Electronic Supplementary Material (ESI) for Analyst.

Supplementary Material

Influence of buried oxide layer of nanostructured SOI surfaces on matrix-free LDI-MS performances.

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Keywords : *nanostructured SOI, metal assisted chemical etching, mass-spectrometry, laser desorption ionization, peptides.*

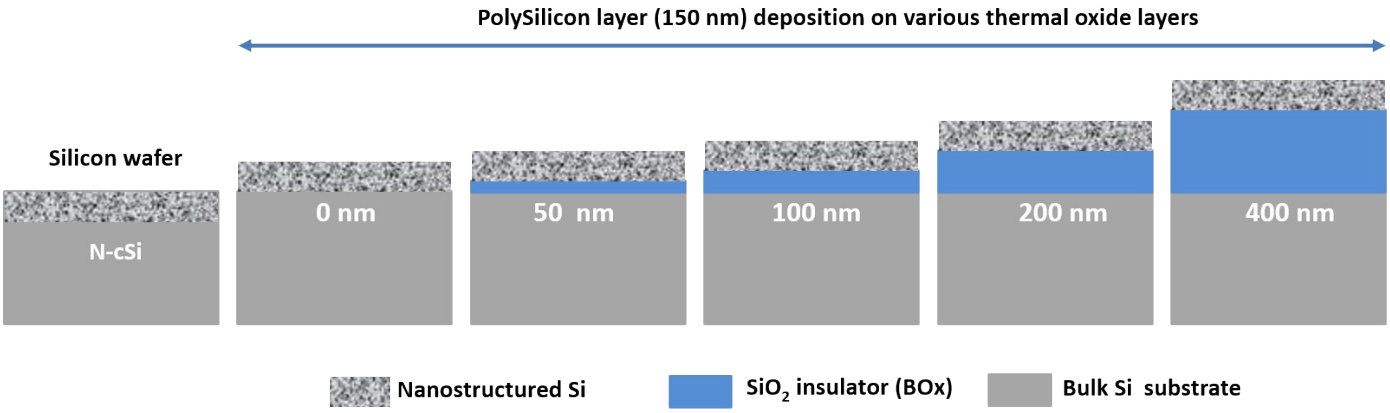


Figure S1: Various silicon substrates used in this study. Crystalline silicon wafer and SOI substrates with PolySi layer thickness of 150 nm deposited on various thermal oxide layers ranging from 0 to 400 nm were submitted to MACE process.

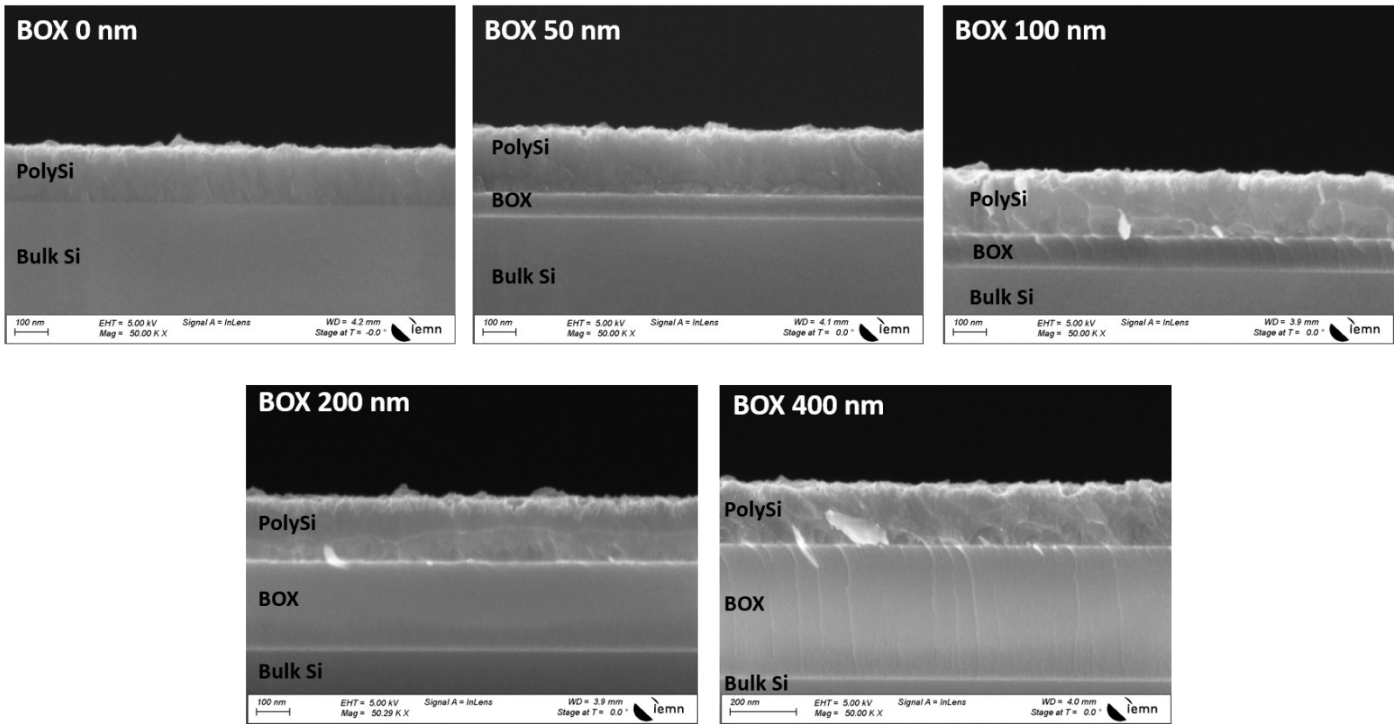


Figure S2: SEM images showing the influence of the etching time on the surface morphologies of SOI substrates.

