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INFLUENCE OF SF_6 COVERAGE ON THE SPUTTERING BEHAVIOUR OF Cr-TARGETS

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If clean metal surfaces are bombarded with energetic ions in the keV range the predominant contribution to the sputtered flux are neutral metal atoms in the electronic ground state. It is well established that a drastic change in the composition of the sputtered flux is observed when the metal surface is covered with oxygen. In this work we report investigations of the influence of SF_6 coverage on the sputtering of a Cr target. The Cr targets have been cooled to approximately 120 K. At room temperature the sticking probability of SF_6 is negligible. Below 170 K SF_6 is physisorbed at the Cr target surface. With increasing coverage by SF_6 the amount of neutral Cr atoms in the ground state is strongly reduced. At the same time the amount of sputtered excited atoms increases with increasing coverage with SF_6.

1. Introduction

The influence of an oxygen coverage on a metal surface on various sputtering parameters has been recently studied extensively [1–5]. In these studies various experimental techniques, such as SIMS, laser-induced-fluorescence or multiphoton-resonance-ionisation, have been used. In our recent publications [1,2] particular emphasis has been laid on the study of sputtered neutral ground state and excited atoms. A common result of all these investigations is the strong decrease of the yield of sputtered neutral ground state atoms with increasing oxygen coverage. The flux of sputtered excited atoms and ions generally increases quite considerably with oxygen coverage (increases by a factor up to 100 have been experimentally observed [1,2,5]) but cannot compensate for the strong decrease of the yield of sputtered neutral ground state atoms (decreases by a factor > 100 have been observed [1,2,6]). The decrease for the total sputtering yield experimentally observed on various metals does not exceed a factor 5.

Various models have been proposed to describe the excitation and ionisation of sputtered particles [5,7–9]. Although there are experimental indications favoring some of these models, at present none of these 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.

In this paper we report experiments similar to those described previously [1,2] for oxygen coverage, but now for various degrees of SF_6 coverage of a Cr metal target. Electronegative adsorbates (e.g. O, Cl, F) have been observed to increase the yield of positive ions during sputtering. Although several experiments have been performed measuring the neutral particle yields for oxygen covered metals, practically nothing is known about the yields of neutral particles from metals covered with Cl or F. However, recently many sputterings experiments have been performed with Cl and F adsorbed on silicon [10–12]. In this case a considerable enhancement of the sputtering yield is observed due to chemical sputtering. We have used SF_6 as a source for F at the Cr metal surface in our experiments. At room temperature the sticking probability of SF_6 is very low. Due to the melting point of SF_6 at −50.5°C, SF_6 physisorbs at the surface, if the target is cooled below −50.5°C. However, contrary to a SF_6 on silicon, no chemical sputtering effects are expected for SF_6 at chromium, because the possible fluorides formed with Cr are not volatile as it is the case for the corresponding SiF_x products, which result in a weakening of the Si–Si bonds [11,12].

2. Experimental

Laser-induced-flourescence-spectroscopy [LIF] and Doppler-shift-laser-flourescence-spectroscopy [DSLFS] have been used to measure the relative sputtering yield and the energy distribution of sputtered neutral ground state atoms. The relative sputtering yield of sputtered excited atoms has been recorded via bombardment-induced-light-emission [BLE]. Experimental details concerning the laser system, detection optics, ion beam source and data acquisition can be found in previous

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papers [13,14]. The typical Ar^+ current density at the target surface was about 6 $\mu A/cm^2$ and the ion energy was in all cases 15 keV.

The SF_6 coverage of the Cr target surface was controlled by varying the SF_6 partial pressure in the UHV chamber. The partial pressure was measured with a quadrupole mass analyzer. The partial pressure and the Ar^+ current density defines the ratio between gas molecules and Ar ions N[gas molecules]/$N[Ar^+]$ striking 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 sticking probability and the sputtering yield have to be known exactly.

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 in situ rotated to enable BLE and LIF measurements. The temperature was measured by a thermocouple. Target temperatures down to approximately 110 K have been achieved.

3. Experimental results

LIF measurements of the yield of neutral Cr ground state atoms sputtered from a Cr target at room temperatures at various SF_6 partial pressures did not show any measurable dependence of the yield of sputtered neutral ground state atoms on the SF_6 partial pressure (up to 5×10^{-5} mbar). This can be easily explained if one assumes that the sticking probability of SF_6 at room temperature is zero. In a second set of experiments the target was kept at 120 K. This temperature is well below the melting point of SF_6 of $-50.5°C$ and, therefore, physisorption of SF_6 is expected. Now, when the SF_6 partial pressure in the target chamber is increased stepwise, one observes a decrease of the yield of sputtered neutral Cr ground state atoms.

