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Spontaneous desorption

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Spontaneous desorption (SD) denotes a process in which atoms and molecules are transferred as singly charged ions from the solid phase into the gas phase. For this purpose the solid sample does not need to be bombarded by particles (keV or MeV ions, electrons) from an external source. An electric field between the sample and an acceleration grid with a field strength at the sample surface below the threshold value for field desorption is the only prerequisite to initiate the SD process. The SD mechanism is the subject of the present paper. A number of experimental results obtained recently are summarized. It follows that SD is a two-step process. Primary ions are field desorbed in a first step from the edges of the grid where an enhanced electric field exists. These ions are mainly molecular ions and stem from adsorbates at the grid. They are accelerated in the electric field between the grid and sample to keV energies and sputter, in a second step, secondary ions from the sample with a sputter yield that exceeds the yield of atomic ions considerably.

I. INTRODUCTION

It is well known that atoms and molecules can be transferred as ions into the gas phase if a solid surface is bombarded by particles (keV and MeV ions, electrons) or photons from an external source. Desorption of ions occurs also in a strong electric field F via field desorption (FD) or field ionization (FI). Threshold field strengths for both processes are $F \geq 10^7$ Vm^{-1} and $F \geq 10^9$ Vm^{-1}, respectively.

It is less well known that atomic and molecular ions can be desorbed without bombarding the sample with particles from an external source if the sample is exposed to an electric field with a field strength below the FD threshold. Della-Negra, LeBeyec, and Håkansson,[1] who observed this phenomenon, named it spontaneous desorption (SD).

The experimental setup suitable to study SD is shown in Fig. 1. The sample S is deposited on a flat metal substrate to which a voltage U of typically ±10 kV is applied. Samples are usually thin films (metals, semiconductors, insulators, organic compounds) with thicknesses of the order of 1000 Å. Typical deposition methods are vacuum evaporation, electrospraying, and the Langmuir-Blodgett dipping technique.[2]

A high-transmission grid G at ground potential is placed in front of the sample at a distance $b \approx 4-5$ mm. The field-free region between G and the ion detector (microchannel plate) MCP with a length of typically 10–20 cm, represents the flight path of the time-of-flight (TOF) mass spectrometer used to analyze the desorbed ions. The latter are called SD ions in the following.

The TOF analysis can be applied because a charged particle with small mass (called trigger particle) is frequently emitted simultaneously with the SD ion. A trigger particle and SD ion that are both normally singly charged gain the same energy in the electric field between sample and grid. The trigger particle arrives, however, at the MCP detector (see Fig. 1) ahead of the SD ion due to its smaller mass. The signals of the detector are both fed into the start and the stop input of a time digitizer (TDC) which determines the time difference between the start and stop signal. The start input of the TDC is inhibited after the first start signal for a preselected time interval during which up to 256 stop events are accepted. In most cases the start signal stems from the trigger particle and is followed by a MCP signal generated by a SD ion. Thus, the TOF difference between the trigger particle and SD ion is measured by the TDC. This TOF difference is proportional to the square root of the mass of the SD ion.

The simultaneous desorption of the trigger particle and

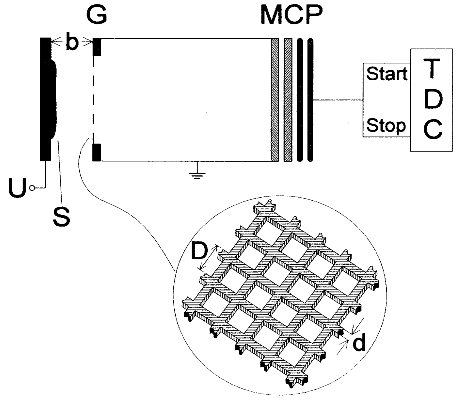

FIG. 1. Scheme of the experimental setup suitable to study spontaneous desorption. S = sample, U = voltage applied to the sample, G = grid, MCP = microchannel plate detector, TDC = time digitizer used to measure the time-of-flight of the desorbed ions. The inset shows a typical grid used for SD investigations. It consists actually of a 2 μm thick Ni foil with rectangular holes. Typical values for d and D are 30 and 1280 μm, respectively (see also Table I). The grids can be purchased from Buckbee Mears Company, St. Paul, MN 55101.

SD ion is a characteristic feature of SD. It occurs almost as a rule if the sample is negatively biased with respect to the grid, i.e., in the negative SD mode. Electrons, and to a smaller extent also H^- ions, are the trigger particles in this case. This means that negative-ion spectra containing at least typical background ions like H^- and $C_nH_m^-$ ions which originate from surface adsorbates (see below) can be easily obtained from all samples by means of the SD method. In many cases, sample specific ions also can be detected in the negative SD mode. Figure 2 shows, as an example, SD spectra of negative ions obtained from an alanine sample. The spectra contain background ions like H^- and $C_nH_m{}^-$ and sample specific ions. The TOF measurements were triggered both by electrons and H^- ions.

