SUPPORTING INFORMATION

Mechanisms of fluorine-induced separation of mass interference during TOF-SIMS analysis

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Table S1. PVD deposition parameters of Zr, Mo and Ag thin films.

Layer	Power mode	Plasma power [W]	Plasma current [mA]	Deposition time [s]	Base pressure [mbar]	Process pressure [mbar]	Argon flow [sccm]
Zr	DC	73	200	1320	4.7×10^{-7}	5.2×10^{-3}	35
Mo	DC	72	200	1760	9.0×10^{-7}	5.0×10^{-3}	20
Ag	DC	111	200	582	5.3×10^{-7}	5.0×10^{-3}	20

Table S2. PVD deposition parameters of AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr multilayer sample.

Layer		Plasma power [W]	Plasma current [mA]	Deposition time [s]	Base pressure [mbar]	Process pressure [mbar]	Argon flow [sccm]
AgMo	Ag	35	80	701	1.6×10^{-8}	5.0×10^{-3}	35
	Mo	86	250				
ZrMo	Zr	93	250	655	2.7×10^{-7}	5.0×10^{-3}	35
	Mo	74	220				
ZrAg	Zr	94	250	618	2.3×10^{-7}	5.0×10^{-3}	35
	Ag	33	80				
Zr		72	200	1322	2.4×10^{-7}	5.1×10^{-3}	35

Table S3: ALD deposition parameters of AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr multilayer sample. 42 cycles were conducted to obtain 5 nm Al_2O_3 thin films.

Precursor				Substrate temperature [ºC]	Argon flow [sccm]
H_2O		$Al(CH_3)_3$			
Precursor temperature [ºC]	Pulse time [ms]	Precursor temperature [ºC]	Pulse time [ms]		
45	0.05	72	0.05	120	50