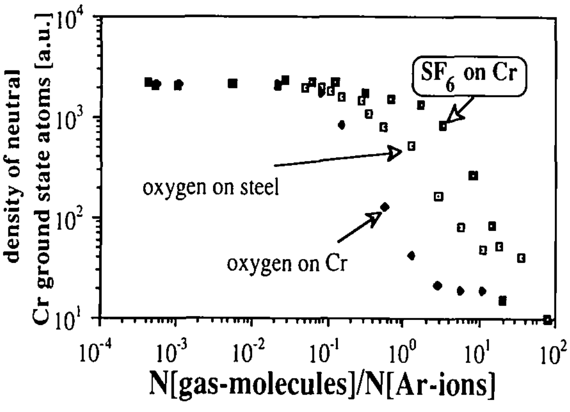

Fig. 1. Dependence of the density of neutral Cr ground state atoms sputtered from a Cr target at 120 K on the ratio $N[SF_6]/N[Ar^+]$ of SF_6 molecules to argon ions striking the target surface per second and cm^2. For comparison the corresponding yields of Cr ground state atom sputtered from a Cr and a stainless steel target at room temperature are plotted as a function of the ratio of oxygen molecules to argon ions.

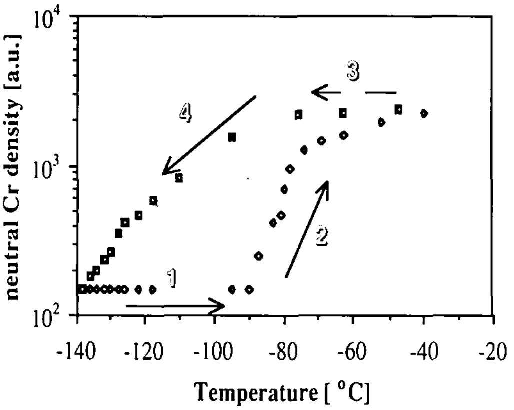

Fig. 2. Dependence of the density of neutral Cr ground state atoms sputtered from a Cr target and exposed to a ratio $N[SF_6]/N[Ar^+] = 100$ on the target temperature.

In fig. 1 the dependence of the yield of sputtered neutral Cr ground state atoms as a function of the ratio $N[SF_6$-gas molecules]/$N[Ar^+]$ is compared to the yield of sputtered neutral ground state atoms as a function of the ratio $N[O_2$-gas molecules]/$N[Ar^+]$. In addition to Cr atoms sputtered from a Cr target also the curve for Cr atoms sputtered from a stainless steel target with 18% Cr is given for comparison. All three curves in fig. 1 exhibit a similarity, where the main result can be summarized that the yield of sputtered neutral ground state atoms decreases to less than 1% of its original value for ratios N[gas molecules]/$N[Ar^+] > 10$.

In order to determine the temperature dependence of the SF_6 coverage of the Cr target, the yield of sputtered neutral ground state atoms has been recorded during increasing the target temperature and simultaneously exposing the target to a SF_6 partial pressure of 1×10^{-5} mbar (ratio N[gas molecules]/$N[Ar^+] = 100$). The heating-cooling cycle is shown in fig. 2.

Besides neutral Cr ground state atoms, sputtered excited atoms have been investigated with BLE. Again the results for SF_6 coverage of a Cr target have to be compared with the behavior for coverage with oxygen. Furthermore, results for coverage with ammonia are given. In fig. 3a the BLE spectrum from 250 to 330 nm is given as obtained for a clean Cr target and Cr targets heavily covered with oxygen, ammonia and SF_6 (ratio N[gas molecules]/$N[Ar^+] \sim 1$). In the spectral region shown in fig. 3a lines from neutral excited Cr atoms and from excited Cr ions have been identified. Fig. 3b shows the yields of sputtered excited neutral Cr atoms and ions as a function of the ratio N[gas molecules]/$N[Ar^+]$.

