High Energy Sputtering from Cleaned Metal Foils*

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Positive and negative secondary ions desorbed from metal foils by bombardment with ^{252}Cf fission products have been investigated by time-of-flight mass spectroscopy. The measurements were performed under UHV conditions using metal foils of Cu, Ni and Al cleaned by Ar-ion etching. Spectra were taken with cleaned surfaces and also under the exposure of H_2, O_2, N_2, CO, C_2H_4, C_2H_6 and C_3H_7OH up to several 100 L. The yields of metal ions from clean metal surfaces are in agreement with Sigmund' theory.

1. Introduction

Fission-fragment induced desorption is usefull in mass spectroscopy of non volatile organic substances. The positive and negative ion mass spectra from organic layers on metallic substrats show in many cases strong lines of undestroyed parent ions and a fragmentation pattern characteristic for the respective compound [1, 2]. The fission fragments lose about 10 keV of their energy on passing a sample of 1 μg/cm^2 thickness. A small fraction of this energy dissipates by atomic collisions, most of the energy might form a high temperatur core [3]. It is, however, hard to understand how these processes can release species of masses up to 2000 AMU with little or even without destruction. Therefore, one of the authors (F. R. K.) suggested [4], that the desorption is associated with a high frequency perturbation of the electron plasma excited during the passage of the fission fragment through the sample material. This collective electron excitation by fast heavy ions has been experimentally verified, for instance, by Vager et al. [5].

So far all mass spectra were taken from samples spread onto a metallic foil by means of an electrospray [6] or other techniques. Surface contaminations were unavoidable. This work presents for the first time fission fragment induced desorption of clean metal surfaces under UHV conditions or under controlled exposure to gases. The intention is to compare yields of secondary ions emitted from states of different binding types. A strong electron plasma perturbation should affect especially polar bounded species.

It is a question, how metal ions from cleaned metal surfaces act. Under poor vacuum conditions such ions have never been observed in our spectra. This finding is contrary to SIMS experiments performed with primary ions in the keV range, where strong lines of the metallic substratum exist in organic mass spectra [7].

Sputter yields of primary ions with energies above 1 MeV follow from P. Sigmund's theory based on an atomic collision model [8]. The experimental results of the present work will be compared with these predictions, but because of the unknown ion-to-neutral ratio the theoretical values have to be considered as an upper limit for desorption by atomic collisions. Total sputter yields at energies up to 80 MeV have been measured by F. Nickel [9] using a 50 nA iodine beam and gold targets. He obtained a yield of about 1/ion at 80 MeV. This value is in close agreement with the theoretical prediction.

2. Experimental Method

So far fission fragment induced desorption has always been studied by time-of-flight (= TOF) spectrometry, which turned out to be very suitable for taking mass spectra but also for measuring energy and angular distributions of the emitted secondary ions [10]. The high energetic primary ions are delivered by the spontaneous fission source ^{252}Cf. As shown in Figure 1, the spectrometer and the fission source are mounted in a spherical UHV chamber, which is coupled to a second vacuum chamber used for exchange and preparation of the samples.

2.1. The Vacuum System

The two chambers manufactured out of stainless steel are connected by a bakeable straight-through valve, through which the sample holder can be moved from the position for cleaning to that for measurement. The spectrometer chamber is evacuated by a 120 l/s ion pump, the preparation chamber