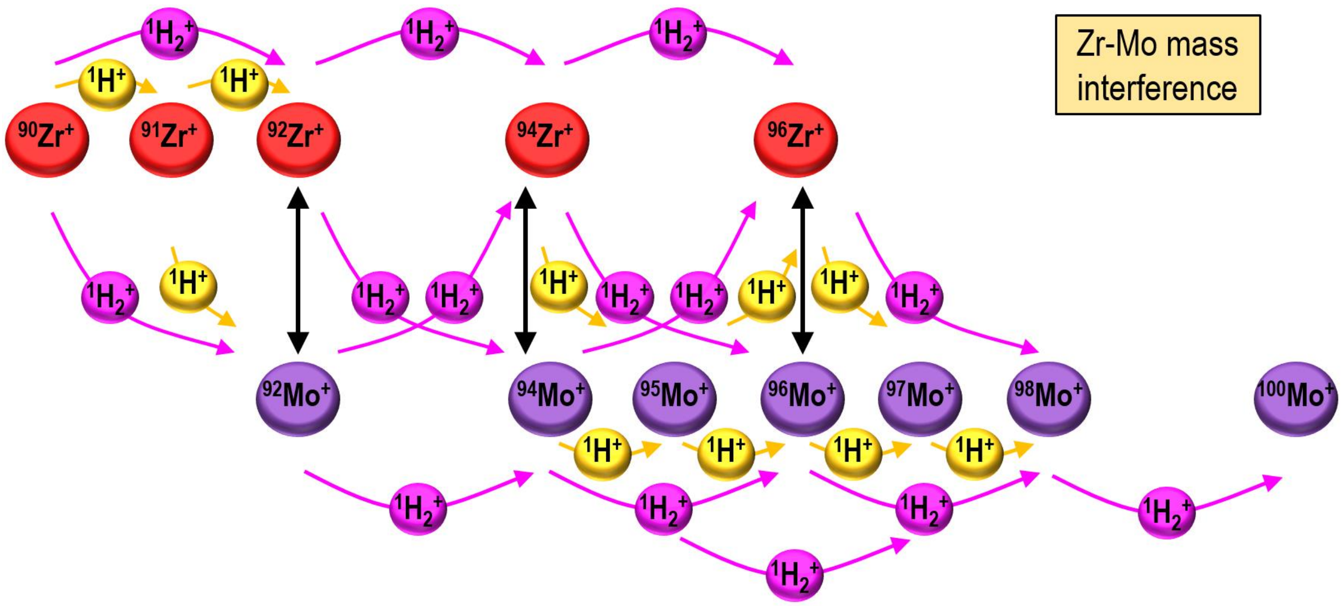

Figure S1. Graphical representation of potential mass interference variants between different metal isotopes (isobaric interference, 1^{st} order mass interference), their hydrides (2^{nd} order mass interference) and dihydrides (3^{rd} order mass interference) in the case of a system containing Zr (given in red) and Mo (given in violet). $^{1}H^{+}$ ions, which contribute to ZrH and MoH ions formation, are shown in yellow. $^{1}H_2^{+}$ ions, which contribute to ZrH_2 and MoH_2 ions formation, are given in pink. The arrows indicate the direction of ions' influence on the signal measured at a given *m/q*. For example, the signal measured at *m/q*= 92, corresponding to $^{92}Zr^{+}$ ions, is a sum of signals coming from $^{92}Zr^{+}$, $^{92}Mo^{+}$, $^{91}Zr^{1}H^{+}$, $^{90}Zr^{1}H_2^{+}$ secondary ions.

Table S4. Natural isotope abundance of Zr, Mo and Ag. Source: TOF-SIMS Explorer version 1.4.4.0 software from TOFWERK.

m/q	90	91	92	94	95	96	97	98	100	107	109
Zr	51.5%	11.2%	17.2%	17.4%		2.8%					
Mo			14.8%	9.2%	15.9%	16.7%	9.6%	24.2%	9.7%		
Ag										51.8%	48.2%

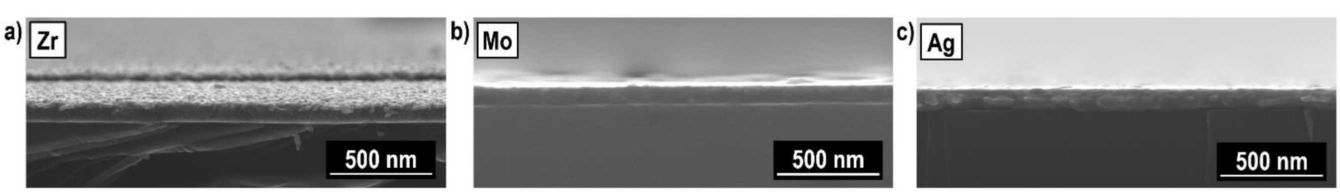

Figure S2. SEM images of mechanically obtained sample cross-sections. The Si substrate is at the bottom. The think film thickness of h_{Zr}=81±3 nm, h_{Mo}=88±4 nm, h_{Ag}=100±2 nm were measured in the case of Zr (a), Mo (b) and Ag (c), respectively.

Table S5. Summary of the thin film thicknesses, *h*, measured on the samples' cross-sections using SEM (Figures S2) and calculated sputtering rates.

Sample	*h* [nm]	Sputtering rate [nm/frame]	
		Without gas	With fluorine gas
Zr	81±3	1.8±0.2	2.8±0.2
Mo	88±4	3.3±0.6	5.9±0.7
Ag	100±2	4.3±0.7	14±3

Table S6: Summary of the results conducted on metal thin films: $t_{interface}$ denotes the time of reaching the interface between the metal thin film and the Si substrate, S_{total} is the total secondary ion signal of a given isotope, the indexes *reference* and *fluorine* refer to the measurements conducted without and with fluorine gas. The given values are the averages of three measurements.