Positive ion spectra can be easily obtained with the SD method from alkali-halide samples. The alkali ion serves as the trigger particle in this case. This is demonstrated in Fig. 3(a), which shows a SD mass spectrum obtained from a CsI sample in the positive SD mode. Other trigger particles observed in the positive SD mode for samples different from alkali halides are H^+, Na^+, and K^+ ions.[3] The simultaneous emission of these ions together with a positive SD ion occurs, however, with rather small probability. Thus, SD spectra of positive ions are normally not obtainable with the TOF method (alkali-halide samples are an exception). In the following, we will deal, therefore, only with the negative SD mode if not stated otherwise.

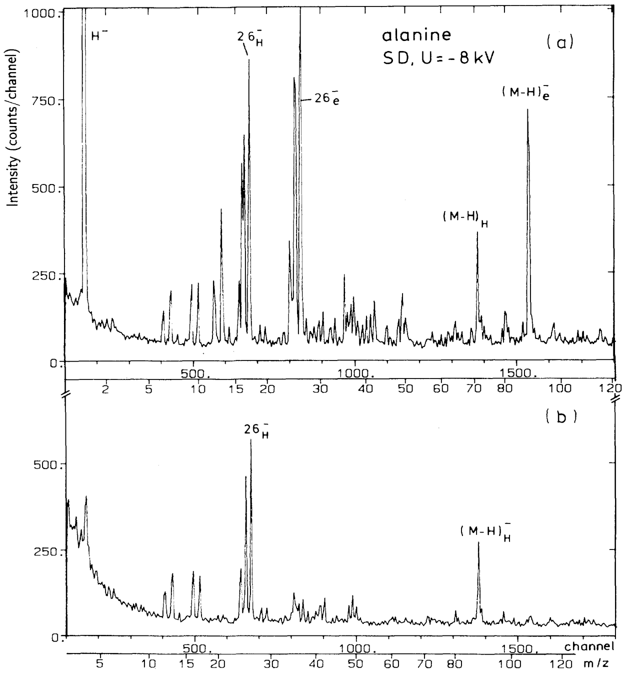

FIG. 2. SD mass spectra of negative ions obtained from an alanine sample. (a) Both electrons and H^- ions served as trigger particles, (b) only H^- ions were used to start the TOF measurement (electrons were deflected by means of a magnet). The trigger particle is indicated by the index *e* (electron) and H (H^- ion), respectively. *M* denotes the alanine molecule.

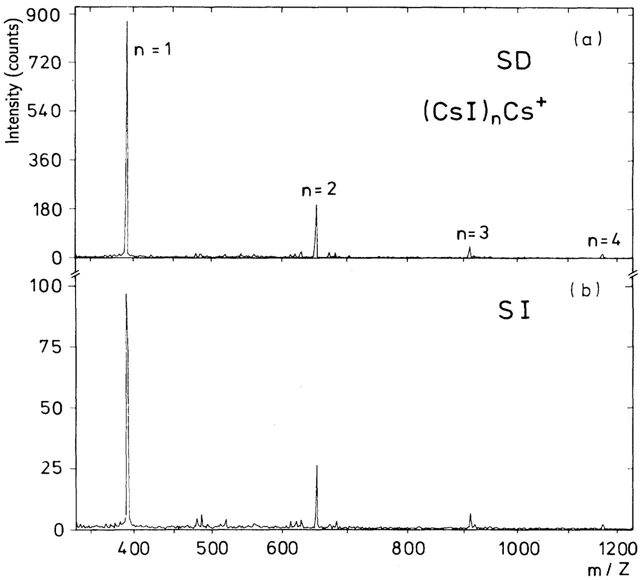

FIG. 3. (a) SD mass spectrum of positive ions from a CsI sample. The Cs^+ ion gave the start trigger, (b) secondary ion (SI) spectrum of CsI obtained with identical experimental conditions as in (a). Both spectra exhibit cluster ions of the type $(CsI)_nCs^+$ with $n=1$–4.

There are several reasons why SD deserves attention: (i) the SD mechanism has to be clarified, (ii) SD affects a number of methods used in mass spectroscopy (MS), like plasma desorption MS or TOF secondary ion MS (SIMS), and (iii) the SD method can be used to build a very simple but effective ion source for TOF mass spectrometers. This article deals with point (i). Recent results from our laboratory which clarify the SD mechanism are summarized in this article.

