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Production and evaluation of micron-sized fine grating having high aspect ratio suitable for time-of-flight mass spectrometer

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Overview

Low-cost grating suitable for orthogonal accelerator of TOF-MS is described (Table 1).

Table 1. Summary of advantages using present grating for TOF-MS.

Feature of grating	Effectiveness	Advantageous for
Fine	Suppress ion divergence	Sensitivity
High transmission	Suppress ion loss	Sensitivity
Thick	Withstand high extraction field	Resolving power/sensitivity/mass accuracy
	Suppress field penetration	Resolving power/low background

Introduction

Ion optical grids are widely used to accelerate or decelerate ions in time-of-flight mass spectrometer (TOF-MS). This "real" grid has the following disadvantages: (a) ion loss on the grids, (b) divergence of ion trajectories due to lens action, and (c) low mechanical strength (Figure 1). To suppress the divergence, it is effective to reduce a pitch of grid [1]. Parallel wire grids (Figure 2a) with 20-um wires at 250-um pitch are available, giving a transmission of 92 %. This kind of grids is especially suitable for ion reflectors. On the other hand, fine electroformed meshes (Figure 2b) are used for orthogonal accelerators; however, thickness of the mesh is limited to typically 10 um by manufacturing reasons. If the extraction field inside the accelerator is increased to improve mass resolving power, mechanical strength is insufficient and these grids would be loosen or broken. It is therefore necessary to develop fine grids with high mechanical strength.

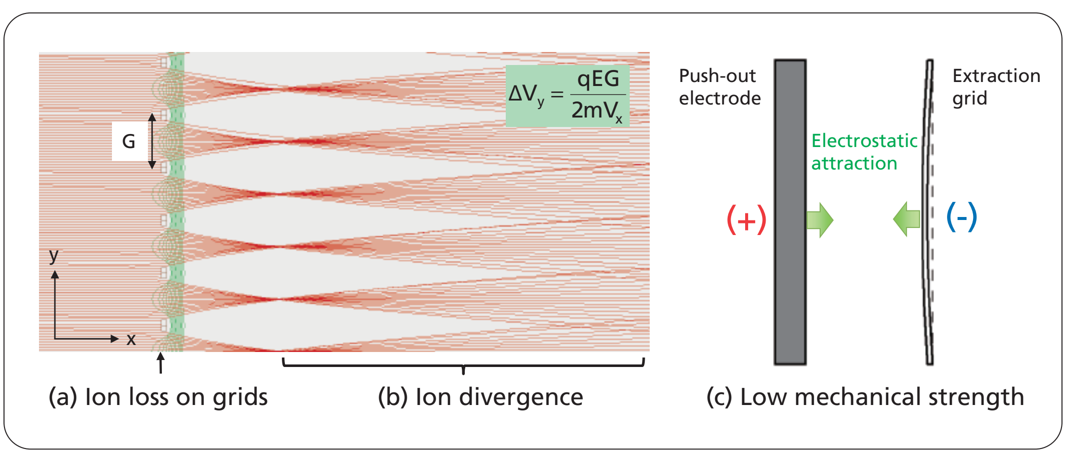
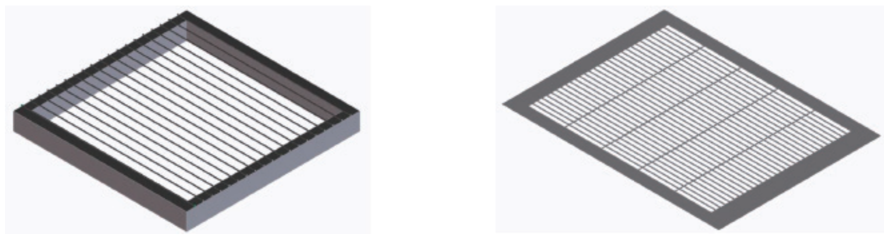


Figure 1 Disadvantages of "real" ion optical grids.



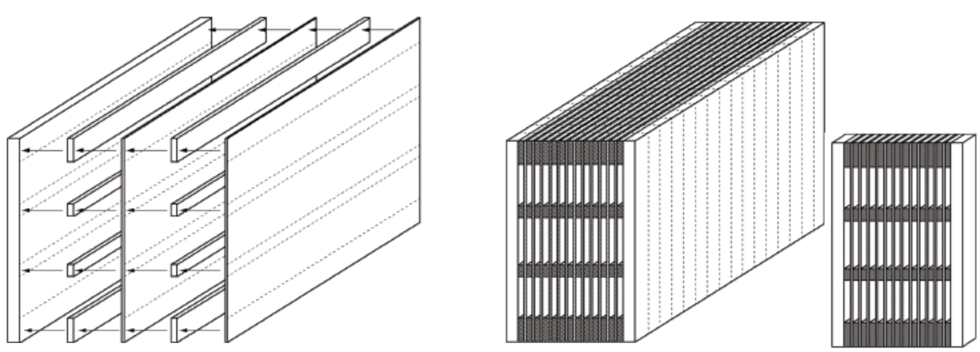
(a) Parallel wire grid
e.g. 20-um wires at 250 um pitch

(b) Electroformed meshes
e.g. 850x85 um pitch

Figure 2 Conventional ion optical grids used for mass spectrometer.