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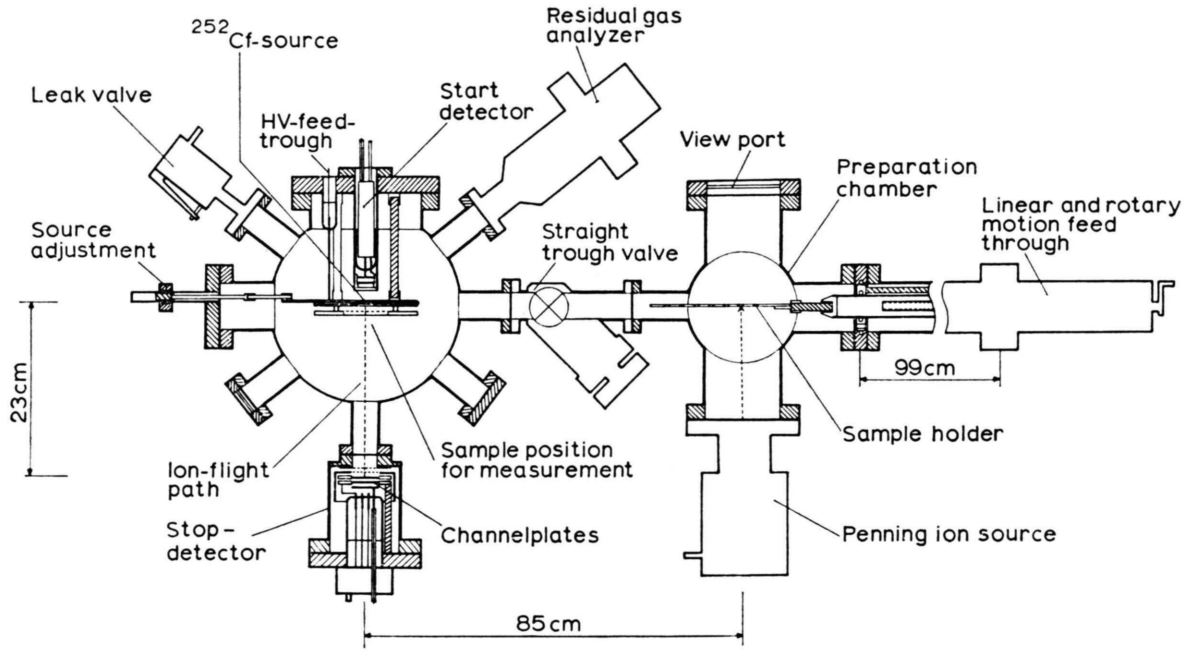

Fig. 1. Schematic drawing of the time-of-flight apparatus.

by a 200 l/s turbopump. Additionally, the pumping power in both chambers can be considerably enlarged by Titanium sublimation pumps cooled by liquid nitrogen traps. If the straight-through valve is closed, the pressure in the spectrometer chamber reaches 5×10^{-11} Torr. With open junction and the sample holder in position for measurement, the pressure goes up to 2×10^{-9} Torr, because the preparation chamber holds only 2×10^{-8} Torr and the slit between the junction wall and the holder shaft is not sufficiently tight.

The partial pressure of residual gases can be controlled by a quadrupol gas analyzer down to 10^{-13} Torr. In order to expose the samples to certain gases, an adjustable leakvalve is connected to containers filled with pure gases.

2.2. *The Samples*

Up to 5 different metal foils are stretched into the sample holder, each with a diameter of 0.6 cm, open in backward and forward direction. The foils have a thickness of 0.5 to 2 mg/cm^2 typically. In the preparation chamber the front surfaces of the sample foils can be cleaned by means of an argon-ion gun of penning type. At a pressure of 1×10^{-7} Torr it takes typically 1 min, to sputter off 30 monolayers of Au with an 2.0 keV Ar beam. After the cleaning procedure of about 1 min needed, the sample is moved into the spectrometer chamber over a distance of 85 cm.

2.3. *The Time-of-flight Spectrometer*

The principal of the TOF technique concerning fission fragment induced desorption has been described elsewhere [1, 10, 11]. The sample holder is inserted into a stainless steel sheet providing a flat plane for the surroundings of the sample. The arrangement of the sample and the fission source is shown in Figure 2. The latter one has a source strength of 2000 fission fragments per sec and is placed 0.5 cm behind the sample foil. That means, all measurements deal with transmission sputtering. The ^{252}Cf is electroplated on a 1.4 mg/cm^2 thick Al foil *.

At each fission process two fragments are emitted in opposite directions. If the first one hits the start detector producing the TOF start signal, the second one passes the sample foil with a probability of about 50%. According to the different fragment energies and the sample-detector distance the start

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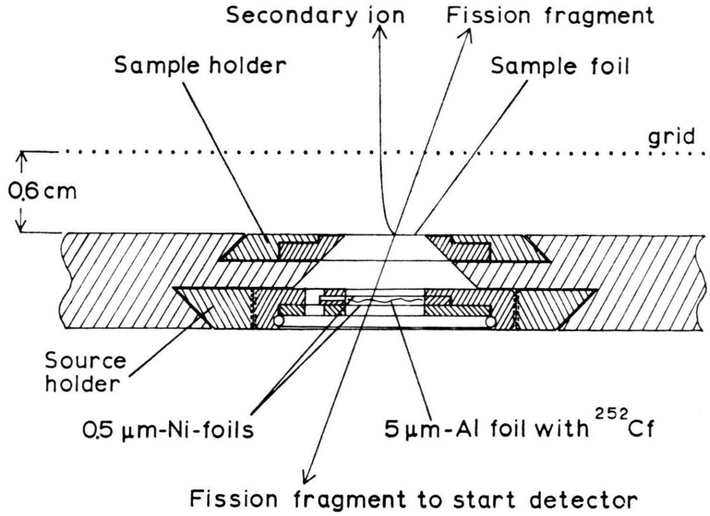

