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62

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65

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PRACTICAL APPLICATION OF A NEXT GENERATION UV MICROCHIP LASER FOR POST-IONIZATION SPUTTERED NEUTRAL MASS SPECTROMETRY

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An apparatus for time-of-flight sputtered neutral post-ionization mass spectrometry has been developed using a newly developed microchip laser having features of small size, high repetition rate, and sub-nanoseconds giant-pulse. The key technique which is realizing such features is microchip resonator, and intense pump-passive Q-switch method. In the current stage of this development, it is temporary constructed on a breadboard. As an example of the performance of the laser, a polymer blend sample was analyzed, and a reasonably good spectrum was obtained in a short period of time.

I. Introduction

Imaging of molecular distribution is needed in various fields such as life sciences and, polymer industries. A promising technique for such imaging is matrix-assisted laser desorption/ionization (MALDI). In this method, large molecular weight molecules are detected directly owing to soft ionization nature. However, the imaging spatial resolution is not enough for single cell imaging or domain visualization of polymers. In contrast, imaging resolution of secondary ion mass spectrometry with a time-of-flight mass spectrometer (TOF-SIMS) reaches to sub-micrometer level. When TOF-SIMS is coupled with a laser for post-ionization of sputtered atoms or molecules, it is called sputtered neutral mass spectrometry (SNMS). The lateral resolution of SNMS is dominated by an ion beam used to sputter which is basically the same as in SIMS. A major advantage of SNMS is that atoms and molecules having low sensitivity in SIMS can be effectively ionized and detected. Previously, SNMS was employed to detect impurities in semiconductors, and grain-boundary segregation of boron^[1]. In particular, higher resolution is needed in the organic and polymer fields, which is relatively easy to attain. In general, a laser system is too large, and only specialists in laser optics are capable of properly operating the lasers optimized for the post-ionization. As a result, the operators cannot concentrate on the analysis. A simple and easy-to-use laser system is the best solution for practical SNMS system. In addition, a laser system requires a large flat stage to align the laser optics. With smaller laser systems such as a flange-mounted type, more analytical scientists would be able to exploit SNMS for organic and polymer sciences. Recently, a high peak power, giant-pulse microchip laser was developed by Prof. Dr. Taira at the Institute for Molecular Science Laser Research Center. The peak power of the microchip laser reached megawatt class at a wavelength of 266 nm within the dramatically down sized laser head toward "Giant Micro-photonics"^[2]. Compared to our previous experiments using the old-type microchip laser

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[3], this UV microchip laser is capable of easily post-ionizing sputtered species from polymer blend surfaces and solids of polycyclic aromatic hydrocarbons (PAHs). We report that the laser SNMS analyses of polymer blend, PAHs and inorganic materials were performed by TOF-SIMS combined with the microchip laser.

II. Experimental

Figure 1 shows the TOF-SIMS apparatus^[4]. This apparatus was developed by Sakamoto et al with support from JST SENTAN. The basic components of this apparatus include an ultrahigh vacuum chamber equipped with a sample stage, a gallium focused ion beam (Ga-FIB) (A&D Co. Ltd.), and a time-of-flight mass spectrometer (TOF-MS) (TOYAMA Co. Ltd.). The samples in the ultra-high vacuum chamber (around 10^{-6} Pa) are bombarded by Ga^+ ions with an acceleration voltage of

