorbates

4.1. Sputtered neutral Cr atoms in the electronic ground state

The most striking consequence of adsorption of electronegative atoms on a metal surface is a total reversal of the composition of the sputtered flux [3]. It has been well known for a long time that electronegative adsorbates enhance the yield of sputtered excited atoms and sputtered ions [6,9,11,18,19]. Information about the influence of electronegative adsorbates on the yield of neutral ground state atoms sputtered from surfaces is relatively new [3,4,8]. Most of these experiments have been performed with O_2 adsorbed at surfaces. The influence of other electronegative adsorbates has been studied only in a limited number of cases, except for an increasing number of experiments investigating chemical sputtering due to chlorine and fluorine on Si [14,15,20].

On most metals investigated, O_2 is chemisorbed on the surfaces by oxidation. This process generally takes place at room temperature. For fluorine adsorption, SF_6 is used in many cases. At room temperature the sticking probability is very low. Therefore, the target has to be cooled down to approximately 130 K in order to observe physisorption.

The influence of electronegative adsorbates on the yield of sputtered neutral Cr atoms in the electronic ground state is very drastic. Because neutral ground state atoms make up 99% or more of the sputtered particles, their behavior and their relevance for understanding the sputtering process is of special importance. Furthermore, it should be mentioned that neutral atoms are used more and more, and very effectively indeed, for surface analysis methods [7,21]. In fig. 1 some examples for the neutral Cr ground state yield are shown as a function of the $N[\text{gasmolecules}]/N[Ar^+]$ ratio. At $N[\text{gasmolecules}]/N[Ar^+] = 10$ the yield has decreased more than a factor of 100 for O_2 as well as for SF_6 adsorption. The experiments with O_2 have been performed at room temperature, the ones with SF_6 at a target temperature of 120 K.

In the this section (fig. 3) we have discussed the influence of the O_2 coverage on the velocity distribution of neutral Cr ground state atoms sputtered from stainless steel containing 17% Cr. The influence of O_2 on the spectra of Cr sputtered from Cr metal show basically the same tendency to broader distributions for an increasing $N[O_2]/N[Ar^+]$ ratio. Similar results have also been found for Ca [17] and Ti [8]. Therefore, it is quite astonishing, that the velocity spectra of neutral Cr atoms sputtered from Cr under SF_6 exposure show contrary results, as far as a broadening of the distribution is concerned [23].

For SF_6 coverage no broadening of the velocity spectrum of sputtered Cr atoms is observed, although the yield itself behaves like we know it from O_2 coverage.

4.2. *Yields of excited neutral Cr atoms and excited Cr ions*

Most of the excited Cr atoms and ions which evolve from the target surface, have lifetimes of the order of 10^{-8} s. They decay within a few mm in front of the target surface and can be detected by recording the spontaneously emitted photons. We have investigated the influence of O_2, SF_6, NH_3, CH_4 and N_2 gases on the sputtering yield of excited Cr ions and atoms. We will restrict the discussion to Cr metal targets. The sticking probability of N_2 is very low and we have observed no measureable dependence of the yield of excited Cr atoms or ions on the partial pressure of N_2. An identical result has been obtained for CH_4 exposure at room temperature and also at 120 K. (The ground state yields have been found to be independent of the CH_4 and N_2 partial pressure too.) Strong effects on yields of excited atoms and ions have been observed for O_2, SF_6 and NH_3 coverage. In fig. 4a the BLE spectrum from 250 to 330 nm is given as obtained for a clean Cr target and Cr targets heavily covered with O_2, NH_3 and SF_6 (N[gasmolecules]$/N[Ar^+] \approx 1$). In the spectral region shown in fig. 5a lines from neutral excited Cr atoms and from excited Cr ions have been identified. Fig. 4b shows the yields of sputtered excited neutral Cr atoms and ions as a function of the N[gasmolecules]$/N[Ar^+]$ ratio.