Fig. 2. Arrangement of the sample foil and the fission source in position for measurement.

signal and the time of the secondary ion production are related to each other with an accuracy of only 2 nsec. This time jitter is the most serious contribution to the time resolution of the TOF apparatus. The start and the stop detector have been described in Ref. [10] and [11]. The latter one is mounted at a flight distance of 23.0 cm providing maximum acceptance for all emitted ions at an acceleration voltage above 1 kV. The mass resolution was found to be 100. The secondary ions have to pass 3 grids on their way to the first channel plate of the stop detector. The first one accelerates them to energies between 0.1 and 10 keV depending on the type of investigations [10]. The two grids in front of the stop detector are used for an additional acceleration (2.8 kV), if the ion energy is too small for detection by a channel plate. The transmission of the grids and the detection efficiency of the channel plates reduce the total acceptance to 0.46 ± 0.13.

The output pulses of the start and stop detector have rise times of about 1 nsec. After pulse shaping their time distance is measured by means of a time-to-pulse-hight converter as described recently [11]. The time distributions are analyzed and registered by an one-line computer.

3. Mass Spectra

3.1. *"Clean Surfaces"*

0.5 µm thick Cu and Ni and 5 µm thick Al foils were cleaned by argon-ion etching for some minutes. The measurements of the TOF spectra were carried out in a vacuum between 4×10^{-10} and 2×10^{-9} Torr. The composition of the residual gas measured with the quadrupol analyzer was found to consist of hydrogen, nitrogen, argon and water. The time period between the end of the cleaning procedure and the end of the measurements was chosen in such that the total exposure to residual gas did not exceed 5 Langmuir (= L). This restricted the measurements usually to less than 10 min. The reproducibility of absolute secondary ion yields was in the order of 30%, whereas the relative intensities of mass lines varied within the statistical error.

The voltage used to accelerate the ions was ±10 kV. Thus even ions with a radial energy of 100 eV should not overstep the acceptance cone of the flight path [10]. The line shapes of the most intensive ions like H^+, H^- and K^+ did not significantly differ from those mass lines obtained with contaminated surfaces. Schematic mass spectra displayed in terms of absolute ion yields per fission fragment are shown in Figs 3 and 4. The values for the yields are uncertain within ±50%. Chance coincidence events due to uncorrelated start and stop signals produced a background represented by a dashed line in both figures. These background events limited the detectable yield of positive ions to 5×10^{-5} and of negative ions to 2×10^{-4}.

The mass spectra show generally strong hydrogen lines – a not surprising fact, because hydrogen is rather abundant in metals. The Na^+- and, particularly, the K^+-lines are surprisingly strong since metals contain only traces of these alkali elements. The absolute yields of the matrix atoms are presented in Table 1 together with cross sections. The latter

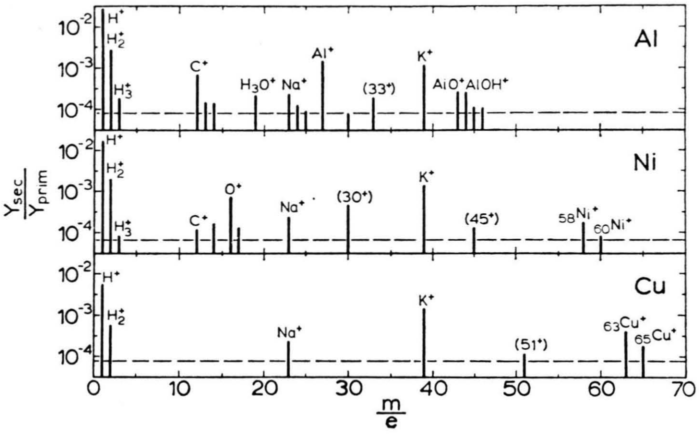

Fig. 3. Mass spectra of positve secondary ions released from clean Al, Ni and Cu foils by bombardment with fission fragments. The dashed line indicates the background.