Isotope	Ga beam current [pA]		Moment of reaching the interface [frames]		Total integrated current [counts/pixel/pA]	
	$I_{reference}$	$I_{fluoriene}$	$t_{interface\_reference}$	$t_{interface\_fluorine}$	$S_{total\_reference}$	$S_{total\_fluorine}$
$^{90}Zr^{+}$	117.3	119	46±2	29±1	(4.0±0.2)×10^{-4}	(1.50±0.02)×10^{-3}
$^{98}Mo^{+}$	118	119.3	27±3	15±1	(3.6±0.2)×10^{-5}	(1.61±0.06)×10^{-3}
$^{107}Ag^{+}$	118	119.3	23±3	7±1	(7±2)×10^{-6}	(3.3±0.3)×10^{-3}

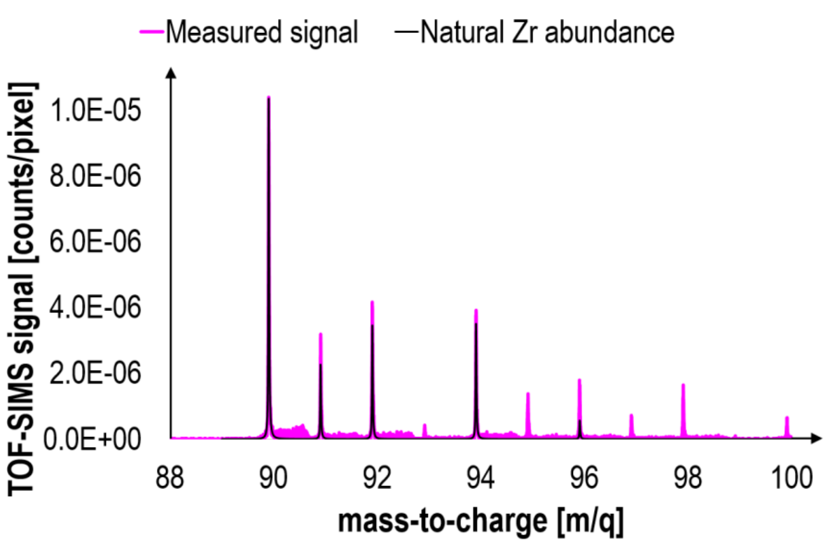

Figure S3. Recognition of mass interference. The measured Zr signal (pink line) in AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr sample is fitted to the Zr natural isotope abundance (black line). The difference between the two lines suggests the contribution of other ions (Mo in this case) to the total measured signal. Data acquired under standard vacuum conditions.