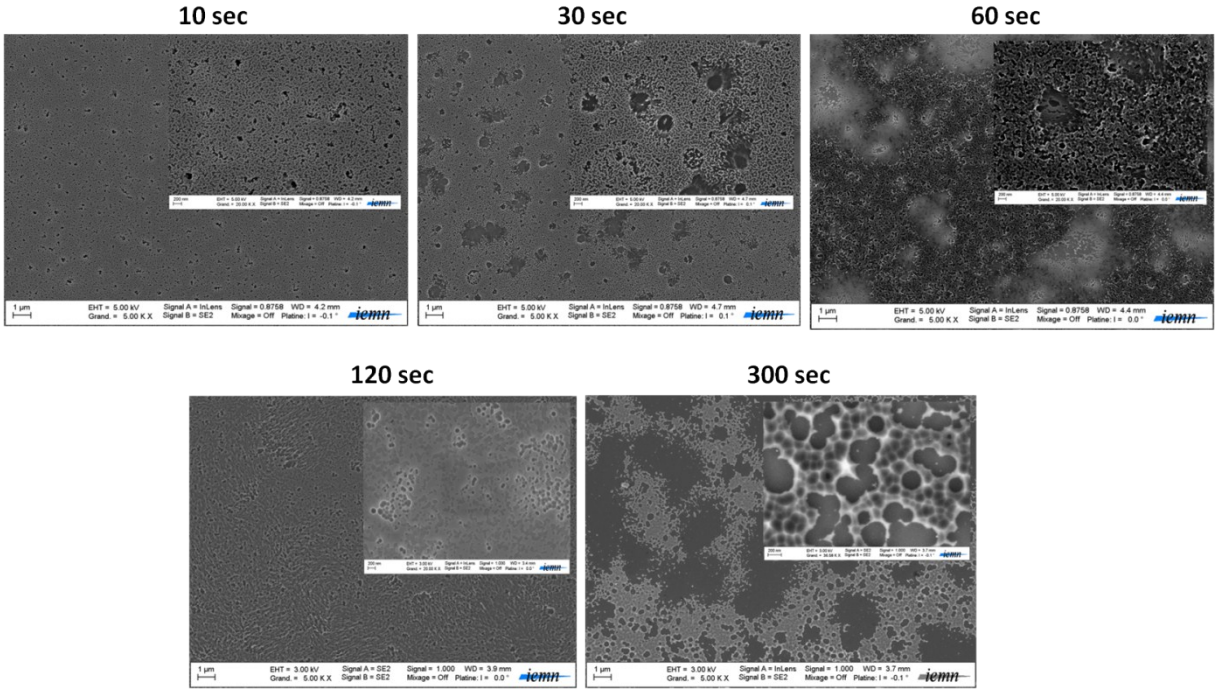


Figure S3: SEM images showing the influence of the etching time on the surface morphologies of SOI substrates.

Nanostructured silicon surface

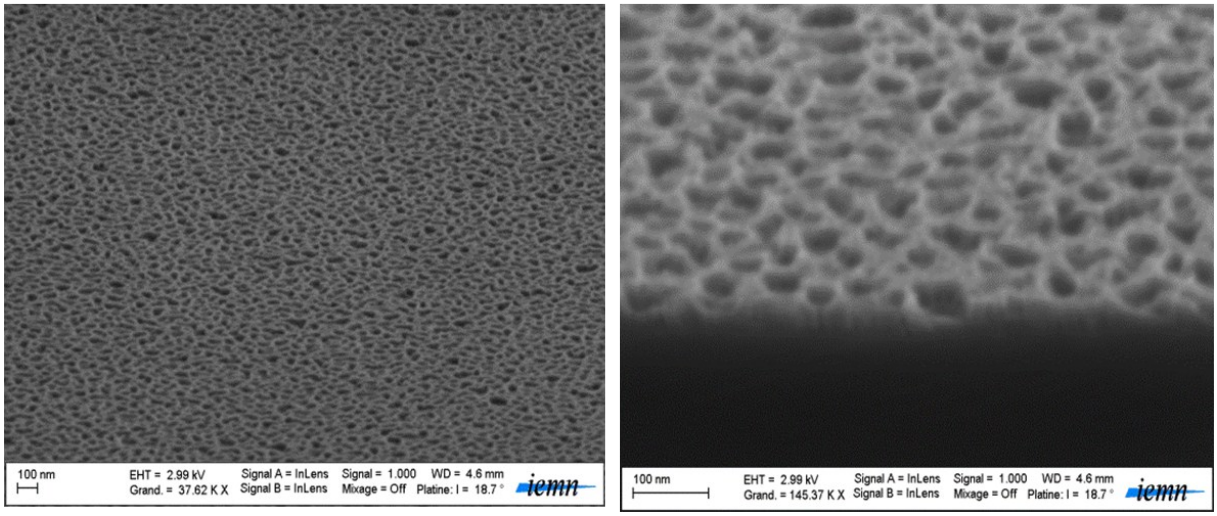


Figure S4: SEM images of crystalline wafer etched *via* MACE process during 10 sec as for SOI substrate.