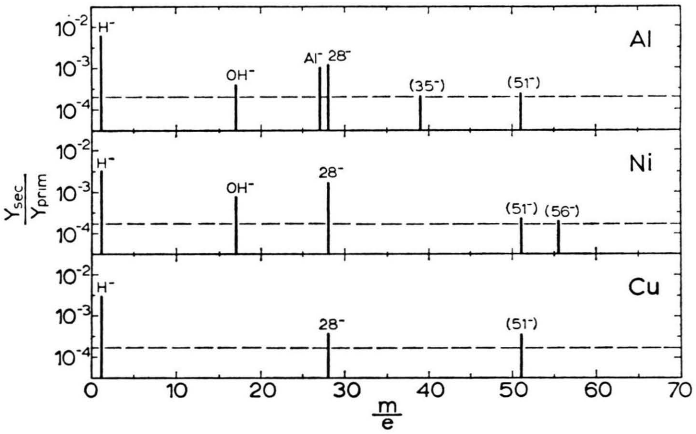

Fig. 4. Mass spectra of negative secondary ions released from clean Al, Ni and Cu foils under the same conditions as in Figure 3.

Table I. Yields and cross sections for secondary ion emission from metal surfaces.

Sample	Absolute yields (ions/f.f.) $\times 10^{-4}$		Cross section (cm^2) $\times 10^{-19}$		Calculated yields (ions/f.f.) $\times 10^{-4}$	
	S^+	S^-	σ^+	σ^-	S_{cal}	S^+_{cal}
Al	20 ± 10	10 ± 4	15 ± 8	7 ± 3	24000	8.5
Ni	5 ± 2	<2	2 ± 1	<1	16000	4
Cu	8 ± 3	<2	3 ± 1	<1	20000	2

ones were estimated assuming that the secondary ions are released from the uppermost boundary of a cristalline structure. In the spectra taken with Al- and Ni-foils, C, CH, CH_2 and O lines are observed indicating that the ion etching was not efficient to eliminate all organic contaminations from the surfaces. An improved cleaning procedure is in progress, where sputtering and heating periods follow alternatively.

3.2. *Surfaces under Gas Adsorption*

After cleaning by ion etching the metal foils were exposed to several 100 L of various gases. During the measuring time of 10 to 15 min the gas pressure was fixed at 3×10^{-7} Torr. For hydrogen, nitrogen, ethane and ethene no reproducible effects specific for the gases were observed, besides the mass pattern due to residual contaminations. The adsorption of oxygen on Ni foils produced a weak O^{2+} line but no enhancement of the O^+ line. The exposure of n-propanol, a rather big molecule, had no peculiar result except of increasing the organic background.

Only the adsorption of carbon monoxide resulted in some remarkable findings. The corresponding mass spectra are presented in Fig. 5. No CO^+ ions

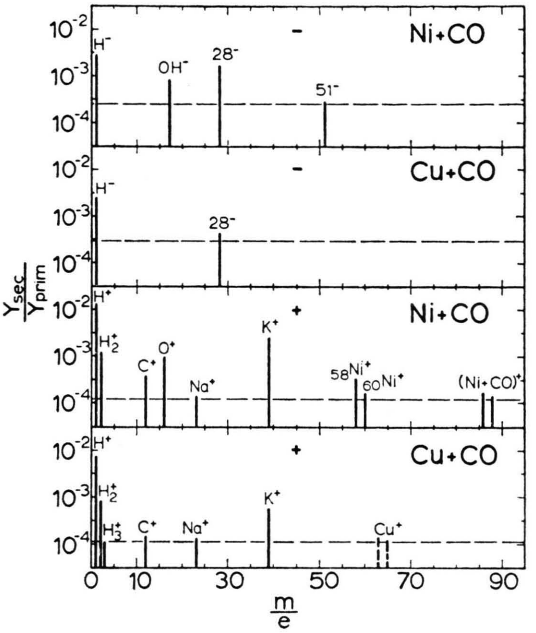

Fig. 5. Secondary ion mass spectra obtained from Ni and Cu surfaces under the exposure of Carbon monoxide.

were found. The 28^- line is a typical background signal in the negative ion spectrum (perhaps N_2^-) but not an indication for the existence of CO^-. Due to theoretical calculations CO^- should be unstable [12]. It has to be mentioned that an ion is detectable with this TOF technique, if its lifetime is of the order of the acceleration time (ca. 100 nsec) or longer.

