MASTIF: Mass analysis of secondaries by time-of-flight technique. A new approach to secondary ion mass spectrometry

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(Received 29 June 1988; accepted for publication 4 May 1989)

A new approach to surface studies by time-of-flight secondary ion mass spectrometry is proposed. The time-of-flight technique is implemented in an unconventional way utilizing a continuous-probing beam. The "birth" moment of the secondary ion is fixed by the detection of secondary electrons emitted when a probing-beam particle strikes the surface. Multichannel mass identification of secondary ions is thus possible using a low-intensity continuous-probing beam, which permits one to study fragile and extremely thin (down to few monolayers) objects, sensitive to damage by intense probing beam and high doses. The technique has been applied to thin (30-Å) self-supporting carbon foil, semiconducting material, and the sensitive surface of a microchannel plate.

INTRODUCTION

Secondary ion mass spectrometry (SIMS) is one of the major techniques in the study of surfaces, ¹⁻³ used for the most diverse problems, which has extended our fundamental and practical knowledge of surfaces in response to the challenges of material science and technology. Though SIMS is most efficient for a number of applications, it is not without its disadvantages and limitations. Therefore, the development of a new approach to SIMS, which may improve its capabilities and permit application to new objects, is of considerable importance.

In a typical SIMS analysis, the surface is bombarded by a collimated beam of noble-gas ions (argon is commonly used) with an energy of several keV. The secondary ions (SI) are collected by the potential applied to the entrance slit of a magnetic or electrostatic mass analyzer. The analyzing field is then changed in order to register a mass spectrum. Therefore, the conventional technique is essentially the consecutive single-channel SIMS, since only one mass is collected at a time and the others are lost. Such an approach requires a highly stable and intense probing beam. The requirement for beam stability limits, in practice, the exposure time. To study trace elements, the high-intensity probing beam is required, being prohibitive to a number of fragile and thin objects, e.g., self supporting thin (≤100 Å) carbon foils. The applications of such foils are increasing in the laboratory and in space experiments. 4-8 Thin foils especially require excellent knowledge of their composition and the state of the surface.

In this article, a new approach to SIMS is proposed which utilizes a continuous-probing beam and concurrent multichannel analysis of secondary ions, enhances sensitivity, and permits a significant decrease in the probing-beam intensity. To demonstrate the technique, secondary ion mass spectra were obtained for a carbon foil (30-Å thickness), a semiconducting material, and the sensitive area of microchannel plate (MCP) surface. What is important is that the surface study of thin foils and MCPs is possible not only in dedicated surface physics experimental facilities, but also

within instruments and devices in which they are installed. Surface analysis can be performed in the actual operating environment of these foils and MCPs. It is difficult to overestimate the importance of the latter if one takes into consideration that for energetic neutral-atom identification, the subtle effects of its interaction with the foil are proposed to be utilized in instruments for future space experiments, 8,9 and that a lot of effort has been spent to improve MCP performance in EUV and soft x-ray astronomy by covering its sensitive surfaces with different layers. 10-13

I. CONVENTIONAL TIME-OF-FLIGHT SIMS

It is obvious that if all masses of secondary ions are detected without loss, the dose and the sample consumption for complete mass analysis could be reduced significantly. The concurrent multichannel mass detection is implemented in time-of-flight (TOF) mass spectrometers.

The TOF SIMS is a well-established technique now, and TOF secondary ion analysis is based on the measurement of the ion flight time across a known distance, providing that the energy (or momentum) is fixed. For the known geometry and fields in the analyzer, the time interval between ion detection and the moment of ion "birth" is mainly a function of the secondary ion mass and only to some extent of the initial ion velocity. The position of the area where the secondary ion is created is well known—this is the interaction region of the probing beam with the object under studyand the initial velocity is not usually very high. All secondary ions are accelerated up to the same kinetic energy (per charge) in the analyzer and the flight times across the same distance are different due to the difference in velocities according to their masses. The scatter of flight time for ions of the same mass is determined by the initial velocity distribution of the secondary ions. Therefore, the TOF analyzer can be used, in principle, to study the initial kinematic parameters of secondary ions.

The moment when a secondary ion is detected at the end of its flight can be fixed with high accuracy (≈ 1 ns) rather easily. The main problem is how to determine the moment of

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the secondary ion "birth." Here, several approaches could be used.