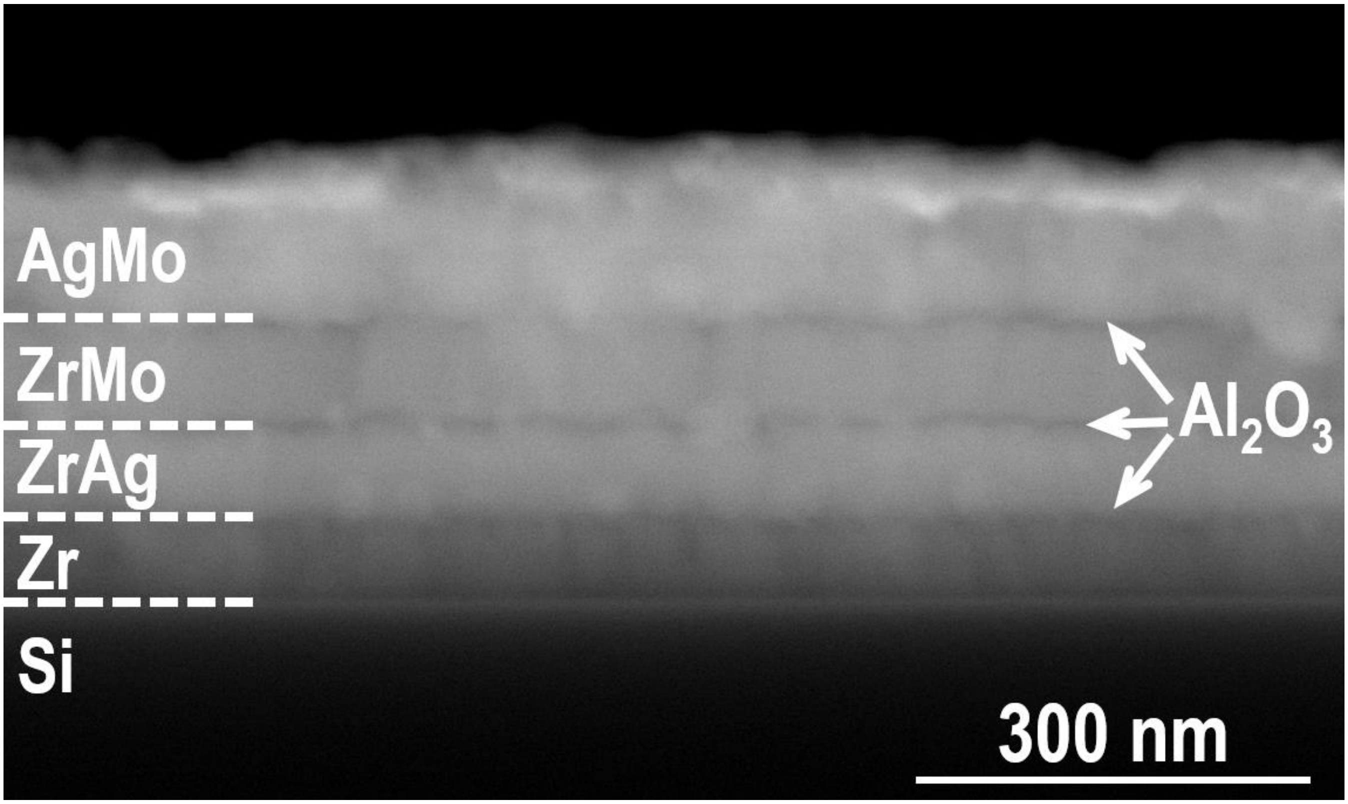

Figure S4. The SEM image of mechanically obtained AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr cross-section. The roughness of the PVD-deposited metallic layers was sufficiently low to prevent potential misinterpretation during further analysis of TOF-SIMS depth profiles. All metallic thin films were well-separated and the layer thicknesses in the order of 100 nm were achieved (i.e. h_{AgMo}=133±9 nm, h_{ZrMo}=77±3 nm, h_{ZrAg}=69±4 nm and h_{Zr}=61±2 nm). The ceramic layers were visible as well but they were too shallow to measure their size.

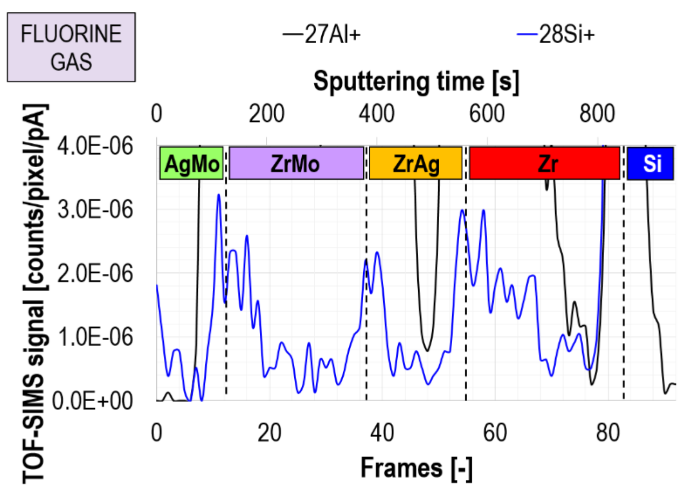

Figure S5. The TOF-SIMS signals depth profiles measured at m/q=27 and m/q=28, corresponding to $^{27}Al^{+}$ and $^{28}Si^{+}$. Data obtained during the fluorine gas-assisted measurement.