II. EARLY EXPLANATIONS

In an attempt to explain the SD mechanism, it was assumed that SD ions originate via a one-step FD process from microtips at the sample surface.[1,4] Subsequent experiments clearly showed that SD cannot be exclusively the result of a one-step FD process.[5–7] Instead, it turned out that at least part of the SD ions result from a sputter process induced by keV ions emerging from the grid[5] (we call these ions primary ions, in the following).

Two mechanisms were discussed for the origin of the primary ions: (i) FD at the grid and (ii) sputtering from the grid induced by keV ions emerging from the sample in a FD process. This means that the SD process was assumed to be either a two-step (FD and sputtering) or a three-step (FD, sputtering, sputtering) process.

In Ref. 5, it is argued that both processes take place. In Ref. 6, it is concluded that SD is a two-step process even though the experimental results obtained do not exclude an interpretation in terms of a three-step process.

III. ROLE OF THE ELECTRIC FIELD

An electric field between the sample and grid of the order of $F \geq 10^6$ Vm^{-1} is a necessary prerequisite for the

SD process to take place. It should be noted that this F value simply results from the ratio of the sample voltage U and the sample-grid distance b (i.e., it corresponds to the field between two plane plates with the distance b and the potential difference U). At a typical distance of $b \approx 4$ mm, SD ions can be observed for a voltage U as low as 2 kV. An increase of U (with $b =$const) results in an exponential increase[7] of the SD rate R (see Fig. 4). R is defined as the number of SD ions desorbed per unit time together with a trigger particle.

An exponential increase of R is to be expected if FD or FI processes contribute to SD. FI can be disregarded, however, because the existing field strengths are considerably smaller than the FI threshold value. The actual field strengths at microtips on the sample or sharp edges of the grid could be sufficiently large (see below), on the other hand, to allow FD processes. An investigation of the dependence of R on U, however, does not allow one to discriminate whether FD takes place at the sample and/or the grid.

A. FD from the sample

A strong argument against the assumption that FD occurs at microtips existing at the sample surface has resulted from the observation that SD ions are desorbed from Langmuir-Blodgett films.[8] These films have a surface which is perfect on the molecular level (as observed with an atomic force microscope). Nevertheless, if FD takes place at the sample surface, one would expect contributions from one-step (direct FD), three-step (FD, sputtering at the grid, sputtering at the sample) and higher-order processes.

To detect ions from a one-step FD process by means of the TOF method requires that these ions emerge simultaneously with a trigger particle (electron, H^- ion). This is not the case in a FD process.[9] Besides this, a pronounced increase of R would be expected if the sample temperature T_S is increased.[10] This was, however, not observed experimentally[11] [see Fig. 5(b)].

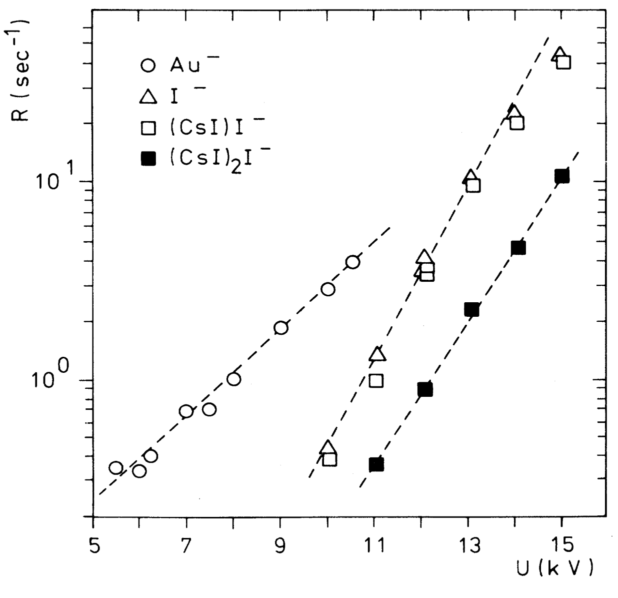

FIG. 4. Dependence of the SD rate R on the sample voltage U for various sample specific ions.

In the case of a three-step process it is not necessary that a trigger particle originates in the FD process at the sample. One would expect, however, a huge background to show up in the TOF mass spectra since roughly 90% of the FD ions from the sample (depending on the transmission T of the grid) would hit the detector without a start trigger. This is not the case, as can be seen in the SD mass spectra shown in this work. Moreover, the background should increase with increasing sample temperature T_S and increasing transmission T of the grid. Both features are not observed (see Figs. 6 and 7).