Historically, the first TOF mass-spectrometers, which date back to the end of the 1940s, 14,15 were developed to study secondary ions produced in a gas phase. Secondary ions are injected into the flight domain by extraction voltage pulses, 16 which can be of special shape, 17 or a pulsed electron beam is used to ionize the gas atoms or molecules. 18,19 These pulses provide the START signals. If the number of secondary ions $N_{\rm SI}$ per one START pulse is $N_{\rm SI} \geqslant 1$, then the TOF spectrum is registered in a "one-shot mode." On the other hand, if $N_{\rm SI}$ is not large enough ($N_{\rm SI} \leqslant 1$), then the TOF spectrum is to be accumulated in the digital memory after a number of START pulses. The secondary ion detection triggers the STOP pulse, the time interval between START and STOP signals is measured, and the corresponding memory cell is incremented.

For present-day surface analysis, the moment of the secondary ion "birth," i.e., the moment of the impact of the probing-beam particle on the surface, is usually fixed by pulsing the beam. The technique is well developed, and usually the pulses are produced by sweeping the beam across the small-diaphragm orifice. 20,21 Because of strong modulation (or electronic "chopping") of the beam, the probing particles may hit the surface only during short (5-10 ns) well-defined time intervals. The moment the beam is "switched on," the START pulse is generated, and ion detection triggers the STOP pulse. Such an approach was successfully implemented in a number of experiments. 22-24 Usually, only one STOP pulse for every START pulse could be registered. The probing-beam intensity is selected in a way to fulfill the condition $N_{SI} \ll 1$, which facilitates the processing of the TOF spectra. In another case, a pile-up spectrumcorrection procedure25 is to be introduced.

Though enjoining such TOF technique advantages as multichannel detection with low dose and low sample consumption and insensitivity to probing-beam intensity variations, this approach is rather inefficient since the beam is "switched on" only during a small part ($\leq 10^{-3}$) of the exposure time. Another drawback is connected with the significant difficulty in shortening ion pulse bunches down to 1 ns in order to match the typical accuracy of fixing the STOP pulses, which is required for high mass resolution.

For the sake of completeness, two more applications of TOF technique (based on pulsing approach) to surface analysis should be mentioned: the atom probe field ion microscope and LAMMA analyzers. In the TOF atom probe field ion microscope, the secondary ions are produced by either a high-voltage pulse^{26,27} or a laser shot.^{28,29} In commercially available LAMMA analyzers,³⁰ the plasma cloud is created by the laser shot at the surface; the ions are extracted, accelerated, conveyed to the detector, and registered by the transient recorder.

II. ALTERNATIVE APPROACH

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The ideal TOF SIMS technique would use a continuous probing beam of arbitrarily low intensity and allow precise independent determination of the time of probe particle impact on the surface. Such an approach was pushed forward earlier and resulted in the development of the TOF technique known as 252 Cf plasma desorption mass spectrometry (252 Cf-PDMS). One of the 252 Cf fission fragments bombards the surface under study and another fragment triggers START pulse. 32,33 Both positive and negative secondary ion spectra can be registered in this way. The same fission fragment which produces desorption of secondary ions can also be used for triggering of the START signal if registered after penetration of the foil supporting the sample. 31,34 The PDMS has proved particularly successful for the large molecules (\gtrsim 10 000 amu) typical for biochemical research.

Ideas rather close to PDMS were used by Doyle et al.³⁵ for the study of the secondary ions produced from a thin foil target by projectile ions with several MeV per nucleon energy. Mass spectrum was measured by the TOF technique: The STOP signals were produced by secondary ions, while the START signals were produced by a detector which registered the probing-beam ions.

The main drawbacks of the described technique can be summarized as follows: (1) Only high-energy particles (capable of the foil penetration) can be used; the physics of their interaction with the surface is quite different from that of "low"-energy ions typical for conventional SIMS. The latter poses difficulties to quantitative mass spectrometry. (2) The fission fragments are varying in their energy and mass; for instance, for ²⁵²Cf more than 40 different pairs of nuclei can be produced with energies from 50 up to 120 MeV. ^{31,33} (3) It is important that the fission source be well protected and contained, since the nuclide ²⁵²Cf does pose a health hazard from its radioactivity and body chemistry. ³¹ (4) The use of multi-MeV accelerators to produce the probing beam does not make the technique easy.

An alternative approach to fix the moment of secondary ion "birth" is possible by the detection of the secondary electrons which may be emitted concurrently with the secondary ions. Though, as will be discussed further, this way of triggering the START pulse has been already used for negative ions, this is the first time that such an approach is proposed and implemented to the positive secondary ions.