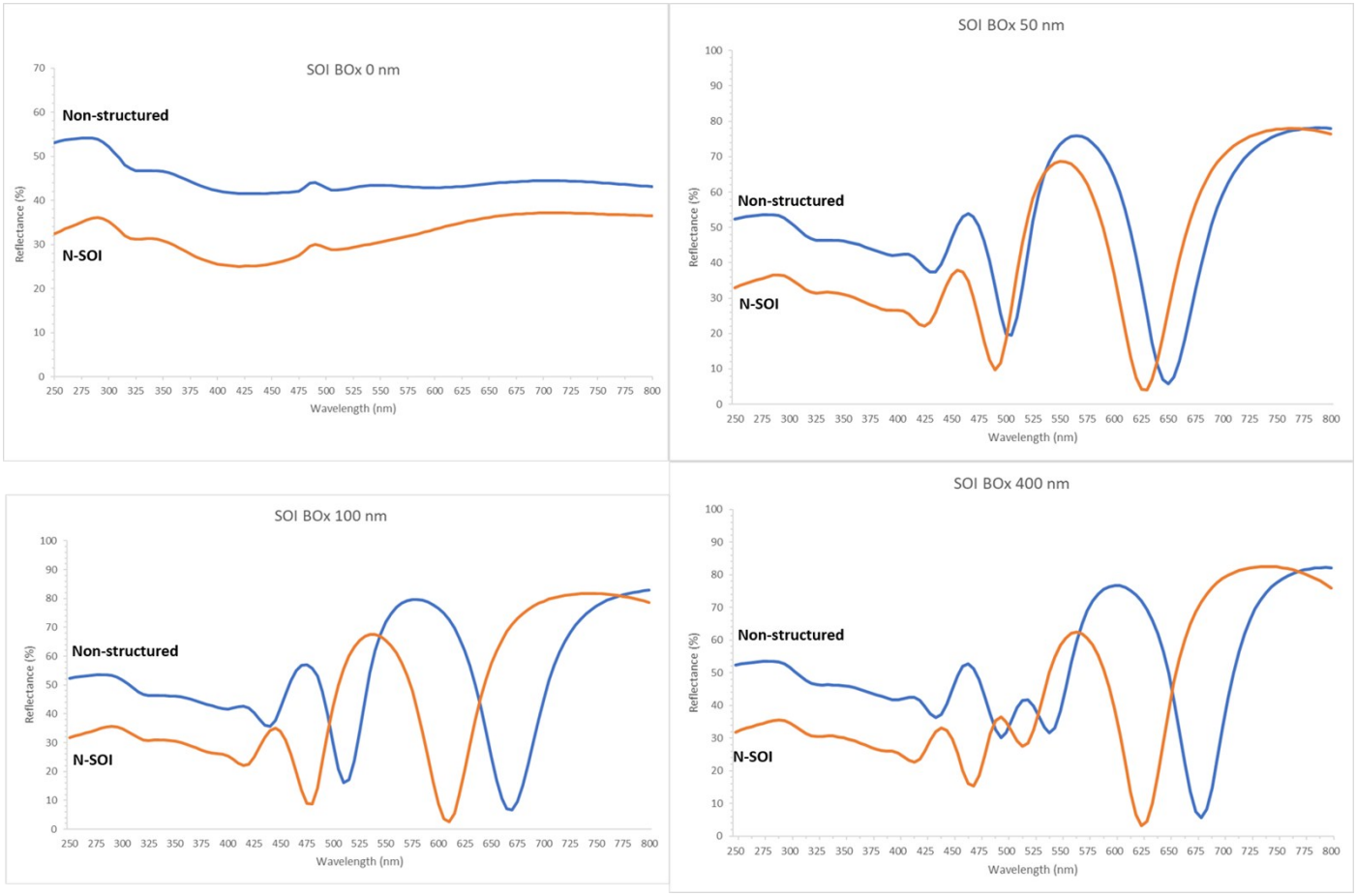


Figure S5: Reflectivity (R%) spectra measurements of the bare SOI and N-SOI (BOx=0, 50, 100 and 400 nm) (etching 10 sec) for wavelengths ranging from 250 to 800 nm.

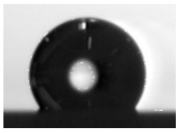
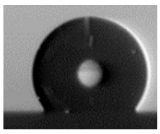
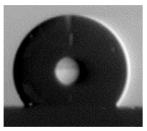
OTS terminated surfaces	Water contact angle (°)	Image of sessile droplet Volume deposited 1µL
SOI ref	108±3	
N-SOI	125±4	
N-cSi	123±4	

Figure S6: Water contact angles on OTS terminated non structured SOI surface and nanostructured SOI and crystalline Si surfaces via MACE process (10 sec etching).

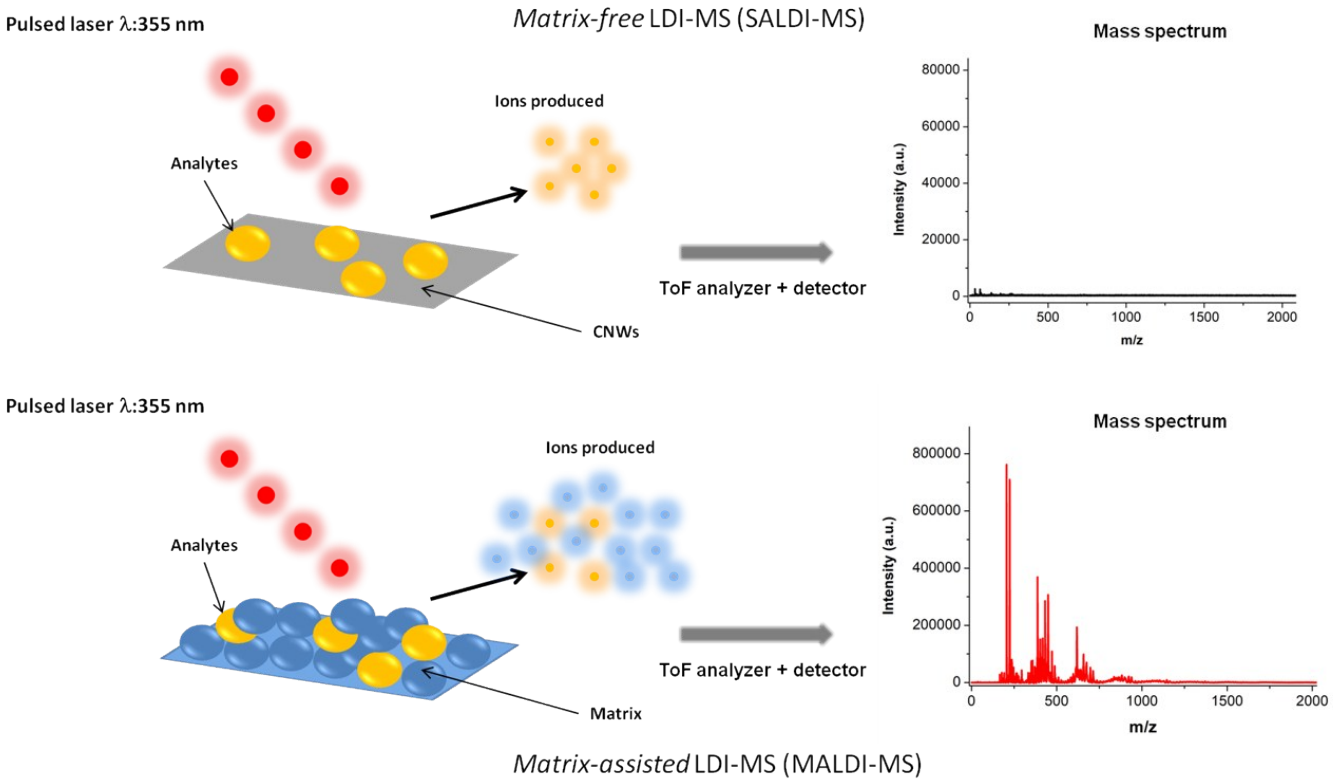


Figure S7: MS spectra obtained from N-SOI (Box 200nm) vs α-cyano-4-hydroxycinnamic acid (CHCA).