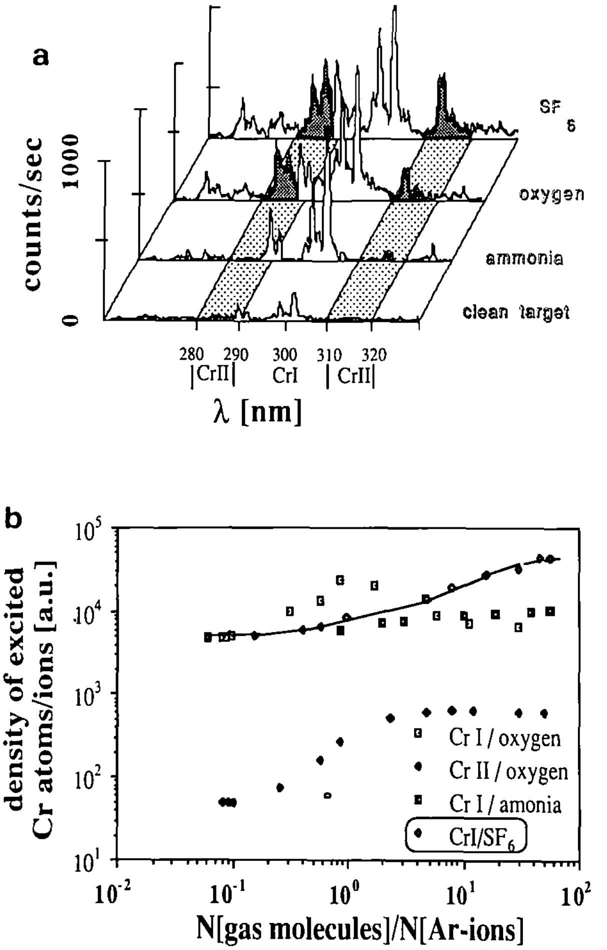

Fig. 3. (a) Part of the BLE spectrum obtained by bombarding clean Cr targets and Cr targets exposed to different gases. The spectra shown for the different gases have been recorded at ratios N[gas molecules]/$N[Ar^+]$ which correspond to a maximal yield of excited Cr atoms or ions. (b) Dependence of the density of excited Cr atoms and ions sputtered from a Cr target at 120 K on the ratio $N[SF_6]/N[Ar^+]$ of SF_6 molecules to argon ions striking the target surface per second 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.

The figure shows very clearly, that

1) In general the yield of sputtered excited neutral Cr atoms and ions increases with increasing ratio N[gas molecules]/$N[Ar^+]$ for all gases and saturates at high coverages.
2) As an exception, for ammonia coverage the yield of excited ions does not increase.
3) For oxygen coverage a maximum for the yield of sputtered excited neutral Cr atoms is observed for $N[O_2]/N[Ar^+] \sim 1$.
4) The increase for excited ions is generally superior to the increase of excited neutrals.
5) In spite of many similiarities between O_2 and SF_6 coverage, differences exist.

In order to increase the gas coverage of the target surface, in our experiments the partial pressure of the gas is increased. As a consequence of this, an interesting observation has been made (see fig. 4).

When the oxygen partial pressure is increased by a certain amount, the corresponding changes in the yields

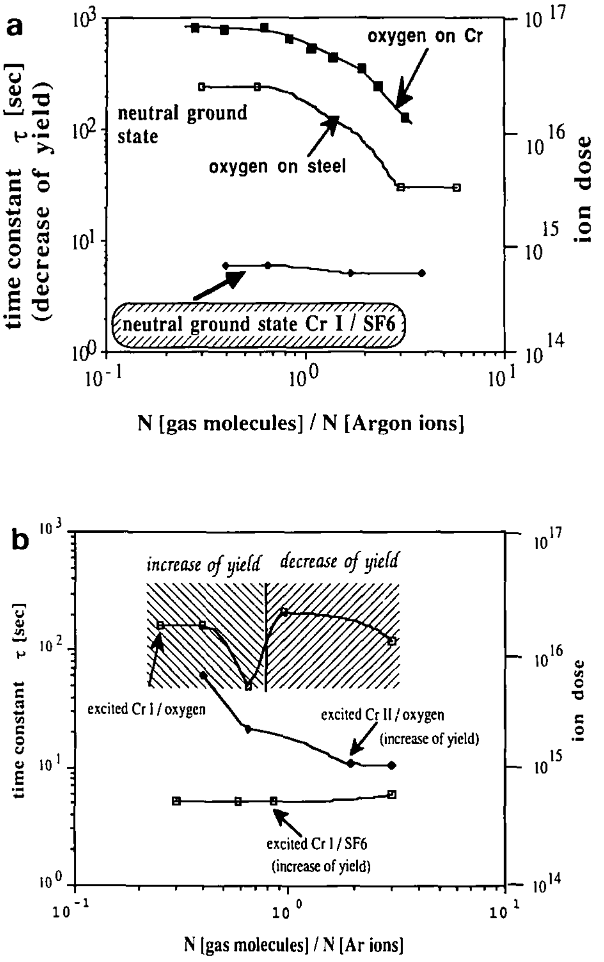

Fig. 4. (a) Time constants (ion doses) for reaching the steady state condition (yield decreases) after increase of O_2 and SF_6 partial pressure for neutral Cr atoms in the ground state as a function of the ratio N[gas molecules]/$N[Ar^+]$. (b) Time constants (ion doses) for reaching the steady state condition (yield increases) after increase of O_2 and SF_6 partial pressure for excited Cr atoms and ions as a function of the ratio N[gas molecules]/$N[Ar^+]$.