A new acronym—MASTIF (mass analysis of secondaries by time-of-flight technique)—was coined for this technique to distinguish it from traditional TOF SIMS and PDMS-TOF, which use the pulsing of either the probing beam or the extraction potential or multi-MeV probing particles.

The main advantageous features of the MASTIF approach are the following: (1) Secondary ion detection is performed in coincidence with secondary electron detection. The coincidence mode makes possible the extraction of faint useful signals (coincidences) from the superior background count rate (even if the signal is much less than the detector's own noise count rate). Valuable instrument housekeeping information on the detection efficiencies, and the probing-beam absolute intensity can be obtained without preliminary instrument calibration. (2) The probing beam is continuous, and as a result, the beam is used with the utmost possible efficiency, there is no need for the rather complex "electronic chopper," and the time of the particle impact on the

surface is fixed with the same accuracy as the secondary ion detection. (3) The probing-beam intensity may be decreased (with a corresponding increase of exposure time) down to, in principle, arbitrarily low values. There is no rigorous requirement upon the probing-beam intensity stability since the spectrum is accumulated in the parallel multichannel mode. (4) The use of the probing ions (atoms) of the same mass and energy as in conventional SIMS make possible application of the vast accumulated data on secondary ion yields under various conditions. It can be claimed, therefore, that the proposed MASTIF provides a quantitative analysis at least to the same extent as conventional SIMS.

Features (1), (3), and (4) are common for both conventional SIMS and MASTIF, but feature (2) is characteristic for the latter only.

Because of these features, trace elements and fragile and/or ultrathin objects sensitive to the damage by the probing beam may be studied. The main disadvantage, inherent to the proposed technique, which limits principally its applications, is that the secondary ions and secondary electrons must be separated (in space and/or time) and detected independently. This demand limits the realm of objects which may be studied.

The MASTIF approach can be rather easily realized if the START and STOP pulses are produced by the particles of the same charge sign, for instance, by electrons and negative secondary ions. In an electrostatic field they acquire different velocities due to the difference in masses and are separated in time. The measurement of the distribution of the time intervals between the detection of the electrons and negative secondary ions gives mass spectrum. Such an approach was realized successfully in spontaneous desorption TOF mass spectrometry³⁶ and for the bombardment of the surface by MeV ions.³⁷

As far as positive-ion SIMS is concerned, the range of applications is restricted to a number of special objects such as thin self-supporting foils, semiconducting materials, and MCP sensitive area surfaces. Only for these objects has the separation of negatively charged electrons and positive ions been realized. The main difficulty arises from the fact that if secondaries of certain charge sign are extracted from the impact point by an external electrostatic field, then the secondaries with the opposite charge sign would be pushed back into the surface from which they have been sputtered.

It is interesting to mention here an attempt³⁶ to obtain positive-ion mass spectra in PDMS-TOF by triggering the START signal by "light" secondary ions (H⁺, Na⁺, K⁺) and STOP signal by heavy secondary ions. Obviously this can be applied only for the study of very heavy secondary ions and the technique difficulties are connected with the problem of START ion identification.

For the sake of completeness, the application of coincidence detection ideas to the analysis of secondary ions produced in the gas phase is worth mentioning. Secondary ion detection in coincidence with the simultaneously born secondary electron was described the first time by Brehm and von Puttkamer.³⁸ In experiments of this type, the gas atoms or molecules are ionized by photons with fixed energy and

the characteristics of secondary ions and photoelectrons are studied.³⁹

III. MASS RESOLUTION

Actual mass resolution of the MASTIF technique is determined by the geometrical characteristics and the electrostatic field of the analyzer as well as by the initial energy distribution of the secondary ions. If no special measures are implemented to focus in time ions with different initial energies, and if the ion acceleration distance is much less than the flight distance, then the mass resolution is

$$\frac{M}{\Delta M} \simeq \frac{1}{2} \frac{E_a}{E_i}$$

where E_a is the energy acquired by an ion after acceleration and E_i is the initial energy of the ion. Obviously, to achieve the high ($\geqslant 100-500$) mass resolution is unrealistic by the straightforward increase of acceleration voltage, since secondary ion energy distribution is characterized by a rather extended high-energetic "tail" (up to $50 \, \mathrm{eV}$).