Another observation which contradicts the possibility of a three-step process is the fact that the SD rate R increases with increasing grid transmission T [see Fig. 8(a)]. In the case of a three-step process one would expect[12] that the rate R decreases from a maximum value at $T=0.5$ for increasing T values ($T>0.5$), in contrast to the experimental observation.[12]

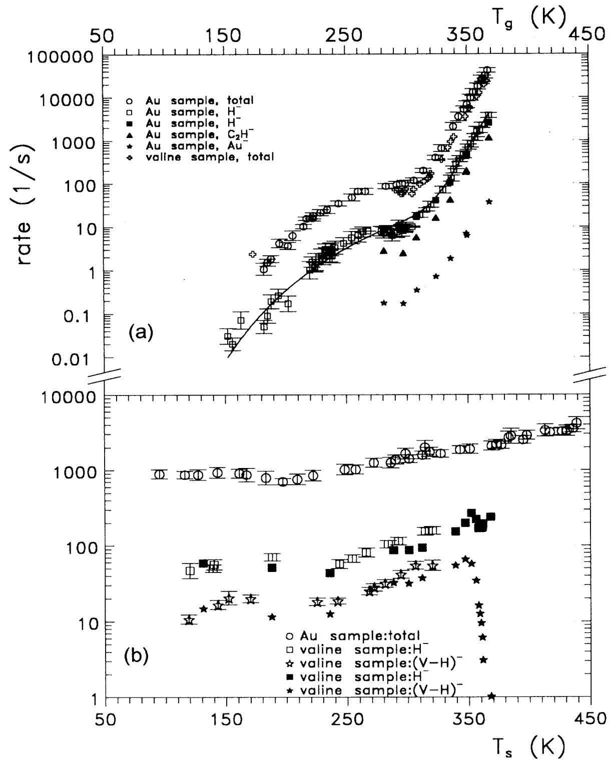

FIG. 5. (a) Dependence of the total SD rates R and rates for different ions from Au and valine samples as a function of the grid temperature T_g. The solid curve represents the function $R \propto e^{-E_1/kT} + e^{-E_2/kT}$ with $E_1 = 0.2$ eV and $E_2 = 1.0$ eV. Note that all $R(T_g)$ curves have the same shape. (b) Dependence of the total SD rate R from an Au sample and of ion rates from a valine sample on the temperature of the sample T_S. V denotes the valine molecule. Open and solid symbols represent measurements performed for decreasing and increasing T_S, respectively.

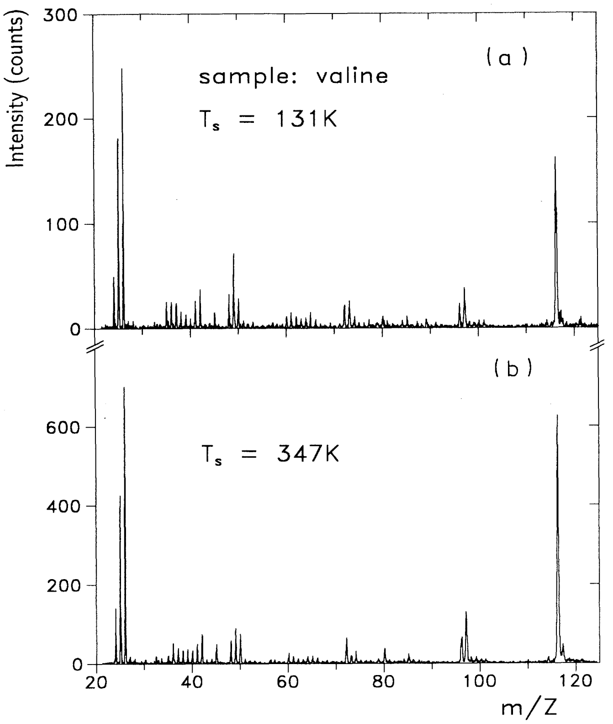

FIG. 6. SD spectra of valine measured at two different sample temperatures T_S. (a) $T_S = 131$ K and (b) $T_S = 347$ K.

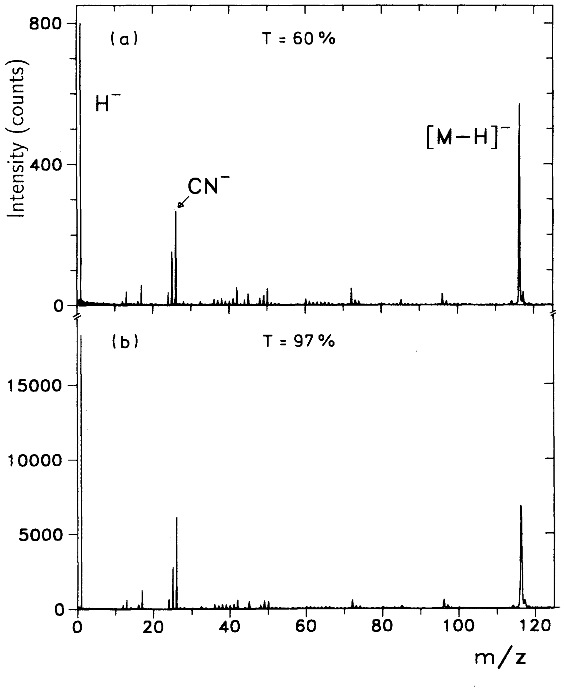

FIG. 7. SD spectra of valine obtained with acceleration grids having different transmission T. (a) $T = 60\%$ and (b) $T = 97\%$.