The adsorption of CO on Ni increased the Ni^+ ion yield by a factor of 2, a similar effect being reported for SIMS experiments in the keV region [13]. Furthermore, a $Ni(CO)^+$ line was observed as well as an enhancement of the C^+ and O^+ lines. There are no similar findings in the case of CO on a Cu surface with the exception of a C^+ line, which is absent in the case of a pure Cu surface. To sum up, the cross sections for emission of C^+ and O^+ ions from a Ni surface are about 3×10^{-19} cm^2, whereas that of CO^+ ions is at least 6 times smaller. The cross section for Ni^+ emission was estimated to be 4×10^{-19} cm^2 and that of $Ni(CO)^+$ ions $(1.5 \pm 0.5) 10^{-19}$ cm^2, assuming that all possible CO sites are occupied.

4. Discussion

The observations in secondary ion emission from organic layers seem to exclude that atomic collision processes are of major importance. This is not necessarily so for matrix ions from clean metal surfaces. The most sophisticated theory dealing with atomic collision sputtering is that of Sigmund [8]. This theory can be extended to very high primary ion energies, if one takes into acount that also the recoil atoms lose a substantial part of their energy in electronic collisions. Therefore, in Sigmund's expressions for sputtering yields at high energies (see Ref. [8], p. 411) the stopping power was folded with $\nu(T)/T$, the fraction of recoil energy lost by atomic collisions. The function $\nu(T)$ was taken from graphs of Thomsen [14]. The total sputtering yields S_{cal} determined by this procedure are given in Table 1. These values are averaged yields of the two most intensive representatives of the light and the heavy fragment group, ^{107}Tc and ^{155}Cs [15]. According to transmission sputtering, the primary ion energy used in Sigmund's formulas was the energy of the fission fragments after their passage through the metal foils. Behind the Ni and Cu foils this energy was calculated [16] to be 96 MeV and 74 MeV for ^{107}Tc and ^{135}Cs, respectively, and behind the Al foil 50 MeV and 30 MeV, respectively.

For the present experiments S_{cal} is only an upper limit, as only charged ions can be studied. Because of the undefined surface structure the Saha-Eggert theorem gives only an order-of-magnitude estimation for the ion-to-neutral ratio. Therefore, experimental ratios were used as measured at bombarding energies of 1 keV with Ar-ions for the regarded metals [17]. The assumption had to be made that the ion-to-neutral ratio does not depend on the primary ion energy. The yields S^+_{cal} calculated for positive secondary ions are shown in Table 1. With regard to the uncertainties of the measurements and calculations, the values of column 2 and 7 are in remarkably good agreement. In two cases the experimental values are higher by a factor $2-4$. Generally any disturbance of a crystalline surface geometry can cause these small enhancements. Therefore, at the present status of the experiments, fission fragment induced desorption of matrix ions from metal surfaces is explainable in terms of Sigmund's atomic collision model.

The mass spectral data obtained from clean surfaces show clearly that no "hot core" model [3] will apply. If only the first monolayer within a hot-core radius of 25 Å would form a plasma of matrix atoms of 2×10^4 K one would expect, using the Saha-

Eggert theorem, charged metal atoms by a factor of nearly 10^3 more abundant than observed. Moreover, under the presented conditions, the behaviour of the Ni-metal surface under CO adsorption is similar to that of the low energy sputtering condition. So, one can argue that collision cascades and their slow atoms reaching the surface play the dominant role in the emission of the metal ions. The collective electronic interaction of the fast fission fragment itself producing electron plasma waves, should not be able to interfere sufficiently with the surface atoms, to eject them. On the other hand, this high-frequent perturbation is able to interact strongly with polarbound species at the surface. Consequently, one is able to explain the high yield of H^+, H^-, Na^+, and K^+ ions, which are one to two orders of magnitude more intensive than the metal ions, though only traces of alkali may be present.

No effects like electron-induced desorption of molecules have been found. The chemical bonds to the surface, e.g. the CO bonds to the Ni surface, are not much affected by this perturbation. Only additional atomic ions were emitted, due to the elemental composition of the molecules adsorbed.

5. Conclusion

The measurements have shown that high energy ion sputtering can be reduced to the well known sputtering effects of low energy ions caused by the collision cascades. Only the desorption of some highly polar bound ions may be due to the perturbation excited by the primary ion. A separation of ionic and electronic perturbation effects does not seem to be possible by this excitation method alone. However, it is necessary to take mass spectra to compare with those shown above, e.g., by means of ultra-short laser pulses, producing electronic perturbation without heating up the surface. Furthermore, it will be necessary to measure the energy and angular distribution of the ions sputtered or desorbed also from clean surfaces in order to understand the excitation mechanism responsible for them.

Acknowledgement

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