Drastic improvement in mass resolution may be achieved if the trajectories of the ions are isochronous, i.e., the time of flight is independent of the initial energy of the secondary ions. Such time focusing was realized by Mamyrin *et al.*⁴⁰ in a rather simple device called a "reflectron." The principle is based on the ideas⁴¹ of turning ions in the electric field. The achievement of time focusing in more complex magnetic and electrostatic analyzers was considered extensively by Poschenrieder.^{42,43}

The same time-focusing technique may be applied for conventional TOF SIMS also; however, the improvement in mass resolution would be less significant due to the rather large uncertainty (typically 5–10 ns) of actual START signal

In this work, no special attempts for time focusing were made. The aim of the work is only to demonstrate that the MASTIF approach can be realized, and the achieved mass resolution is modest at best (\approx 20). For real surface MASTIF analysis, either reflectron or Poschenrieder analyzer designs should be implemented.

IV. EXPERIMENTAL DEMONSTRATION

Several simple experimental detector systems were built and tested to evaluate the proposed technique.

A. Experimental arrangement

It is important that both detector systems and corresponding electronics can be based on standard commercially available elements. MCP stacks are used for particle detection, and the detector system can be built as a rather compact device. Overall dimensions are confined within limits $10\times10\times12$ cm³ and the secondary ion total flight distance is 6–7 cm only. Even for high acceleration voltages (up to 10 kV), time of flight is 1–2 μ s for heavy ions ($M \approx 1000$ amu). Typical timing accuracy for MCP detectors is 1 ns, which makes feasible mass resolution up to 500. Relatively small flight distances (and corresponding low probability for the

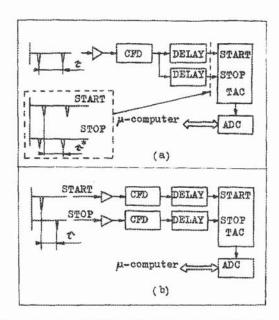


FIG. 1. Principal scheme of time-of-flight measurements: (a) single-channel mode; (b) two-channel mode; τ : time interval between START and STOP signals; τ *: time interval actually measured in single-channel mode. CFD: constant fraction discriminator; TAC: time-to-amplitude converter; ADC: analog-to-digital converter.

ion to be lost due to the interaction with residual gas) allow functioning of the device in rather poor vacuum conditions, such as the pressure 10⁻⁵ Torr, which is required for the MCP detectors.

Two modes are possible for the measurement of time intervals between START and STOP signals: single-channel and two-channel modes. In the single-channel mode, both the START and STOP signals are sent through the same signal line [Fig. 1(a)]. The signal from the MCP detector is amplified by a fast amplifier (FA) and the standard pulse is formed by a constant fraction discriminator (CFD). Timing accuracy better than 1 ns can be achieved with CFD. Two delay lines are used to arrange the proper sequence of pulses at START and STOP inputs of the time-to-amplitude converter (TAC). If the pulses after CFD are delayed more in STOP line than in START line, then the same pulse would trigger both START and STOP inputs of TAC. To avoid this effect, pulses in START line are delayed more than in STOP line. Then, the START input of TAC is triggered by the first pulse in the pair and the STOP input is triggered by the second pulse, and the time interval between two pulses is measured [Fig. 1(a)]. The pulse height at TAC output is digitized by an analog-to-digital converter (ADC) and is sent to a microcomputer which accumulates TOF (and, correspondingly, mass) spectrum. In the two-channel mode, START and STOP signals are sent through separate lines and the scheme is shown in Fig. 1(b). We built our electronic system on the basis of CAMAC, and it is convenient that all necessary modules (FA, CFD, DELAY, TAC, 10bit ADC) are available commercially.

Not all START signals are accompanied by STOP pulses and vice versa, and on average, START signals (secondary electrons) are more frequent than STOP ones (secondary ions). Therefore, events are possible when the

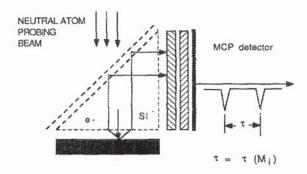


FIG. 2. Negative-ion MASTIF. Single-channel mode of TOF analysis is performed.

START signal is produced by one probing-beam particle, and the STOP signal by another one. The probing beam is a random flux of particles, and the probability of such false coincidences is proportional to the square of the probing-beam intensity. So for the beam intensity resulting in emission of 10^4 secondary particles per second, there will be approximately 1% of such false coincidences if maximum time of flight in the detector system is $1~\mu s$. Decreasing of the probing-beam intensity is the way to reduce the probability of such events.