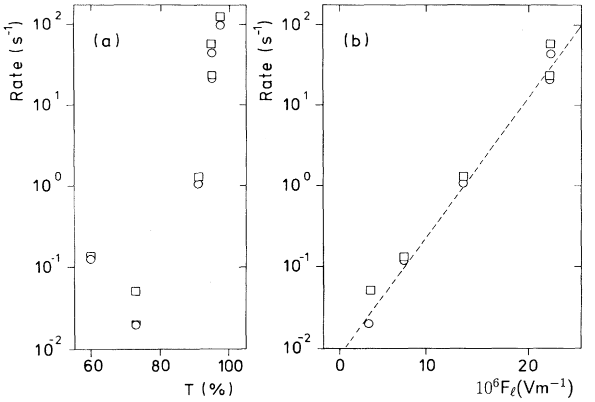

FIG. 8. (a) Dependence of the SD rate R on the transmission T of various grids and on the local field strength F_l of the electric field at the edges of these grids (b). F_l values have been calculated by the code SIMION (Ref. 13) (see Table I). The sample investigated was valine. (□) and (○) denote the desorption rate of the H^- and the deprotonated valine ion (negatively charged), respectively.

B. FD from the grid

All experimental facts discussed in Sec. III A contradict an interpretation of SD in terms of a one-step or three-step process. This means that a two-step process (i.e., FD from the grid, sputtering from the sample) seems to be the only alternative. We thus have to test if the experimental facts discussed above as well as additional results are in favor of such an explanation of SD.

The following observations support the assumption that FD occurs at the grid: (i) the SD rate R increases rapidly with increasing grid temperature T_g [see Fig. 5(a) and Ref. 11], (ii) the local electric field F_l at the edges of the grid is of the same order of magnitude as the threshold value for FD[12] (see Table I and Fig. 9), and (iii) R increases exponentially with increasing F_l at the grid[12] [see Fig. 8(b)].

In addition, it should be noted that a trigger particle does not need to be desorbed together with a massive ion in the FD process at the grid (in contrast to an assumed one-step FD process from the sample). Moreover, the observed small background in the TOF mass spectra, which does not depend on the transmission of the grid (see Fig. 7), is compatible with an interpretation of SD being a two-step process initiated by FD ions from the grid. Since the desorption occurs from regions at the grid exhibiting an enhanced electric field F_l and since the desorbed ions stem mainly from adsorbates on the grid (as will be shown below), the desorption process was termed field-enhanced desorption of adsorbates (FEDA) in Ref. 14.

IV. SPUTTERING AS FINAL STEP

The interpretation of the SD in terms of a two-step process assumes that the final step is a sputter process. If this is the case, the following facts (among others) should be valid: (i) negative ions should be frequently sputtered

TABLE I. Local-field strengths F_l of the electric field at the edges of different grids of the type shown in Fig. 1 as calculated with the program SIMION (Ref. 13) (see also Fig. 9). Note the relationship between F_l and the transmission T of the grids. The SD rates obtained with the various grids are shown in Fig. 8. lpi is an abbreviation for lines per inch.

Grid type	d (μm)	D (μm)	T(%)	F_l(10^6 Vm^{-1})
20 lpi	30	1280	95	22.7
30 lpi	42	850	91	14.4
40 lpi	140	630	60	7.3
333 lpi	10	70	73	3.4

together with an electron or a H$^-$ ion by keV ions, (ii) SIMS spectra should exhibit similar features as SD spectra, and (iii) the SD rate should increase in a similar way as the SIMS rate for decreasing sample thickness.

In Ref. 15 it was shown that electrons or H$^-$ ions are, indeed, frequently sputtered by keV ions together with negative ions. In the same investigation it was found that positive ions are normally not sputtered in coincidence with H$^+$ or other low-mass ions from samples other than alkali halides (see above). The latter explains why SD mass spectra of positive ions are normally not obtainable with the TOF method.