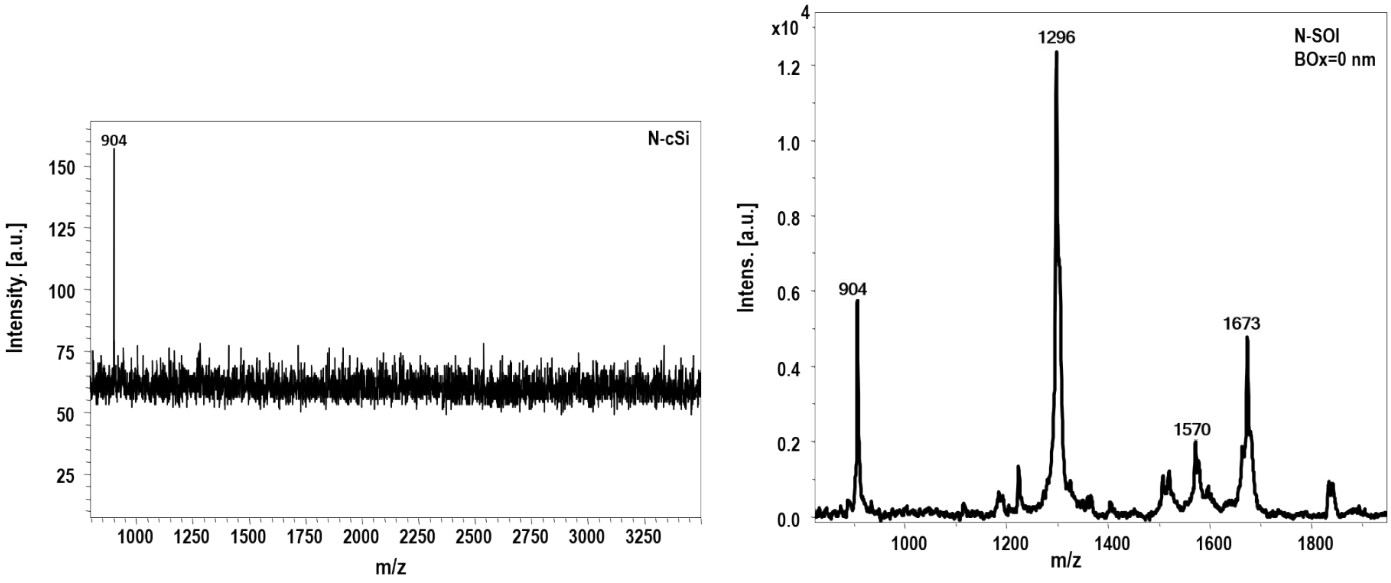


Figure S8: MS spectra obtained from solution containing - Des-Arg[1]-Bradykinin m/z 904; Angiotensin I m/z 1296; Neurotensin m/z 1673 at 50 fmol/µL and Glu[1]-Fibrinopeptide B m/z 1570 at 10 fmol/µL on N-cSi (left) and N-SOI (BOx=0nm) substrate.

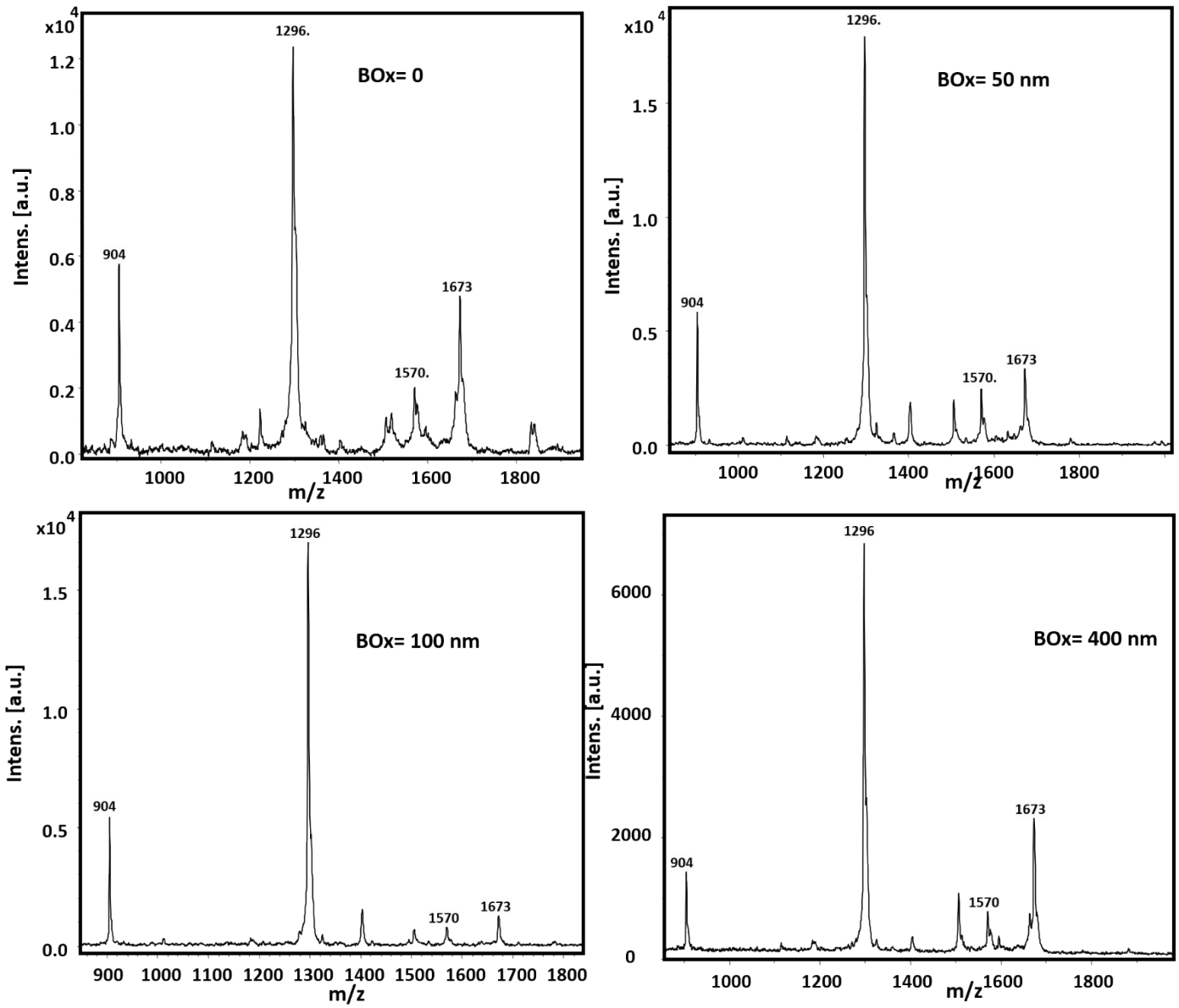


Figure S9: MS spectra obtained from solution containing - Des-Arg[1]-Bradykinin m/z 904; Angiotensin I m/z 1296; Neurotensin m/z 1673 at 50 fmol/µL and Glu[1]-Fibrinopeptide B m/z 1570 at 10 fmol/µL on N-SOI substrate with various Box layers: 0, 50, 100 and 400 nm.