All results described further were obtained at a typical count rate of 10^2-10^3 s⁻¹ for electrons. Count rates for secondary ions were somewhat lower, $10-10^2$ s⁻¹, and coincidence (i.e., TOF event) count rate, 1-30 s⁻¹.

B. Negative ions

The most simple implementation of the MASTIF idea is for negative ions. Figure 2 shows the setup. Probing-beam atoms bombard the surface under study. An ion probing beam also may be used; however, in that case, the effect on ion trajectories due to electrostatic fields in front of the surface must be taken into account. The secondaries-electrons and negative ions-are accelerated by the nearest grid. The positive secondary ions are pushed back into the surface. After a turn in the electrostatic mirror, particles reach detector D. Fine, high-transmission harp grids are preferable for use in an electrostatic mirror. The particles are registered by a chevron MCP stack detector. The energy per charge gained by each secondary is the same. This results in different velocities for the secondaries (and corresponding separation in time) according to their masses. Electrons reach the detector first. Afterwards, the secondary ion arrives. This technique utilizes the single-channel mode of TOF analysis. Such an approach was realized for negative secondary ion TOF SIMS earlier. 36,37 The approach has the advantage of simplicity but also several disadvantages.7,44 In particular, afterpulses, which are often observed in secondary electron multipliers, may create some problems.

The two-channel TOF analysis was realized for a thin (30-Å) self-supporting carbon foil (Fig. 3). If the foil is "thin," then electrons produced within the foil bulk near the point of particle impact on the input surface have a good chance of reaching and escaping the output surface of the foil. The electrons are registered by detector D_1 , which provides the START signal.

Secondary ion mass spectrometry

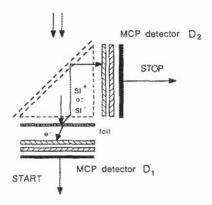


FIG. 3. Two-channel TOF mode for thin-foil analysis by MASTIF. Ions of any selected charge sign may be analyzed.

The secondary ions of any selected charge sign (depending on the extraction potential) may be accelerated and registered by detector D_2 . The portion of a typical TOF spectrum for negative secondary ions from the carbon foil is presented in Fig. 4. The probing beam is 3-keV argon atoms; the carbon foil thickness is 30 Å. The emitted secondary ions were accelerated to 2100 eV. A total of about 3×10^4 events were accumulated in this spectrum. The calculated mass differences (in atomic mass units) are shown between adjacent mass peaks. The identification of the mass peaks clearly indicates that the carbon foil is covered by a "dirty" layer. The mass resolution for such a simple setup having a low acceleration voltage is better than 10. The spectrum of negative ions obtained in the single-channel mode (Fig. 2) from the same foil was similar to that shown in Fig. 4. Obviously, in that case, any conducting surface could be studied in the same mode as the thin foil. The use of the uncharged particles in the probing beam and its low intensity make this approach also promising for the poorly conducting surfaces.

C. Positive ions

Applying the negative acceleration voltage, the positiveion spectrum was obtained from the same foil (the portion of the spectrum is shown in Fig. 5). The experimental conditions for this spectrum were almost the same as for the spectrum in Fig. 4. The energy of secondary positive ions after

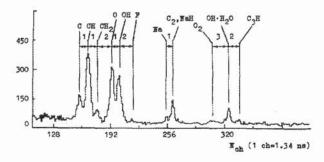


Fig. 4. A portion of the TOF spectrum (negative ions) obtained from carbon foil (30-Å thickness). Probing beam: 3000-eV argon atoms. The energy of the secondary ions after acceleration is 2100 eV. Calculated mass differences (in amu) between peaks are shown. Mass resolution $M/\Delta M \approx 20$.

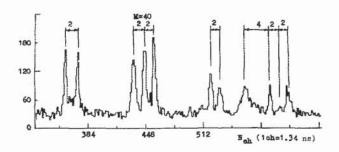


FIG. 5. A portion of the TOF spectrum (positive ions) obtained from carbon foil (30-Å thickness). Probing beam: 3000-eV argon atoms. The energy of the secondary ions after acceleration is 2000 eV. Calculated mass differences (in amu) between peaks are shown. Mass resolution $M/\Delta M \cong 20$.

acceleration was 2000 eV. The mass spectrum for positive ions is more abundant in lines when compared with that of negative ions. The mass resolution is better than 20.