Methods

We produced a grid with pitches and a transmission similar to those of the conventional electroformed fine meshes, but the thickness was much increased up to 2 mm. This micron-sized fine “grating” having high aspect ratio was made as follows (Figure 3). First, a plurality of thin plates made of stainless steel were stacked with keeping spaces between them by sandwiching a large number of spacers made of stainless steel, and bonded together to form an integrated block by diffusion bonding (Figure 3a). Secondly, the integrated block was cut in round slices at predetermined intervals by wire-cut discharge machining (Figure 3b). A number of gratings were obtained from one block. By this production method, machining cost per one grating was much reduced.



(a) Bonding of metal pieces

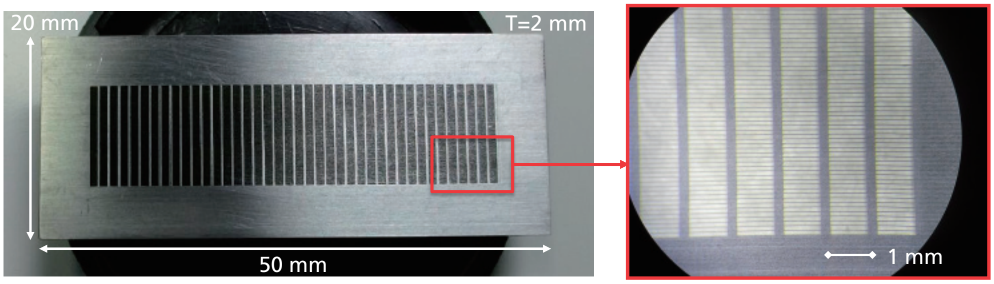
(b) Cutting block

Figure 3 Production of micron-sized fine grating with high aspect ratio.

Result

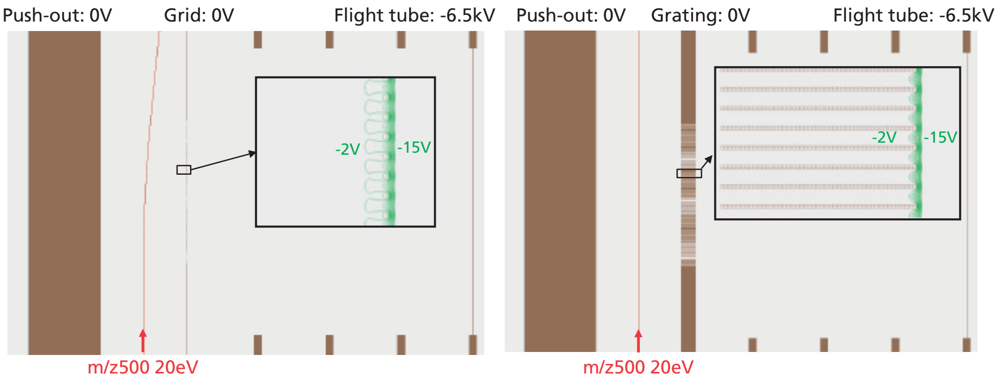
Production of micron-sized fine grating

We produced a fine grating having pitches of 100x1000 um, transmission of 70 %, and thickness of 2 mm (Figure 4). This grating has two advantages. The first is increment of the mechanical strength. To improve resolving power in orthogonal acceleration TOF-MS, it is effective to reduce turn-around time of ions by increasing the extraction field; this will cause the deformation of grids. This adverse effect can be avoided by increasing the strength by using the grating. The second is suppression of field penetration inside the accelerator. When ions are introduced between the push-out electrode and the extraction grid, if the thickness of the grid is thin, a high voltage applied to the flight tube penetrates into the acceleration region. As a result, ions introduced are bent (Figure 5a), and the resolving power and/or the signal intensity will be lowered. Also, ions continue to flow into the flight tube, causing a background noise. To suppress this penetration in the prior art, a potential barrier is formed by using a plurality of grids at some interval apart. However, this has the following problems. (1) These grids are needed to align with high accuracy to keep high transmission. (2) The voltages applied to them need to be timing-controlled independently, thus the cost increases. (3) The jitter of these voltages can result in adverse effect for mass accuracy. Contrary to the conventional grid, our grating can completely avoid the field penetration as confirmed by simulation study (Figure 5b).



(a) General view (b) Enlarged view

Figure 4 Photograph of micron-sized fine grating with high aspect ratio.