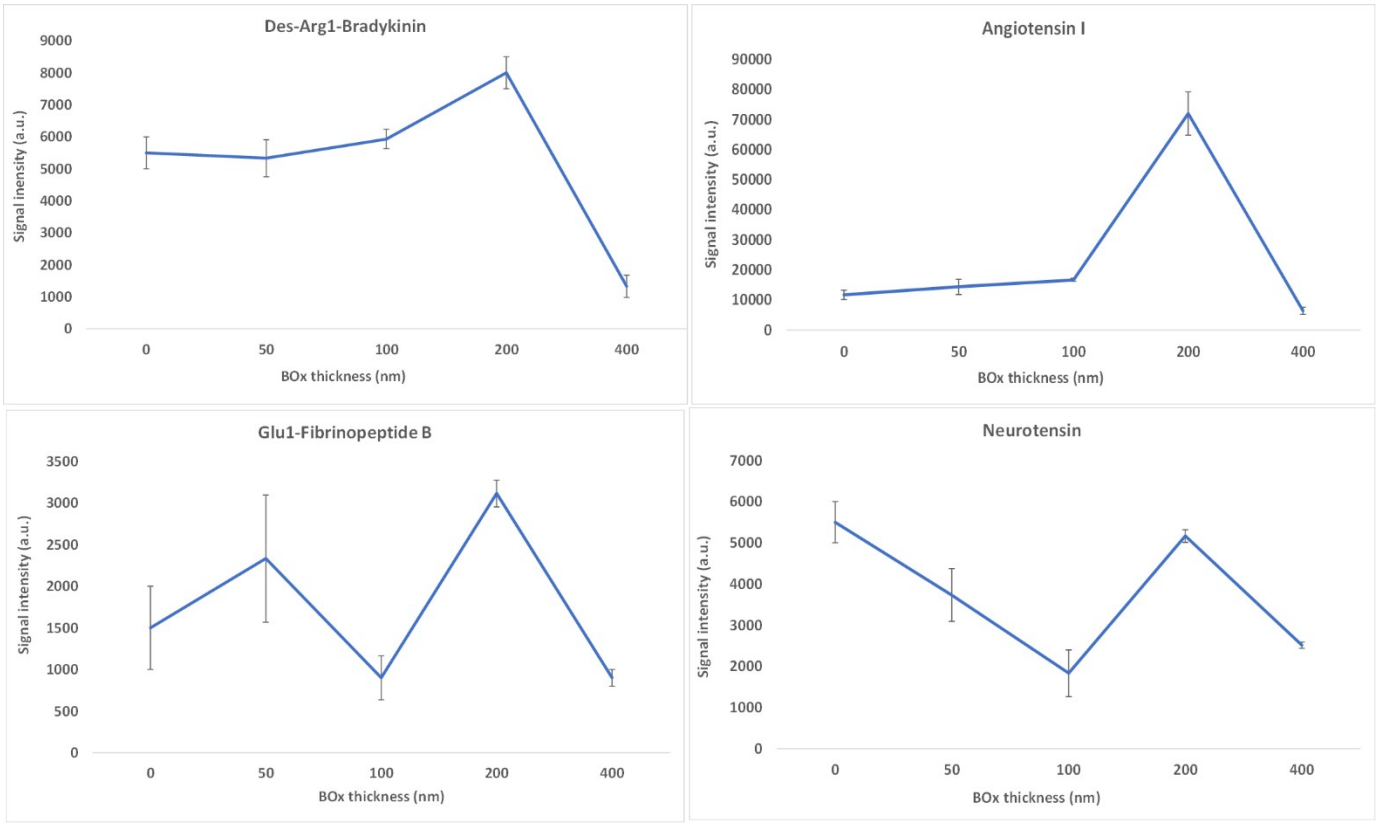


Figure S10: MS signal intensities obtained for peptides solution 1 from N-SOI with different BOx layer thicknesses. Signal variation have been calculated from 3 spots/surface and from 3 different surfaces. Data shown as mean ± SD, n = 6.

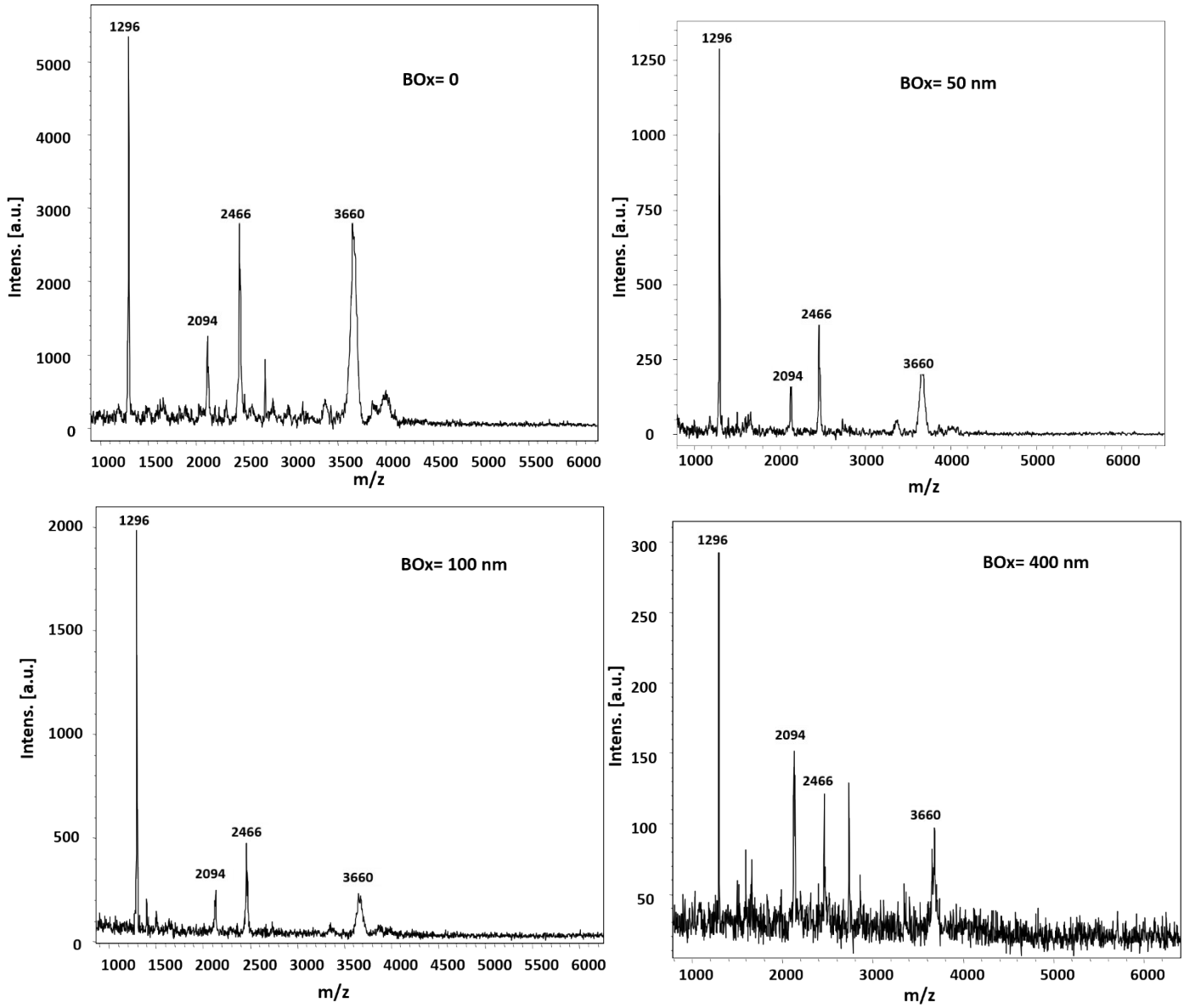


Figure S11: MS spectra obtained from solution containing - Angiotensin I m/z 1296; ACTH (clip 1–17) m/z 2094; ACTH (clip 18–39) m/z 2466; ACTH (clip 7–38) m/z 3660 and Insulin m/z 5734 at 50 fmol/µL on N-SOI substrate with various BOx layers: 0, 50, 100 and 400 nm.