D. Microchannel plate surface

One important case where positive-ion MASTIF could be implemented is shown in Fig. 6. A sensitive area of a MCP is bombarded by probing-beam atoms. Secondary electrons initiate an electron avalanche in the MCP stack and produce the START pulse. The STOP signal is triggered by the detection of a positive secondary ion SI^+ . Secondary ions can be produced from semiconducting glass (the microchannel walls) and/or from a conducting metal layer. If an ion barrier film is attached to the MCP, this film will be the source of the secondary ions. Since the triggering of D_1 is the neces-

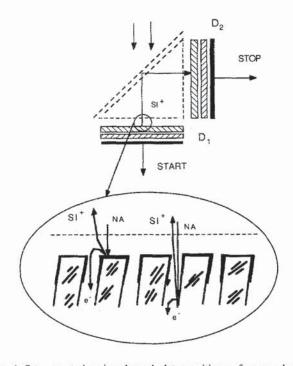


FIG. 6. Setup to study microchannel plate sensitive surface area by the MASTIF technique. NA: neutral atom of the probing beam. Secondary ions are emitted either from the semiconducting glass microchannel walls or from the metal layer.

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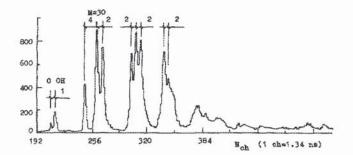


Fig. 7. A portion of TOF spectrum (positive ions) obtained from MCP sensitive surface area. Probing beam: 3000-eV argon atoms. The energy of the secondary ions after acceleration is 2000 eV. Calculated mass differences (in amu) between peaks are shown. Mass resolution $M/\Delta M \approx 20$.

sary condition for registering a TOF event, then only secondary ions emitted from those parts of the MCP surface that take part in the detection of particles be studied by MASTIF. This technique gives the opportunity to monitor the condition of the sensitive surface area of the MCP. The latter is important for EUV and soft x-ray astronomical detectors, where different layers (mainly alkali halides) have been tested to cover MCP surfaces to improve their characteristics in the desired wavelength range. The secondary ion spectrum, obtained from the sensitive area surface of the MCP (a portion is shown in Fig. 7), is obviously rather complex and abundant in peaks. Some peaks are widened due to the dependence of the energy acquired by ion on the place of its "birth" in microchannel.

E. Semiconducting surface

Positive secondary ion MASTIF can also be realized for a semiconducting material (or the thin layer, e.g., monolayer, covering such a surface). The principal scheme is shown in Fig. 8. The rectangular plate $(24\times20~\text{mm}^2)$ of semiconducting material (Zn_2TiO_4) was bombarded by a collimated beam (argon atoms, 3000 eV). A voltage U=800~V was applied across the plane. Secondary electrons were accelerated in one direction and were registered by detector D_1 . Secondary ions were accelerated in the opposite direction and, after a reflection in the electrostatic mirror, were registered by detector D_2 . The detection of an electron triggers the START pulse and the detection of an ion the STOP pulse for the TOF analyzer. The electrostatic mir-

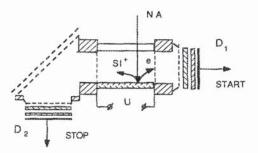


FIG. 8. Setup for positive secondary ion MASTIF of a semiconducting surface. D_1 : electron detector; D_2 : ion detector; U: applied voltage across the semiconducting plate under study.

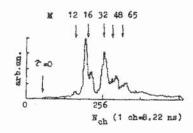


FIG. 9. TOF mass spectrum (positive ions) from the semiconducting material (Zn_2TiO_4). Arrows indicate calculated positions (in amu) of the mass peaks. Mass resolution $M/\Delta M \cong 5$.

ror is necessary to prevent ion feedback between D_1 and D_2 . The other reason why the ion detector is not situated symmetrically with the electron detector is that part of the primary-beam particles could be reflected as neutrals from the surface under bombardment and be registered by D_2 . These reflected atoms produce a very broad peak in the TOF spectra covering secondary ion peaks. The typical TOF spectrum is shown in Fig. 9. Calculated positions of some mass peaks are indicated by the arrows. The achieved mass resolution is $M/\Delta M \approx 5$. The enhancement of voltage and the implementation of the time focusing are the ways to improve the mass resolution.