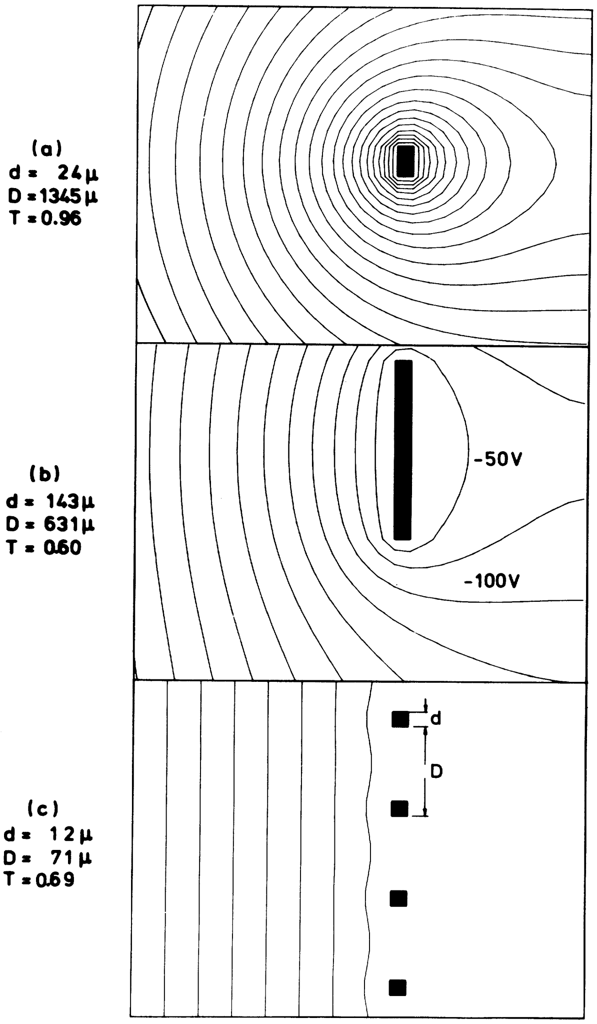

FIG. 9. Equipotential lines in front of the grid (solid bars) calculated with the code SIMION (Ref. 13) for three different grids with geometrical parameters (d,D) close to those of the grids used to determine the dependence of R on the transmission T [see Fig. 8(a)].

The similarity of SD and SIMS spectra has been demonstrated in Ref. 15. In this work, both SD and SIMS spectra were recorded for several samples with identical experimental conditions. As an example, Figs. 3 and 10 display mass spectra of CsI and Cd arachidate obtained with both methods. The similarity of SD and SIMS spectra does not only hold for the mass region containing sample specific ions but also for the small-mass region (see Fig. 11). In this region one observes mass peaks which have to be attributed to H_2O and C_nH_m contaminants on the sample surface. These peaks normally do not show up in a FD mass spectrum and were thus taken as an argument against an interpretation of SD in terms of a one-step FD process by the authors of Ref. 5.

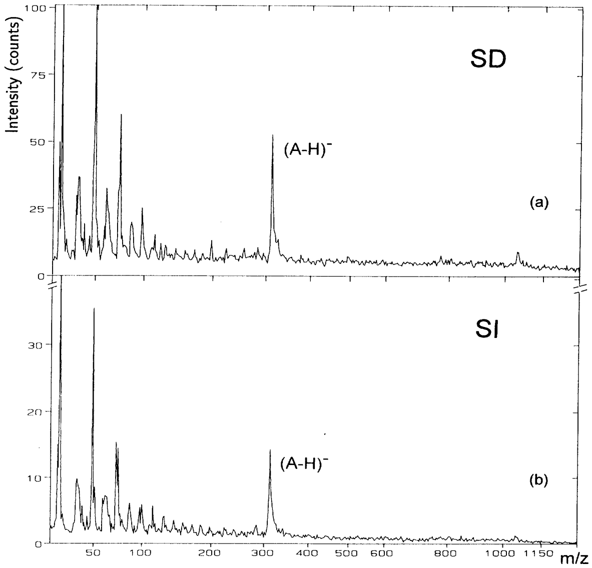

FIG. 10. (a) SD and (b) secondary ion (SI) spectra of a Cd arachidate sample (Langmuir-Blodgett film of three monolayers Cd arachidate on a Si substrate) obtained with the same experimental conditions. A denotes the arachidic acid molecule.

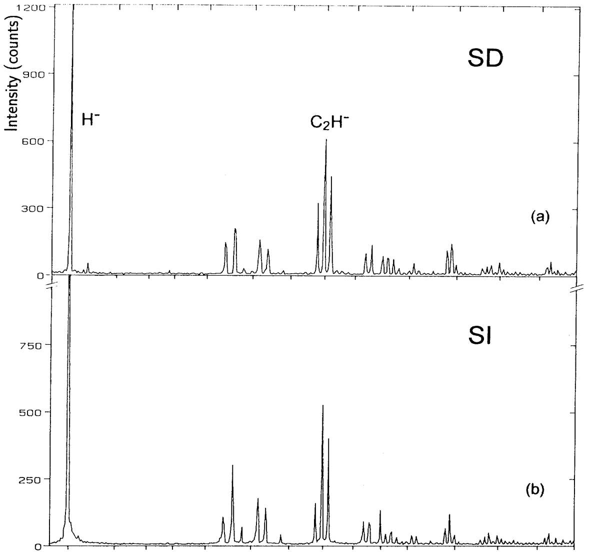

FIG. 11. (a) SD and (b) SI spectra of a gold sample showing the low-mass region ($m = 1-80$ u). Both spectra were obtained with identical experimental conditions. Identically the same spectra were obtained with both methods for all other samples investigated.