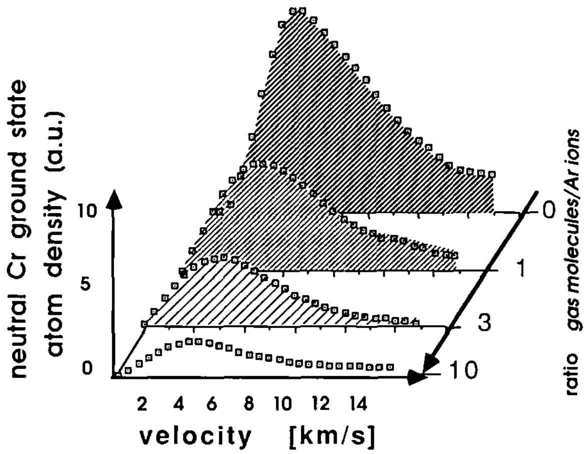

Fig. 5. Velocity spectra of sputtered Cr neutral ground state atoms for different ratios $N[SF_6]/N[Ar^+]$. The target temperature was kept at 120 K. No shift of the maximum in the velocity distribution is found.

(*this is valid for neutral ground state and excited atoms*) are characterized by a remarkable time dependence. 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 flux in the order of 5×10^{16} argon ions/cms^2. As an exception, this effect has not been observed 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. Furthermore, as it can be seen in fig. 4, the time constants (or corresponding ion doses) to reach the steady state conditions of the yields vary with the ratio N[gas molecules]/$N[Ar^+]$.

The energy spectrum of sputtered particles can give us a more detailed information about the sputtering mechanisms and, possibly, the excitation mechanisms involved [14,15]. The surface binding energy can be determined from the maximum of the energy spectrum. In recent experiments [6,14,15] it has been observed that the stepwise oxidation of a metal target goes hand in hand with a broadening of the velocity distribution of the sputtered neutral metal atoms detected in the electronic ground state. For SF_6 coverage we have found contrary results as shown in fig. 5.

Although the decrease of the yield of sputtered neutral ground state atoms for SF_6 coverage is comparable to the decrease under oxygen coverage, the velocity spectra do not show a broadening in the case of SF_6 coverage.

4. Discussion

At this point the question of whether the influence of SF_6 adsorption on Cr metal surfaces results basically in the same sputtering phenomena as oxygen coverage is legitimate. The experimental results for the yield of sputtered neutral ground state atoms under exposure of a Cr target to a SF_6 atmosphere can principally be interpreted in two ways:

1) The Cr target surface is simply covered with an increasing number of SF_6 layers and finally only SF_6 or SF_6-fractals are sputtered. A similar case has been reported for Si sputtering under SF_6 coverage below 60 K [11].
2) SF_6 adsorbed at the surfaces decomposes and Cr-fluorides are formed with increasing quantity at the surface and, also due to implantation, in the first few layers of the target. (A similar mechanism is assumed to happen for oxygen coverage.) For SF_6 physisorbed at Si an identical process has been used to explain the enhanced sputtering yields at 100 K target temperature [11,12]. If this is what happens, we assume an increasing amount of Cr to be sputtered in the form of molecules. This would also explain the reduction of the yield of sputtered neutral ground state atoms.

The experimental data of the neutral ground state yield for themselves cannot satisfactorily distinguish between these two mechanisms. The shape of the velocity spectra of sputtered neutral ground state atoms could yield some additional information. According to the broadening of the velocity spectra for oxygen coverage of a Cr target, we also would expect a similar effect for SF_6 coverage if process 2, mentioned above is predominantly taking place. The insensitivity of the velocity spectra in the present case, however, might lead one to the conclusion that the target surface is simply *covered* with SF_6 (process 1).

On the other hand, the experimentally found behavior of sputtered excited Cr atoms tends to contradict the theory of process 1, because it cannot explain the enhancement of sputtered excited atoms with increasing coverage.

To our opinion the arguments based on the excited atoms are stronger than the doubts that might be caused by the results for the velocity spectra. The broadening of the velocity spectra for oxygen is not fully understood at present. In spite of the striking similiarities 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 (fig. 4). For oxygen exposure ion fluxes in the order of 10^{16} ions/cm^2 are necessary to establish a steady state condition. This could be explained with a considerable influence of implanted oxygen on the yields of neutral ground state and excited Cr atoms. For SF_6 the steady condition for all yields is reached practically immediately after the pressure increase. Evidently, the topmost layer has an essential influence of 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 in 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.

5. Conclusions

The influence of gases with electronegative constituents like F on a Cr target surface has consequences on most of the global sputtering parameters (yields in different states) which are comparable to those caused by oxygen exposure. The microscopic mechanisms, however, might be different to some respect.

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