The time interval between detection of the secondary electron and the secondary ion depends upon the mass of the ion and the position of the area where it is sputtered from the surface. If the position is fixed, then the device performs as a mass analyzer. On the other hand, if the mass of the secondary ion is known (this could be achieved by covering the semiconducting material by an appropriate layer, say, LiF), then this device would perform the function of a one-dimensional position-sensitive detector. Actually, this device (Fig. 7) was proposed initially 45 to be implemented in this capacity in the modified version of a space instrument for the study of the interstellar helium-atom fluxes in interplanetary space. 46

V. DISCUSSION

The experimental realizations of the MASTIF principle, which are described above, clearly show the feasibility of the approach. Though mass resolution achieved is at best modest, it may be improved significantly by an increase in the acceleration voltage (say, up to 10 kV) and by implementation of the time-focusing technique. The accuracy to fix the moment of the electron and/or ion detection is about 1 ns. For realistic flight distances, this accuracy would not pose a limitation on the acceleration voltage enhancement.

Among immediate possible applications of the proposed technique are studies of thin foils and the sensitive surface areas of MCPs under operational conditions. The information on afterpulses in MCP detectors when energetic ions and neutrals are registered may also be obtained. One of the possible sources of afterpulses is the secondary ion emission from microchannel wall following the impact of the particle to be detected. The indirect proof that such a mechanism may be involved is the observation⁴⁴ that afterpulses are rather frequent events when heavy atoms are registered and

are rare events for hydrogen atom detection.

The coincidence mode, implemented in MASTIF, provides an opportunity to increase significantly the dynamic range of conventional SIMS, i.e., to register trace elements. Therefore, a search for negative ions which were not yet detected from certain elements may be performed. Such elements as Sc, Mn, Zn, Sr, and Hf are immediate candidates for such a search, and the metastable negative ions created in sputtering also may be studied.

A new approach to secondary ion mass spectrometry described in this article offers advantages for the study of certain objects and, as any new technique, may find new and unexpected applications.

ACKNOWLEDGMENTS

A part of this article was written during my stay at FOM-Institute for Atomic and Molecular Physics, Amsterdam. I would like to acknowledge the Institute for hospitality and Stichting voor Fundamenteel Onderzoek der Materie for financial support.

- ¹H. Liebl, J. Phys. E 8, 797 (1975).
- ²H. W. Werner, in Electron and Ion Spectroscopy of Solids, edited by L. Fiermans, J. Vennik, and W. Dekeyser (Plenum, New York, 1978), p.
- ³H. Liebl, Anal. Chem. 46, 22A (1974).
- ⁴R. L. Wax and W. Bernstein, Rev. Sci. Instrum. 38, 1612 (1967).
- ⁵F. Busch, W. Pfeffer, B. Kohlmeyer, D. Schüll, and F. Pühlhoffer, Nucl. Instrum. Methods 162, 587 (1979).
- G. Gloeckler and K. C. Hsieh, Nucl. Instrum. Methods 165, 537 (1979). ⁷M. A. Gruntman and V. A. Morozov, J. Phys. E 15, 1356 (1982).
- 8M. A. Gruntman and V. B. Leonas, in Proceedings of International Workshop on Problems of Physics of Neutral Particles in the Solar system, Zakopane, Poland (Space Research Centre, Polish Academy of Sciences, Warsaw, 1985), pp. 99-120 and 151-179.
- 9K. C. Hsieh and C. C. Curtis, in Proceedings of 4th International Workshop on Interaction of Neutral Gases with Plasma in Space, Radziejowice, Poland (Space Research Centre, Polish Academy of Sciences, Warsaw, 1987), pp. 73-78.
- ¹⁰C. Martin and S. Bowyer, Appl. Opt. 21, 4206 (1982).
- 11G. W. Fraser, M. A. Barstow, J. F. Pearson, M. J. Whitely, and M. Lewis, Nucl. Instrum. Methods Phys. Res. A 224, 272 (1984).
- ¹²O. H. W. Siegmund, E. Everman, J. V. Vallerga, J. Sokolowski, and M. Lampton, Appl. Opt. 26, 3607 (1987).
- ¹³D. G. Simons, G. W. Fraser, P. A. J. de Korte, J. F. Pearson, and L. de Jong, Nucl. Instrum. Methods Phys. Res. A 261, 579 (1987).