The dependence of the SD rate and the SIMS rate on the sample thickness [i.e., point (iii) from above] is identical. This has already been shown by Bolbach *et al.*,[16] who used samples consisting of Langmuir-Blodgett films deposited on a hydrophobic substrate. The same result was found in our laboratory. Thus, all three facts are compatible with the assumption that the final step of SD is a sputter process.

V. NATURE OF PRIMARY IONS

In this section the nature of the primary ions originating via FD from the grid is discussed. For this purpose, the dependence of the SD rate R on the time t elapsed after applying the voltage U to the sample was investigated (see Fig. 12). The rapid decrease of R which finally ends up in a constant value signals that two competing processes are involved. The equilibrium between both is considerably disturbed when U is applied to the sample. The two processes are desorption and adsorption of adsorbates from and on the surface of the grid. In fact the time dependence of Fig. 12 can be described (solid lines in Fig. 12) by the relationship,

$$R(t) \propto e^{-Dt} + A(1-e^{-Dt}) ,$$

where D and A are the desorption constant and the adsorption rate (assumed to be constant), respectively. It is interesting to note that $R(t)$ curves with similar shape were measured for various SD ions emerging from different samples. This indicates clearly that $R(t)$ reflects the time dependence of the number of adsorbate ions being desorbed via FD from the grid.

A satisfactory fit for the curves shown in Fig. 12 is obtained only if two sets of D and A values are used simultaneously. This means that mainly two groups of adsorbates with different constants D and A contribute to the SD process. A similar conclusion can be drawn from the dependence of R on the grid temperature T_g. The $R(T_g)$ curves can be fitted by

$$R(T_g) \propto \sum_i \exp(E_i/kT) ,$$

where $i = 1,2$ [solid line of Fig. 5(a)]. The E_i values are 0.2 and 1.0 eV, respectively, and must be attributed to binding energies of two different groups of adsorbates.

The most convincing evidence that primary ions stem from adsorbates deposited at the grid results from an investigation performed in ultrahigh-vacuum.[14] In this experiment the grid was sputter cleaned in an UHV apparatus by means of an Ar gun. The SD rate recorded after sputter cleaning at a pressure of 10^{-9} mbar was found to be one order of magnitude smaller than the rate measured before at the same pressure.

It is reasonable to assume that water vapor and C_nH_m

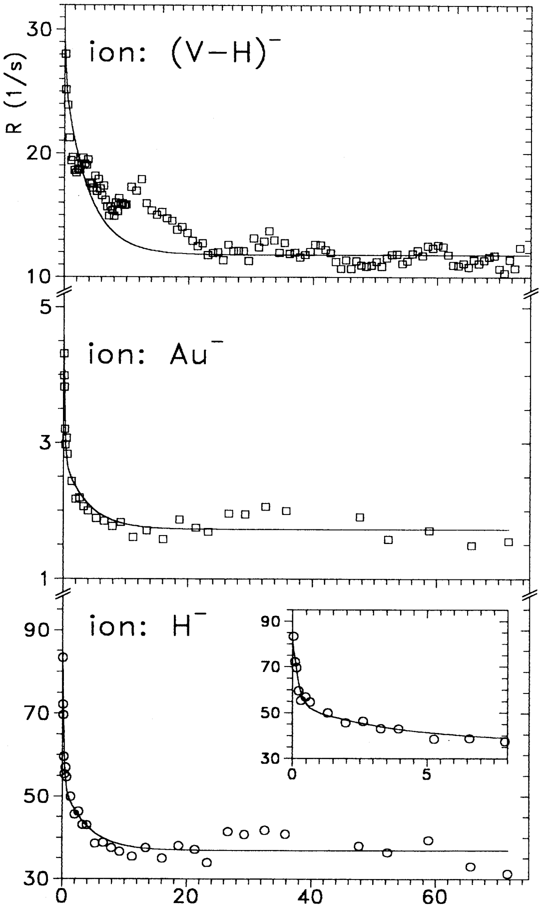

FIG. 12. Dependence of the SD rate R on the time elapsed after applying the voltage U to the sample. Samples were Au and valine (V denotes the valine molecule). The solid lines represent the functions $R(t) \propto \sum_i \{e^{-D_i t} + A_i(1-e^{D_i t})\}$ with $i = 1,2$ (see text).