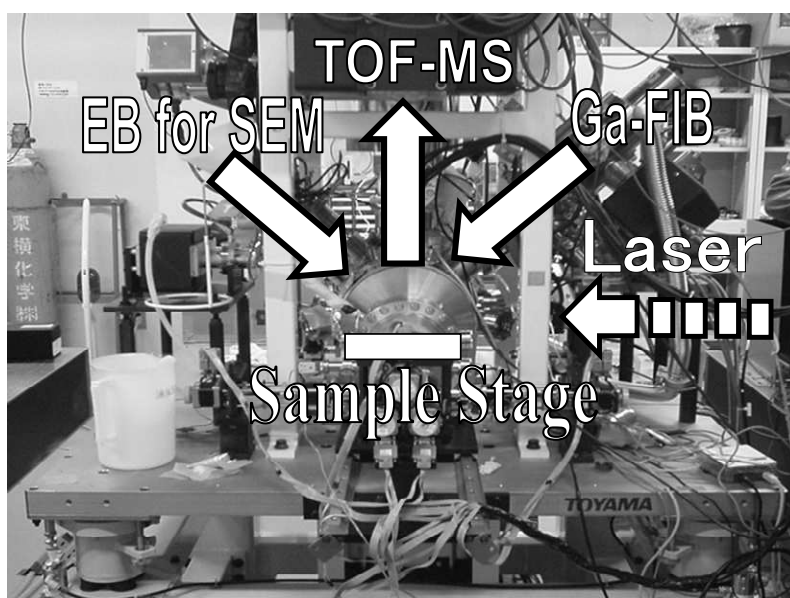


Figure. 1. Photograph of a Ga-FIB-TOF-SIMS apparatus with a scanning electron microscope for observation of samples, Ga focused ion beam gun, time of flight mass spectrometer, an x-y-z-tilt-rotation sample stage (five axis sample stage).

30 kV at an incident angle of 45° . During the data acquisition, the Ga-FIB was operated in a pulsed mode synchronized with the laser post-ionization processes. In this study, the pulse width and repetition rate of the Ga-FIB were 200 ns and 100 Hz or 1 kHz, respectively. A quartz cylindrical lens was placed in the laser path to focus it just above the sample surface. Neutral sputtered species (single atoms and molecular species) ejected from the sample surfaces were photo-ionized by the pulsed laser irradiation from the axis parallel to the sample surface. For laser post-ionization of sputtered neutrals, precision delay generators (DG535 and DG645, Stanford Research Systems, Inc., USA) were synchronized with the system. Two types of microchip lasers were used as the first and second prototype versions. Figure 2 shows a photograph of the first version mega-watt microchip laser head. This laser head is very compact and can be held by hands. The laser wavelength is 266 nm and pulse width is 150 ps, with 100 Hz repetition rate at a 4.3 MW peak power^[5-7].

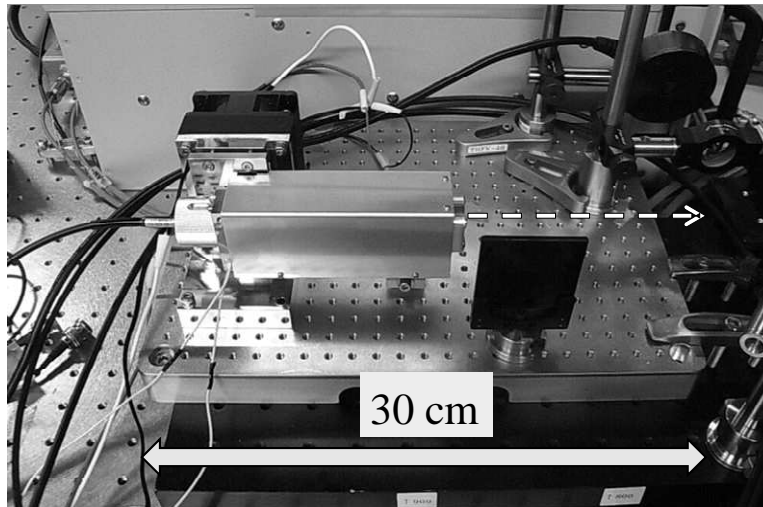


Figure. 2. A photograph of the first version megawatt micro-chip laser head including nonlinear crystals on a bread-board. The bread-board size is 30 cm \times 30 cm. The micro-chip laser head size is 12 cm \times 5 cm \times 6 cm. The laser head is connected to a pumping diode laser through a optical fiber (5 m length).

III. Results and discussion

Figures 3 and 4 show the mass spectra in laser SNMS analysis of a blend polymer composed of polystyrene and poly-hydroxy-styrene using a microchip UV laser at each repetition rate, respectively. The monomers of polystyrene (PS, $m/z = 104$) and poly-hydroxy-styrene (PHS, $m/z = 120$) were clearly detected. Using a focus lens, a fragment ion peak of PHS ($m/z = 94$) was found in both experiments. This result shows the defocus or non-focused lens are needed depending on the appropriate ionization volume.

