Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Nanophotonic Ion Production from Silicon Microcolumn Arrays**

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[**] Financial support by the Chemical Sciences, Geosciences and Biosciences Division within the Office of Basic Energy Sciences of the U.S. Department of Energy (DE-FG02-01ER15129) and from the George Washington University Research Enhancement Fund (GWU-REF) is acknowledged.

Experimental

Materials. Low resistivity (0.001-0.005 Ωcm) p-type mechanical grade, 280±20 μm thick silicon wafers were purchased from University Wafer (South Boston, MA). HPLC grade substance P, leucine enkephalin, verapamil, and reserpine were purchased from Sigma Chemical Co. (St. Louis, MO).

LISMA production. Silicon wafers were cleaved into approximately 3×3 mm^2 chips and cleaned in deionized water and methanol baths. In a Petri dish the chips were submerged in deionized water and exposed to ~600 pulses from a mode-locked frequency-tripled Nd:YAG laser with 355-nm wavelength and 22-ps pulse length (PL2143, EKSPLA, Vilnius, Lithuania) operated at 2 Hz repetition rate. The laser was focused by a 25.4 cm effective focal length UV

grade fused-silica lens (Thorlabs, Newton, NJ) to create a 1 mm diameter spot and 0.13 J cm^{-2} fluence.

Mass Spectrometry. For the ion yield measurements the LISMA was attached to a solid insertion probe using double-sided conductive carbon tape. Subsequently, 1.5 μL of the ~10^{-6} M aqueous analyte solution was deposited and air-dried on the LISMA surface. A home-built linear TOF-MS with τ = 4-ns pulse length nitrogen laser (VSL-337ND, Laser Science Inc., Newton, MA) excitation at 337 nm was used for all desorption ionization experiments. A planoconvex focusing lens created a laser spot with a diameter of ~150 μm. In the MALDI experiments, the DHB and analyte were deposited onto a polished silicon wafer to provide a substrate material similar to the LISMA experiments. In all of the experiments, ion yields were based on the peak areas of the relevant ions.

Angle of incidence experiments: Three different facets were machined on the cylindrical stainless steel probe tip to produce 0°, 15° and 45° angles of incidence. These facets accommodated the LISMA chips for the angle of incidence studies. By rotating a particular facet into the beam path, the ion yield for the corresponding angle could be determined.

Polarization experiments: The nitrogen laser beam was polarized by an uncoated Glan-Taylor calcite polarizer (GL10, Thorlabs, Newton, NJ). In order to maintain a constant laser pulse energy of ~10 μJ, the polarized beam was attenuated using a continuously variable neutral density filter (NDC-50C-2M, Thorlabs, Newton, NJ). The attenuated beam was focused onto the sample surface with a fused-silica lens (Thorlabs, Newton, NJ).

Ion yield vs. incidence angle for substance P

To demonstrate the strong dependence of the ion yield on the incidence angle for larger biomolecules, the neuropeptide substance P was deposited onto the LISMA structure. While an abundant *m/z* 1347 molecular ion peak was observed for 45°, at 15° the signal was dramatically reduced, and at 0° it disappeared altogether (see panel (a) in Figure S1). To verify that this effect was not a result of the varying ion collection efficiencies, MALDI experiments were performed with DHB matrix on the same facets of the probe. The resulting MALDI spectra for 0° and 45° incidence angles are shown in panels (b) and (c) of Figure S1, respectively. It is clear from this data that, in contrast to the LISMA results, the MALDI signal does not show a significant

dependence on the angle of incidence. These findings in combination with the data presented for verapamil (m/z 454) demonstrate that the strong dependence on the incidence angle of the desorption laser beam holds at higher molecular weights.