The observations shown in fig. 4 can be summarized as follows: (1). In general the yield of sputtered excited neutral Cr atoms and ions increases with an increasing N[gasmolecules]$/N[Ar^+]$ ratio for all gases and saturates at high coverages. (2) As an exception, the yield of excited ions does not increase for ammonia coverage. (3) For oxygen coverage a maximum for the yield of sputtered excited neutral Cr atoms is observed for $N[O_2]/N[Ar^+] \approx 1$. (4) The increase for excited ions is generally superior to the increase of excited neutrals. (5) In spite of many similarities between O_2 and SF_6 coverage, differences exist.

In fig. 5 the occupation of exited energy levels of sputtered Cr atoms are plotted as a function of their potential energy. The data can be fitted by a Maxwell–Boltzmann distribution assuming a temperature of approximately 4500 K for clean and covered targets.

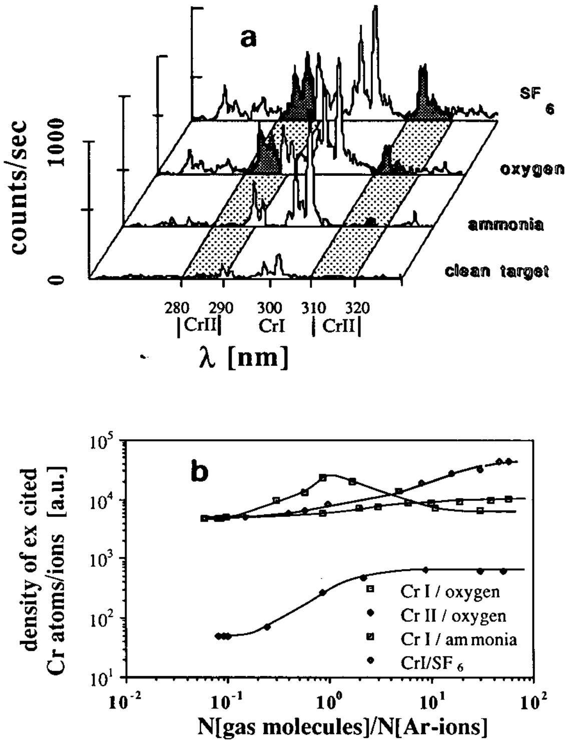

Fig. 4. (a) Part of the BLE spectrum obtained by bombarding clean Cr targets and Cr targets exposed to different gases. The spectra shown for the different gases have been recorded at ratios N[gasmolecules]$/N[Ar^+]$ which correspond to a maximum yield of excited Cr atoms or ions. (b) Dependence of the density of excited Cr atoms and ions sputtered from a Cr target at 120 K on the ratio $N[SF_6]/N[Ar^+]$ of SF_6 molecules to argon ions striking the target surface per sec per 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 has been measured and for determining the yields of excited Cr ions the fluorescence intensity of the 283.5 nm transition line has been measured.

We would like to stress that by fitting the data in fig. 5 and giving temperatures associated to the Maxwell–Boltzmann fits we do not imply that the LTE model [9,22] describes the physics of the excitation during sputtering. Furthermore, the two regions shown in fig. 6 might have some physical origin. Up to about 4.5 eV the logarithm of the population of the energy levels follows pretty well a straight line. Above 5 eV the data