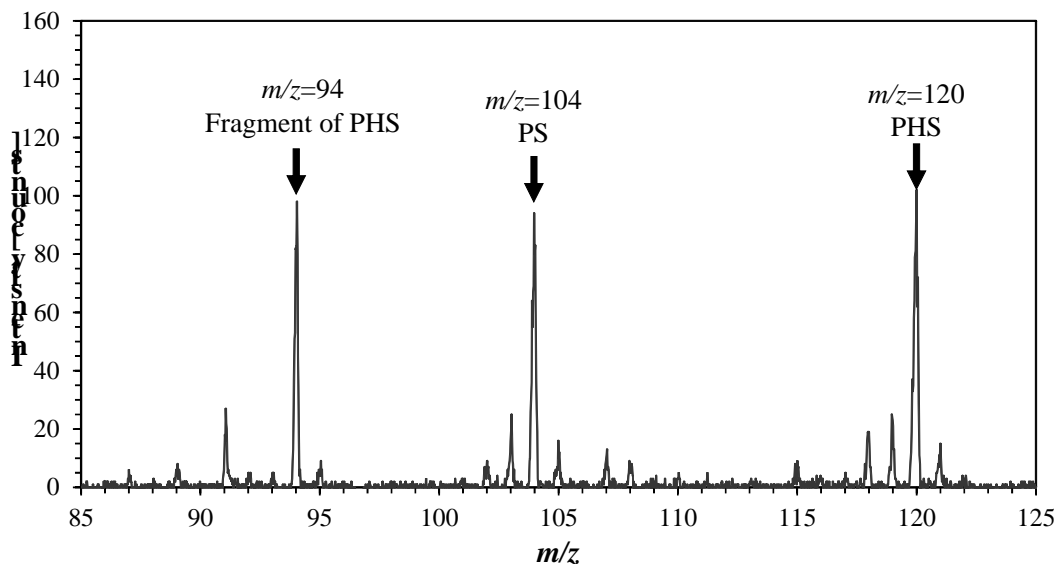


Figure. 3. Laser SNMS mass spectrum of a polymer blend. The laser used here is the first prototype. The repetition rate was 100 Hz and the beam energy was 350 μ J/pulse.

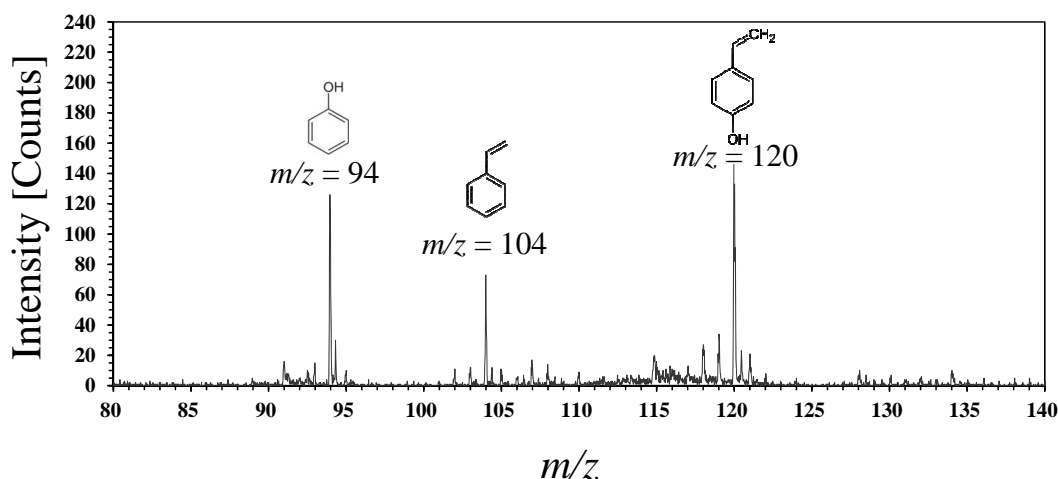


Figure. 4. Laser SNMS mass spectrum of a polymer blend (polystyrene and poly-hydroxy-styrene). The laser repetition rate was 1 kHz (2nd prototype) and the beam energy was 70 μ J/pulse.

IV. Conclusion

A polymer blend was analyzed using a laser SNMS method. A photoionization laser, megawatt class UV microchip laser was used for the first time. The laser repetition rate was 100 Hz or 1 kHz, and the laser wavelength was 266 nm. Each monomer ion was clearly detected from a polymer blend.

Acknowledgment

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