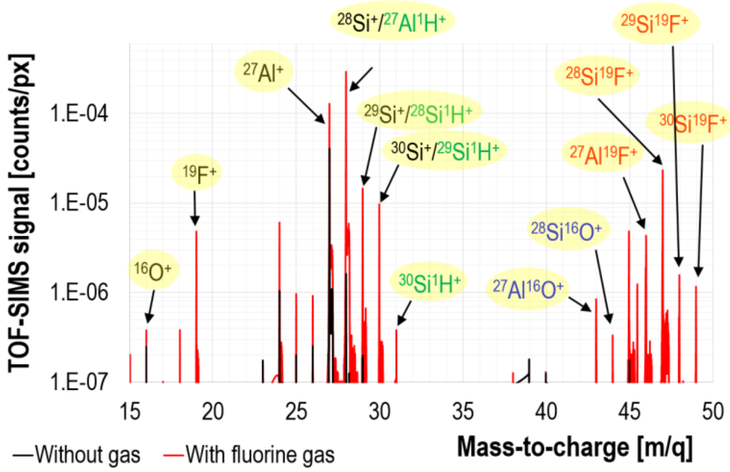

Figure S6. Part of AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr mass spectrum corresponding to Al- and Si-containing ions. Contribution of $^{29}Si^{16}O^+$ and $^{30}Si^{16}O^+$ions to the signals measured at m/q=45 and m/q=46 are negligible due to the low contribution of ^{29}Si and ^{30}Si isotopes to the Si natural isotope abundance (i.e. 92.2% ^{28}Si, 4.7% ^{29}Si, 3.1% ^{30}Si) and relatively low $^{28}Si^{16}O^+$ signal. Note logarithmic scale.

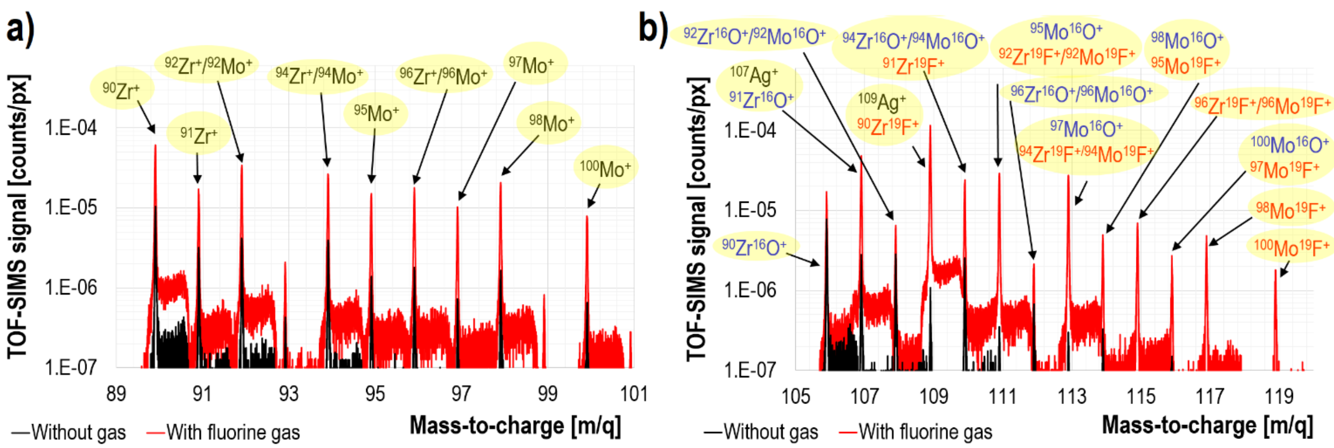

Figure S7. Comparison of mass spectra obtained for AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr under standard vacuum conditions (black lines) and in the presence of fluorine gas (red line). A) a mass spectrum range corresponding to Zr and Mo ions, b) a mass spectrum range corresponding to Ag ions as well as Zr- and Mo- oxides and fluorides.