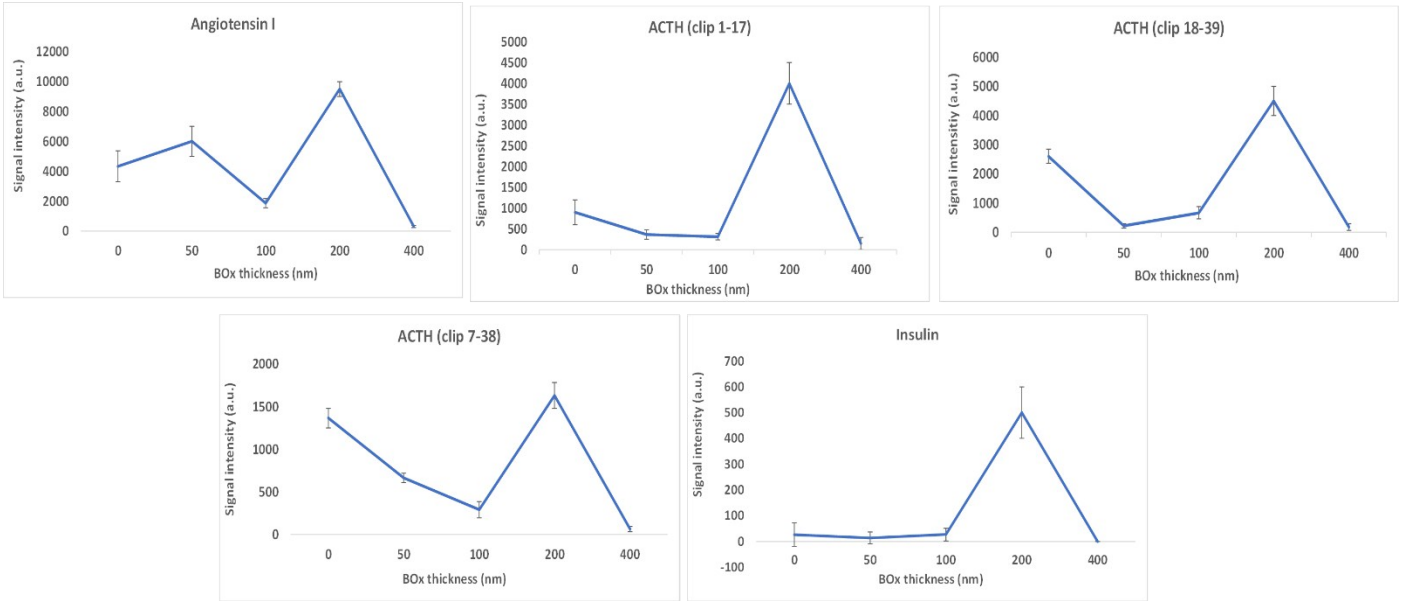


Figure S12: MS signal intensities obtained for peptides solution 2 from N-SOI with different BOx layer thicknesses. Signal variation have been calculated from 3 spots/surface and from 3 different surfaces. Data shown as mean ± SD, n = 6.

Table S1: S/N obtained for peptides solutions 1& 2 from different N-SOI surfaces. Signal variation have been calculated from 3 spots/surface and from 3 different surfaces. Data shown as mean ± SD, n = 6.

Table S1 : Signal to noise ratios obtained from peptides solutions 1 & 2 on different N-SOI surfaces.
Signal variation have been calculated from 3 spots/surface and from 3 different surfaces. Data shown as mean ± SD, n = 6.

Box thickness (nm)	904	1296	1570	1673
0	29 (9%)	64 (13%)	15 (33%)	11 (9%)
50	69 (11%)	122 (17%)	35 (32%)	58 (17%)
100	50 (5%)	172 (3,5%)	10 (29%)	13 (31%)
200	70 (6%)	642 (10%)	20 (5%)	54 (3%)
400	9 (26%)	161 (18%)	3 (11%)	24 (3%)

Box thickness (nm)	1296	2094	2466	3660	5734
0	21 (24%)	12 (33%)	7 (9,5%)	10 (8,5%)	-
50	94 (16,5%)	3 (31%)	7 (35%)	8 (8,5%)	-
100	21 (17%)	3 (24%)	6 (31%)	4 (32%)	-
200	121 (5%)	60 (12,5%)	52 (11%)	27 (9%)	10 (20%)
400	19 (24%)	5 (30%)	5 (62%)	3 (45%)	-

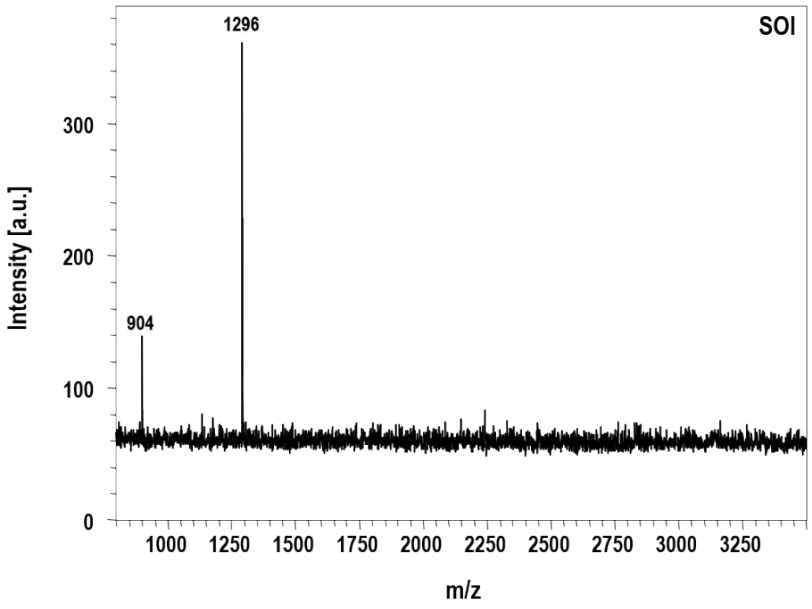


Figure S13: MS spectrum obtained from solution containing - Des-Arg[1]-Bradykinin m/z 904; Angiotensin I m/z 1296; Neurotensin m/z 1673 at 50 fmol/µL and Glu[1]-Fibrinopeptide B m/z 1570 at 10 fmol/µL on SOI (BOx=200 nm) substrate.