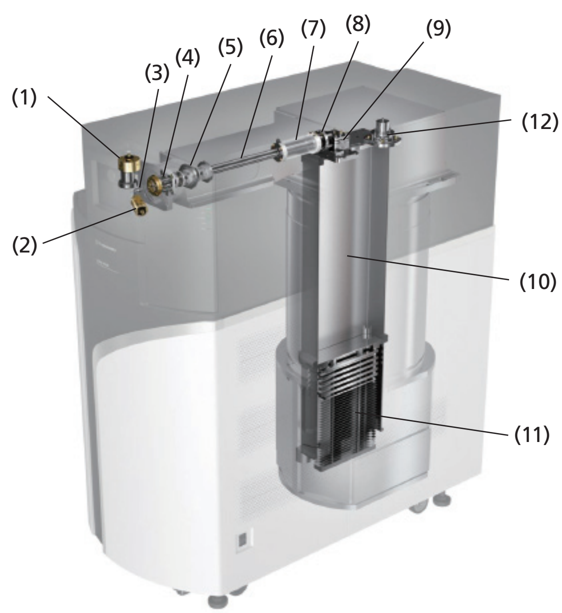
(a) Conventional grid (T=10um, G=0.1mm) (b) Present grating (T=1mm, G=0.1mm)

Figure 5 Field penetration through grid/grating. Green lines indicates contours.

Application to orthogonal-acceleration TOF-MS

To evaluate the effectiveness experimentally, the grid was introduced into an orthogonal acceleration TOF-MS (Figure 6). Briefly, high-efficiency ion guide, quadrupole, and the UFsweeper III Collision Cell are all part of the UFMS technologies established for the LCMS-8060. The speed and sensitivity gained by the UFMS architecture are in complete synergy with the following technologies for maximizing mass accuracy and resolving power. The present grating (UFgrating) makes it possible to improve both resolving power and sensitivity by increasing extraction field. Since deformation of the grid electrode during ion ejection can be suppressed, the reproducibility of each ion ejection is improved, contributing to high mass accuracy. Furthermore, the penetration of electric field from the flight tube is completely suppressed, so background ions during data collection can be removed.

An "ideal" reflectron (iRefTOF) is another key technology of the present TOF-MS enabling to obtain both high resolving power and high sensitivity at the same time. When high extraction field is used for the accelerator, energy spread of ejected ions becomes large. Since the energy-focusing ability is low in a reflectron consisting of uniform electric fields, which is widely used, it is necessary to reduce ion spatial spread inside the accelerator to obtain high resolving power at the sacrifice of the sensitivity. We adopted the reflectron consisting of the non-uniform field; this "ideal" electric field enhances the energy-focusing ability while minimizing both the divergence of the reflected ion trajectories and the time-aberration caused for the ions on a path dislocated from the central axis of the reflectron.



LCMS-9030

(1) Heated ESI Probe
(2) Reference Sprayer
(3) Desolvation Line
(4) UF-Qarray
(5) UF-Lens
(6) Quadrupole
(7) UFsweeper III Collision Cell
(8) UFaccumulation
(9) UFgrating
(10) UF-FlightTube
(11) iRefTOF
(12) Funnel MCP

Figure 6 Experimental setup of a new orthogonal-acceleration TOF-MS.

As a test of the system, mass spectrum of $Na(NaI)_n$ was obtained (Figure 7a). Although the pulsed voltages were applied to both the push-out electrode and the extraction grating, the observed TOFs plotted against the square root of the theoretical masses were completely straight within 1 ppm over the whole mass range (Figure 7b). The background due to stray ions were completely suppressed.

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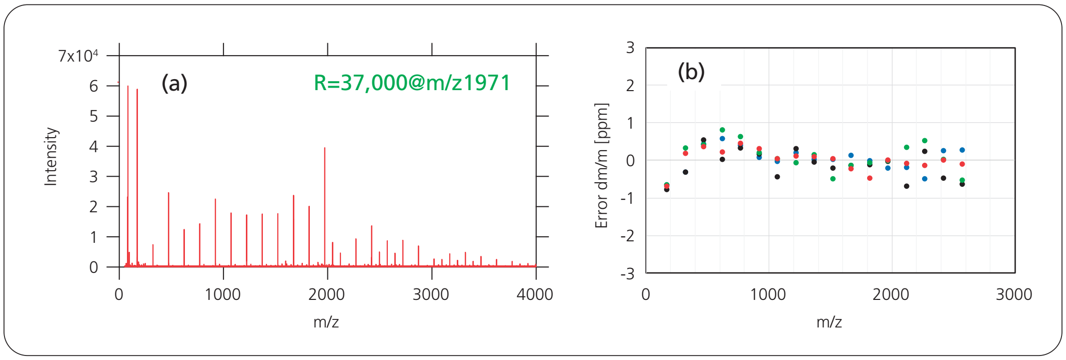

Figure 7 (a) Mass spectrum of $Na(NaI)_n$. (b) Observed mass error plotted against m/z. Different colours indicate independent measurements.

Conclusions

Low-cost grating which contribute to high resolution, high sensitivity, and high mass accuracy of TOF-MS was produced and experimentally verified.

References

[1] M. Guilhaus, D. Selby, and V. Mlyuski, Mass Spectrom. Rev. 19 (2000) 65-107.

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