molecules from pumping oil contribute mainly to the adsorbates in question, if the TOF spectrometer is run in a high-vacuum chamber equipped with diffusion or turbomolecular pumps. This can be demonstrated if the SD rate is determined with the same spectrometer at the same pressure (10^{-7} mbar in our case) both in an UHV and a high-vacuum chamber. The rate measured in UHV is at least one order of magnitude smaller than the rate determined in high vacuum. The same conclusion can be drawn from the observation that the SD rate decreases considerably if a cold trap around the spectrometer (positioned in high vacuum) is cooled down to liquid-nitrogen temperature.

The adsorbates in question are, of course, also deposited at the sample surface and thus, have to show up in the SD mass spectrum. In fact H^-, O^-, OH^-, and $C_nH_m{}^-$ ions dominate the SD spectrum (see Fig. 11) which is evidence for the assumed nature of the adsorbates delivering the primary ions for the SD process. Sputtering from the sample surface occurs with a high sputter yield due to the mainly molecular nature of the primary ions. This is known from sputter experiments with molecular species[17,18] which showed that the sputter yield of a molecular ion exceeds the summed yields of the constituent atomic ions by a considerable margin.

VI. CONCLUSION

A large number of experimental observations clearly shows that SD is a two-step process. The first step is a FD process. Ions originating from adsorbates (mainly water vapor and hydrocarbons) on the grid are field desorbed in the enhanced field at the edges of the grid (field-enhanced desorption of adsorbates). The desorbed ions are accelerated to keV energies between the grid and sample. They hit the sample surface and sputter secondary ions (SD ions) in a second step. Since the SD ions are analyzed by means of the TOF mass spectrometry, one can view SDMS as a special form of TOF SIMS induced by molecular ions.

The present work gives the parameters necessary to optimize the SD ion rate. This allows one to build a very sufficient ion source for keV molecular ions which can be used to sputter secondary ions with high efficiency. On the other hand, the source itself can deliver ions with high efficiency from a sample to be investigated by any mass spectrometry tool.

ACKNOWLEDGMENT

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[1] S. Della-Negra, Y. LeBeyec, and P. Håkansson, Nucl. Instrum. Methods Phys. Res. B **9**, 103 (1985).

[2] G. G. Roberts, Adv. Phys. **34**, 475 (1985).

[3] B. Nees, R. Schmidt, Ch. Schoppmann, and H. Voit, Int. J. Mass Spectrom. Ion Proc. **94**, 305 (1989).

[4] M. Salehpour and J. E. Hunt, Int. J. Mass Spectrom. Ion Proc. **85**, 99 (1988).

[5] S. Della-Negra, C. Deprun, Y. LeBeyec, F. Röllgen, K. Standing, B. Monart, and G. Bolbach, Int. J. Mass Spectrom. Ion Proc. **75**, 319 (1987).

[6] C. D. McAfee, E. F. Da Silveira, and E. A. Schweikert, Int. J. Mass Spectrom. Ion Proc. **97**, 311 (1990).

[7] B. Nees, R. Schmidt, Ch. Schoppmann, and H. Voit, Int. J. Mass Spectrom. Ion Proc. **94**, 205 (1989).

[8] R. Schmidt, D. Brandl, Ch. Schoppmann, H. Voit, T. Kröhl, D. Johannsmann, and W. Knoll, Int. J. Mass Spectrum. Ion Proc. **99**, 223 (1990).

[9] F. Röllgen (private communication).

[10] H. D. Beckey, *Principles of Field Ionization and Field Desorption Mass Spectroscopy* (Pergamon, Oxford, 1977).

[11] Ch. Schoppmann, D. Brandl, and H. Voit, Nucl. Instrum. Methods Phys. Res. B (to be published).

[12] Ch. Schoppmann and H. Voit, Mass Spectrom. **7**, 446 (1993).

[13] D. A. Dahl and J. E. Delmore (unpublished).

[14] Ch. Schoppmann, D. Brandl, and H. Voit, Int. J. Mass Spectrom. Ion Proc. **121**, 87 (1992).

[15] Ch. Schoppmann, D. Brandl, and H. Voit, Int. J. Mass Spectrom. Ion Proc.. **124**, 79 (1993).

[16] G. Bolbach, S. Della-Negra, C. Deprun, and Y. LeBeyec (unpublished).

[17] M. G. Blain, S. Della-Negra, H. Joret, Y. LeBeyec, and E. A. Schweikert, Phys. Rev. Lett. **63**, 1625 (1989).

[18] Ch. Schoppmann, diploma thesis, University of Erlangen-Nürnberg, 1989.