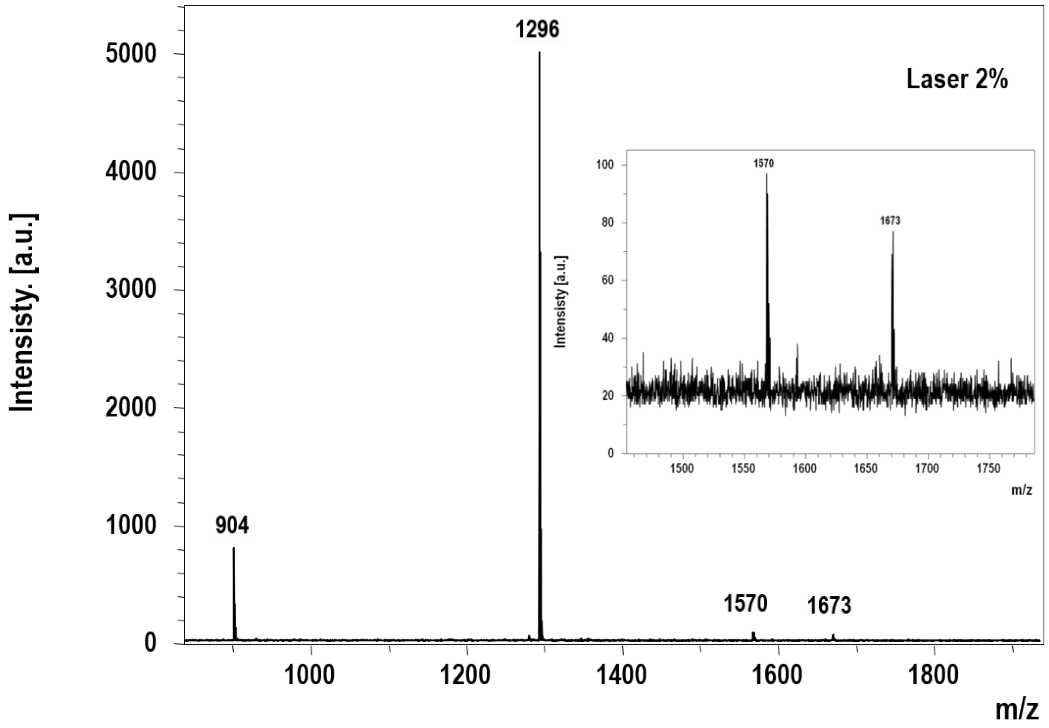


Figure S14: MS spectrum obtained from peptide solution 1 containing - Des-Arg1-Bradykinin m/z 904; Angiotensin I m/z 1296; Neurotensin m/z 1673 at 50 fmol/µL and Glu1-Fibrinopeptide B m/z 1570 at 10 fmol/µL on N-SOI (BOx=200 nm) substrate at low laser fluence.

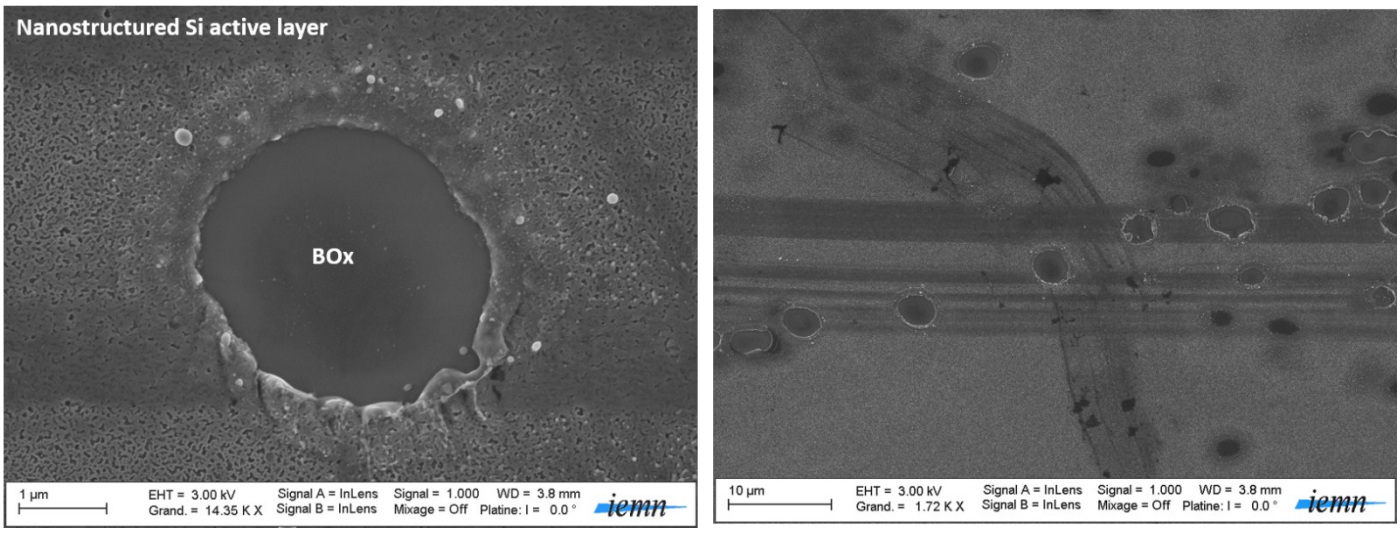


Figure S15: SEM images showing craters after high laser fluence impacts on N-SOI surface.