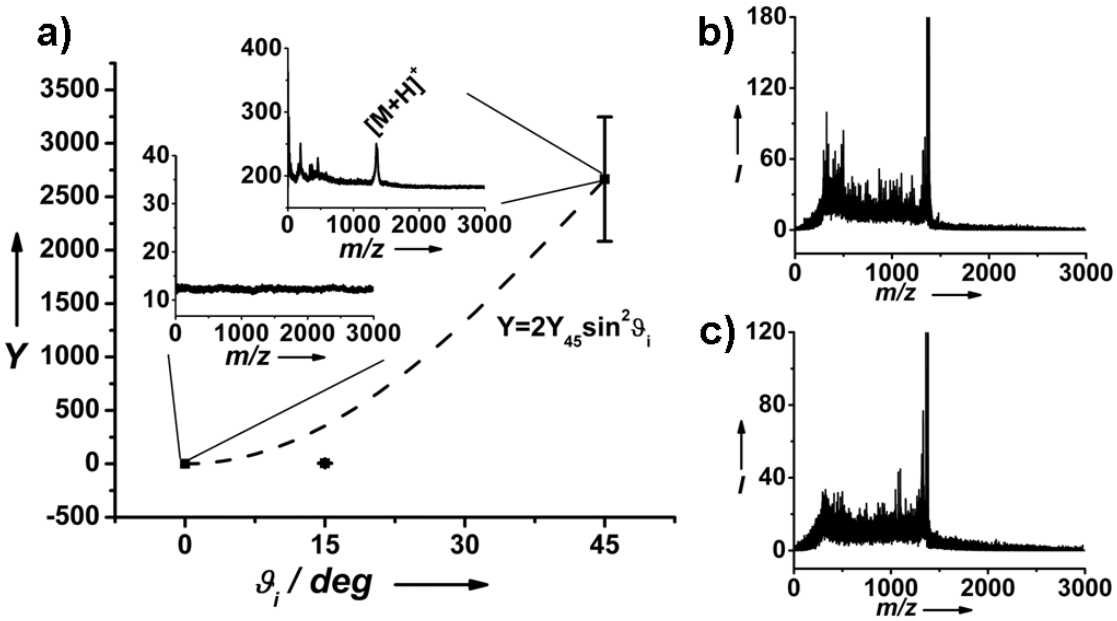

Figure S1: a) Ion yields for substance P desorbed from LISMA between incidence angles 0° and 45°. Insets show the LISMA mass spectra for 0° and 45°. MALDI experiments with DHB matrix show no change in the spectra for incidence angles b) 0° and c) 45°. A simple model prediction, analogous to Eq. (1), is shown by the dashed line.

Polarization dependence for reserpine, leucine enkephalin and substance P

To see if the observed strong effect of the laser beam polarization on the ion yield was dependent on the nature or the molecular weight of the analyte, experiments were carried out with reserpine (*m/z* 609), substance P (*m/z* 1347) and leucine enkephalin (*m/z* 556). Whereas unpolarized and p-polarized laser pulses of approximately the same energy produced similar LISMA spectra with little change in molecular ion abundances, the s-polarized beam produced no spectra for reserpine and substance P and only marginal signal for leucine enkephalin (see Figure S2).