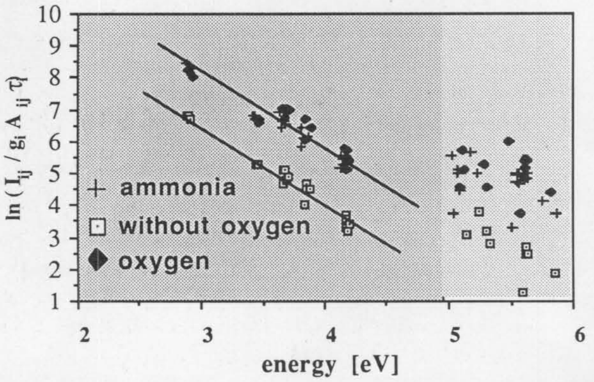

Fig. 5. The population of different electronic energy levels of sputtered excited Cr atoms is obtained from the fluorescence intensities of different transition lines observed in the measured BLE spectrum. $\ln((I_{ij}/g_i)A_{ij}\tau_i)$ is plotted as a function of the energy of the energy levels. (I_{ij} is the measured fluorescence intensity, g_i is the statistical weight of the level, A_{ij} is the dipole martrix element of the transition line and τ_i is the total lifetime of the upper level. The product $A_{ij}\tau_i$ is the branching ratio from the upper level.)

are much more scattered and, therefore, a reasonable fit is difficult. This could be explained by the increasing experimental error due to the low intensities of these transitions lines, but the relative abrupt change seems to suggest a physical origin.

4.3. Time dependence of yields

The changes in the measured sputtering yields exhibit a typical time dependence. In general, steady state conditions (as far as the yields are concerned) are reached within a characteristic time delay after the partial pressure of the gas is increased. Furthermore, it turns out that this time dependence is a function of the stage of surface coverage as characterized by the $N[\text{gasmolecules}]/N[\text{Ar}^+]$ ratio. The characteristic time constants are, of course, directly related to the ion dose to which the target is exposed after the increase of the partial pressure. In fig. 7 these time constants (ion doses) are plotted as a function of the $N[\text{gasmolecules}]/N[\text{Ar}^+]$ ratio.

The time constants vary by two orders of magnitudes, depending on the species observed and the kind of adsorbate. Furthermore, a change of the time constant is observed as the $N[O_2]/N[\text{Ar}^+]$ ratio is increased. In general, the steady state values are reached only after the target has been exposed at the increased O_2 partial pressure to an ion dose in the order of 5×10^{16} argon ions/cm². As an exception, this effect has been observed in a much less pronounced way for excited Cr ions and oxygen coverage. For SF_6 coverage this effect has not been observed at all, neither for neutrals nor for ions. Finally, the time constants varied also with the target material. For metal Cr the time effect was very pronounced. For Cr incorporated in stainless steel the time constant was considerably lower.

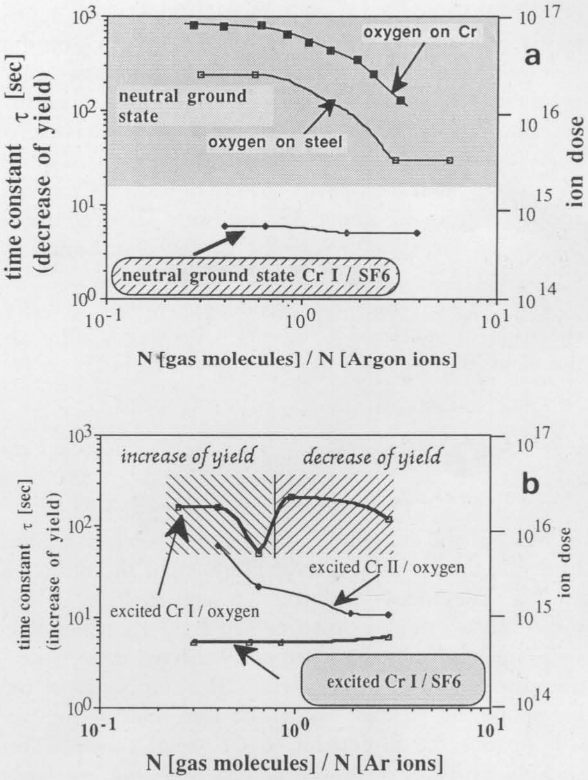

Fig. 6. (a) Time constants (ion doses) for reaching the steady state condition (yield decreases) after increase of the O_2 and SF_6 partial pressures for neutral Cr atoms in the ground state as a function of the ratio $N[\text{gasmolecules}]/N[\text{Ar}^+]$. (b) Time constants (ion doses) for reaching the steady state condition (yield increases) after increase of O_2 and SF_6 partial pressures for excited Cr atoms and ions as a function of the ratio $N[\text{gasmolecules}]/N[\text{Ar}^+]$.