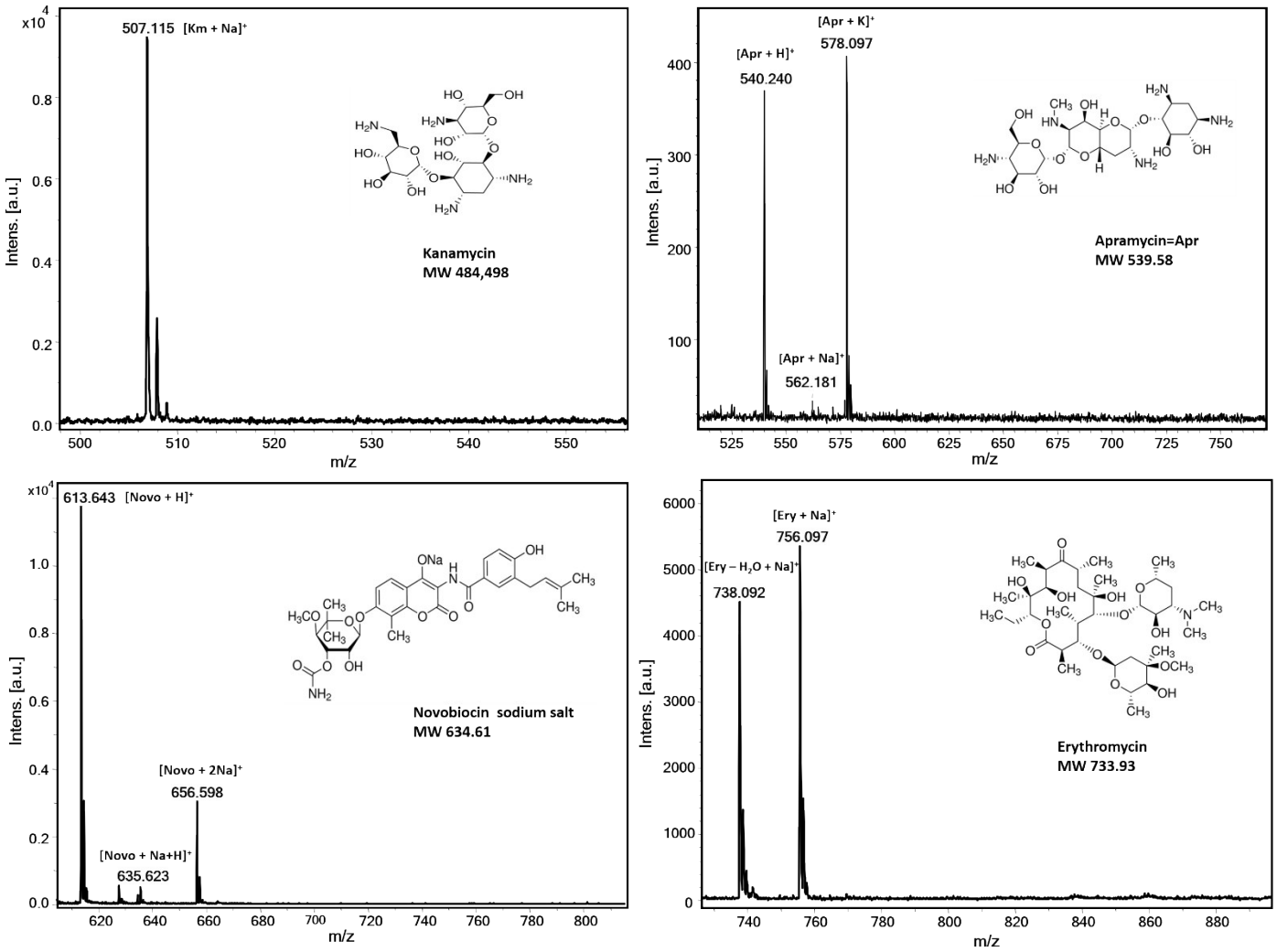


Figure S16: Mass spectra of four antibiotics: Kanamycin, Apramycin, Novobiocin, Erythromycin. The concentration was 100 µg/mL in 10 mM NaCl aqueous solution.

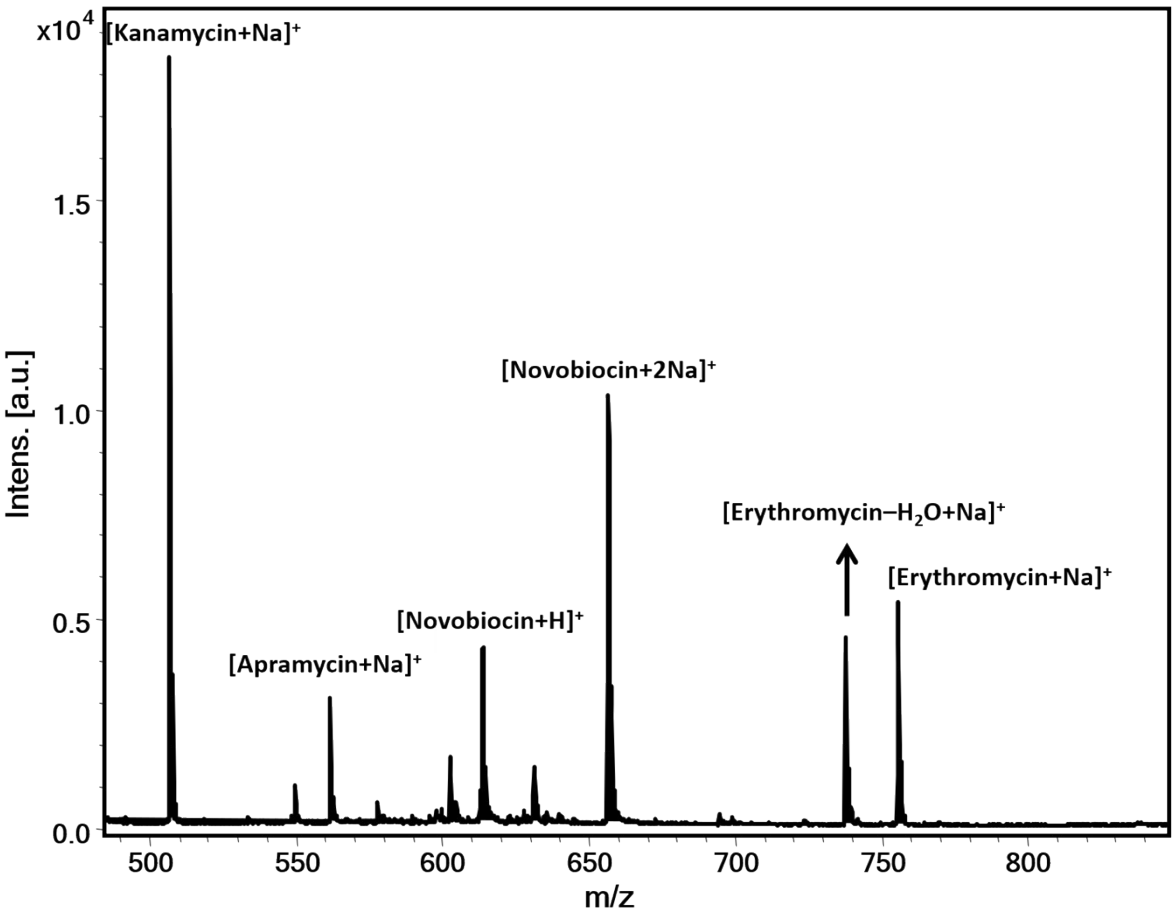


Figure S17: Mass spectrum obtained from the mixture of four antibiotics in positive ion mode. The concentration for each peptide was 100 µg/mL in presence of 10 mM NaCl aqueous solution.

Table S2: S/N obtained from antibiotics solutions peptides solutions on N-SOI surface (Box 200 nm). Signal variation have been calculated from 3 spots/surface and from 3 different surfaces. Data shown as mean ± SD, n = 6.

Table S2 : Signal to noise ratios obtained from antibiotics solution on N-SOI surface (Box 200 nm).
Signal variation have been calculated from 3 spots/surface and from 3 different surfaces. Data shown as mean ± SD, n = 6.

Antibiotics on N-SOI (Box 200 nm)	Cumulated S/N (SD%)	Ion	Detected in mixture
Kanamycin	300 (20%)	$[M+Na]^+$	Yes
Apramycin	80 (30%)	$[M+H]^+$, $[M+Na]^+$, $[M+K]^+$	Yes
Novobiocin	900 (22%)	[M+H]+, $[M+2Na]^+$, $[M+Na+H]^+$	Yes
Erythromycin	250 (20%)	$[M-H_2O+Na]^+$, $[M+Na]^+$	Yes