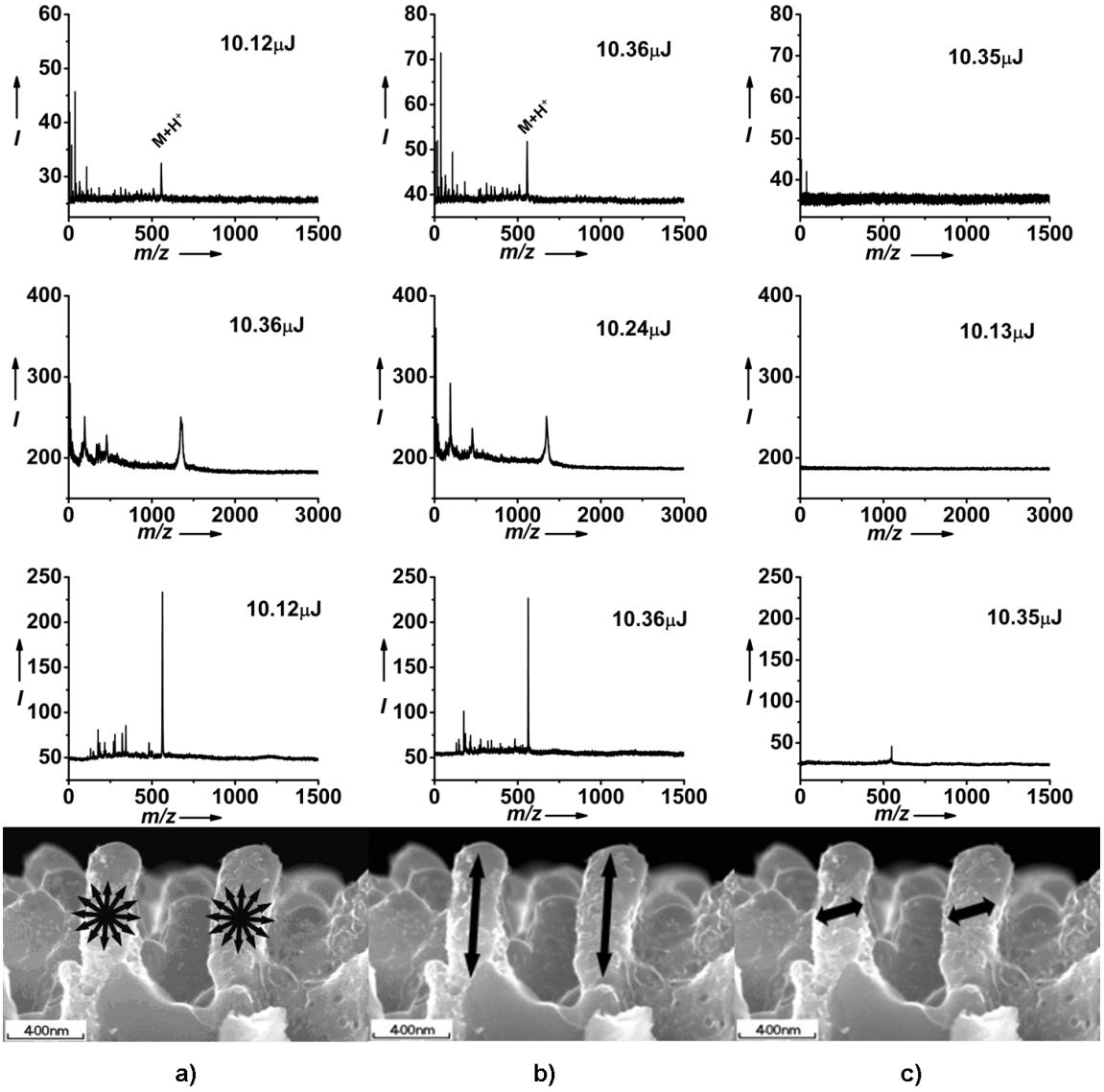

Figure S2: Reserpine (top row), substance P (second row), and leucine enkephalin (third row) spectra from LISMA were compared for laser desorption ionization experiments with unpolarized a), p-polarized b) and s-polarized c) rays. The p-polarized beam had similar ionization efficiency to the unpolarized one, whereas no or marginal signal was detected with the s-polarized ray. All experiments were conducted with ~10 μJ laser pulse energies.

Ion yield as a function of laser intensity

In MALDI experiments the ion yield as a function of incident laser intensity, I_i, shows threshold behavior followed by a strong non-linear response. Figure S3 shows that ion production from LISMA also exhibits a threshold but, in the studied range, the intensity dependence appears to be linear. This is consistent with the assumption that the desorption and ionization processes are driven by the axially absorbed laser energy,

$$I_{\perp} = I_i \sin^2 \vartheta_i \cos^2 \varphi_i ,$$

for constant angles of incidence and polarization.

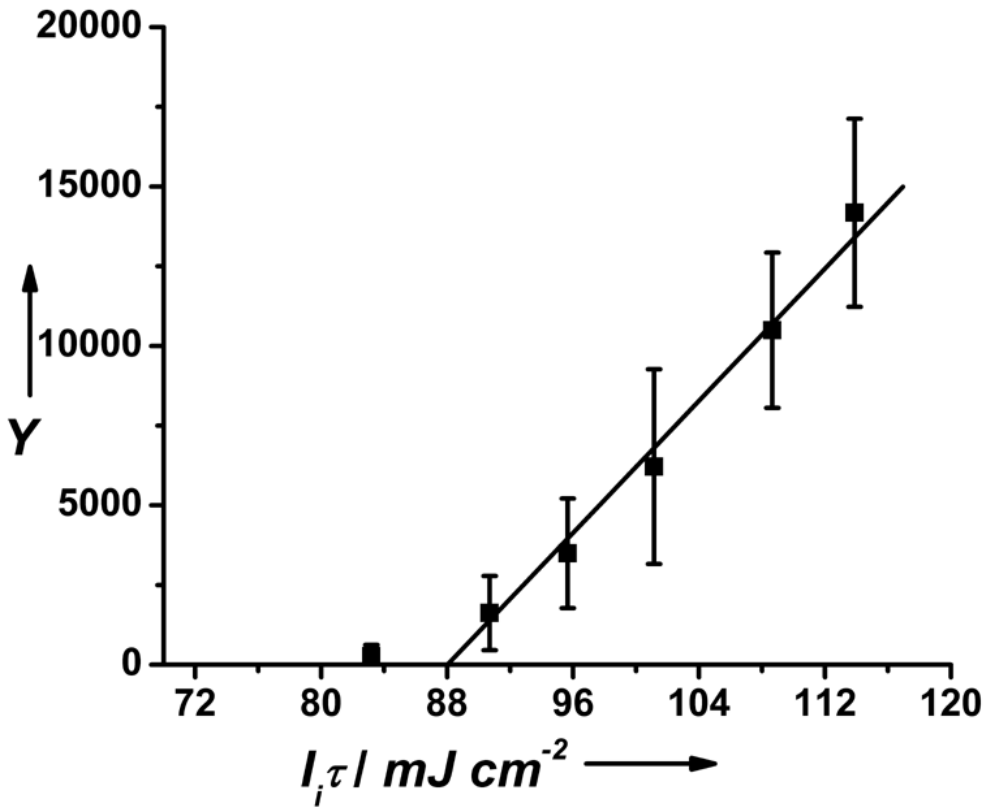

Figure S3: Above a threshold, the ion yield of verapamil shows linear laser intensity, I_i, dependence. For constant angle of incidence and polarization this relationship is analogous to Eq. (1).