- ¹⁴W. E. Stephens, Phys. Rev. 69, 691 (1946).
- ¹⁵A. E. Cameron and D. F. Eggers, Jr., Rev. Sci. Instrum. 19, 605 (1948).
- ¹⁶W. C. Wiley and I. H. McLaren, Rev. Sci. Instrum. 26, 1150 (1953). ¹⁷J. A. Browder, R. L. Miller, W. A. Thomas, and G. Sanzone, Int. J. Mass
- Spectrom. Ion Phys. 37, 99 (1981).
- ¹⁸R. D. Andresen and D. E. Page, Nucl. Instrum. Methods 98, 595 (1972). ¹⁹K. Sattler, J. Mühlbach, E. Recknagel, and A. Reyes-Flotte, J. Phys. E 13, 673 (1980).
- ²⁰J. H. Neiler and W. M. Good, in Fast Neutron Physics, edited by J. B. Marion and A. L. Fowler (Interscience, New York, 1960), Pt. 1, p. 509.
- ²¹D. Rathmann, N. Exeler, and B. Willerding, J. Phys. E 18, 17 (1985).
- ²²Y. S. Chen, G. L. Miller, D. A. H. Robinson, G. H. Wheatly, and T. M. Buck, Surf. Sci. 62, 133 (1977).
- ²³S. B. Luitjens, A. J. Algra, E. P. Th. M. Suurmeijer, and A. L. Boers, J. Phys. E 13, 665 (1980).
- ²⁴J. W. Rabalais, J. A. Schultz, R. Kumar, and P. T. Murray, J. Chem. Phys. 78, 5250 (1983).
- ²⁵P. B. Coats, J. Phys. E 5, 148 (1972).
- ²⁶E. W. Müller, J. A. Panitz, and S. B. McLane, Rev. Sci. Instrum. 39, 83 (1968).
- ²⁷O. Nishikawa, K. Kurihara, M. Nachi, M. Konishi, and M. Wada, Rev. Sci. Instrum. 52, 810 (1981).
- ²⁸T. T. Tsong, S. B. McLane, and T. J. Kinkus, Rev. Sci. Instrum. 53, 1442
- ²⁹T. T. Tsong and Y. Liou, Phys. Rev. Lett. 55, 2180 (1985).
- 30 P. Feigle, B. Schueler, and P. Hillenkamp, Int. J. Mass Spectrom. Ion Phys. 47, 15 (1983).
- ³¹B. Sundqvist and R. D. Macfarlane, Mass Spectrom. Rev. 4, 421 (1985).
- 32D. F. Torgerson, R. P. Skowronski, and R. D. Macfarlane, Biochem. Biophys. Res. Commun. 60, 616 (1974).
- ³³R. D. Macfarlane and D. F. Torgerson, Int. J. Mass Spectrom. Ion Phys. 21, 81 (1976).
- ³⁴A. Hedin, P. Hakansson, and B. U. R. Sundqvist, Int. J. Mass Spectrom. Ion Phys. 75, 275 (1987).
- 35 B. L. Doyle, P. S. Peercy, T. J. Gray, C. L. Cocke, and E. Justiniano, IEEE Trans. Nucl. Sci. NS-30, 1252 (1983).
- ³⁶S. Della-Negra, C. Deprun, Y. Le Beyec, F. Röllingen, K. Standing, B. Monart, and G. Bolbach, Int. J. Mass Spectrom. Ion Phys. 75, 319
- ³⁷M. Salehpour, D. L. Fishel, and J. E. Hunt, J. Appl. Phys. 64, 831 (1988).
- ³⁸B. Brehm and E. von Puttkamer, Z. Natürforsch. 22a, 8 (1967).
- 39J. J. Butler, D. M. P. Holland, A. C. Parr, R. Stockbauer, and R. Buff, J. Phys. E 18, 286 (1985).
- ⁴⁰B. A. Mamyrin, V. I. Karataev, D. V. Shmikk, and V. A. Zagulin, Zh. Eksp. Teor. Fiz. 64, 82 (1973) [Sov. Phys. JETP 37, 45 (1973)].
- 41S. G. Alikhanov, Zh. Eksp. Teor. Fiz. 31, 517 (1956) (in Russian).
- ⁴²W. P. Poschenrieder, Int. J. Mass Spectrom. Ion Phys. 6, 413 (1971).
- ⁴³W. P. Poschenrieder, Int. J. Mass Spectrom. Ion Phys. 9, 357 (1972).
- 44M. A. Gruntman and V. A. Morozov, Preprint No. 667 (Space Research Institute, Academy of Sciences, Moscow, 1977).
- ⁴⁵M. A. Gruntman and V. B. Leonas, Preprint No. 825 (Space Research Institute, Academy of Sciences, Moscow, 1983).
- ⁴⁶H. Rosenbauer, H. Fahr, E. Keppler, M. Witte, P. Hemmerich, H. Lauche, A. Loidl, and R. Zwick, in The International Solar Polar Mission-Its Scientific Investigations, ESA SP-1050, 1983, p. 123.