5. Discussion

A variety of sputtering yield data and energy distributions have been obtained by LIF, DSLFS and BLE for Cr sputtered from various targets and under different surface conditions. The results obtained for Cr sputtered from metal, oxide, carbide and alloy targets are consistent among each other as far the yields are concerned. This is true for the yield values (their porportionality to the Cr bulk concentration) and for their dependence on surface contaminations by electronegative adsorbates. In the case of Cr_2O_3, however, the yield of neutral Cr ground state atoms is far less than the Cr bulk concentration. This is quite reasonable, if one takes into account the influence of oxygen on the sputtering yields. However, the fact that the sputtering yield of neutral Cr ground state atoms from Cr_2O_3 is only a factor of 50 lower than the corresponding yield from Cr metal, whereas the yields found for O_2 exposure of a Cr metal target are reduced by a factor more than 100, is worth noting. A possible hint for an explanation could be found in the time dependence of the sputtering yields as shown in fig. 6. The Cr-oxide formed at the surface after the increase of the partial pressure of O_2 is one source for excited atoms (and causes the reduction of sputtered neutral ground state atoms). Due to ion bombardment oxygen is implanted in target and/or a different oxide is formed in the first few layers of the bulk. This represents an additional source for sputtered excited atoms. In a Cr_2O_3 compound this second process might be inhibited.

The surface binding energy of Cr in different matrices shows variations between 3 eV for Cr_3C_2 and 5 eV for stainless steel. For Cr metal (4.2 ± 0.2) eV have been found in good accordance with the tabulated heat of sublimation of 4.2 eV.

The influence of adsorbates on all sputtering values is far reaching and represents itself in drastic yield changes and changes of the energy distributions. The influence of electronegative adsorbates is particularly pronounced and has been studies on behalf of O_2 and SF_6 coverage. The results obtained for O_2 and SF_6 should be compared with each other under the perspective, whether the influence of SF_6 adsorption on Cr metal surfaces results basically in the same sputtering phenomena as oxygen coverage. A more detailed discussion of this problem can be found in ref. [23]. In this article it is shown that a similar process can be assumed to happen for O_2 ans SF_6 exposure. Cr oxides and Cr fluorides formed at the surface or in the uppermost target layers are responsible for the sputtering behavior.

The broadening of the velocity spectra for oxygen is not fully understood at present. In spite of the striking similarities between oxygen and SF_6 coverage, differences have been observed. The yield of sputtered excited Cr atoms shows a maximum for oxygen exposure, which has not been found for SF_6 exposure. Perhaps more striking is the time dependence of the yields after the partial pressure of the gas is increased. For oxygen exposure ion fluxes of the order of 10^{16} ions/cm^2 are necessary to establish a steady state condition. This could be explained by a considerable influence of implanted oxygen on the yields of neutral ground state and excited Cr atoms. For SF_6 the steady state condition for all yields is reached practically immediately after the pressure increase. Evidently, the topmost layer has an essential influence on most of the sputtering yields studied. These assumptions are also confirmed experimentally in a slightly different way: when the gas partial pressure after oxygen exposure is reduced to its background levels (typically within 15 s) the original yield values are reached after being exposed to ion fluences of the order of 10^{16}–10^{17} ions/cm^2. After SF_6 exposure ion fluxes in the range of 10^{14} ions/cm^2 are sufficient to establish the original values.

Finally we would like to emphasize the differences observed for neutral excited atoms and excited ions. For O_2 and SF_6 coverage the increase of ions is superior to the increase of excited neutrals. Ions also show a less pronounced time dependence than neutrals. For NH_3 coverage the ion to neutral ratio is inversed.

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