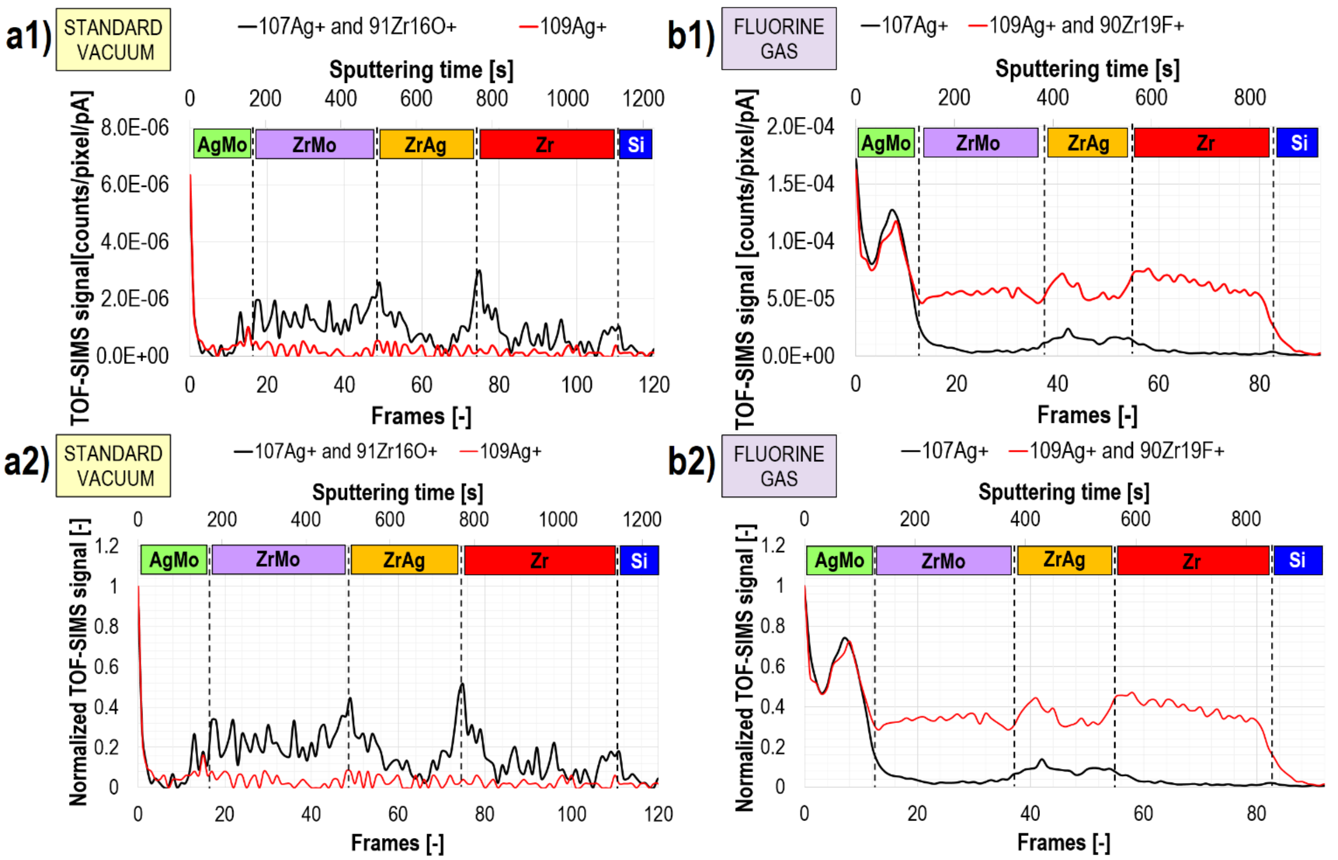

Figure S8. TOF-SIMS depth profiles of signals at m/q=107 and 109, corresponding to $^{107}Ag^{+}$ and $^{109}Ag^{+}$, respectively, measured without (a1 and a2) and with (b1 and b2) fluorine gas. Figures a1 and b2 are given in absolute values, whilst Figures a2 and b2 show values normalized to 1.

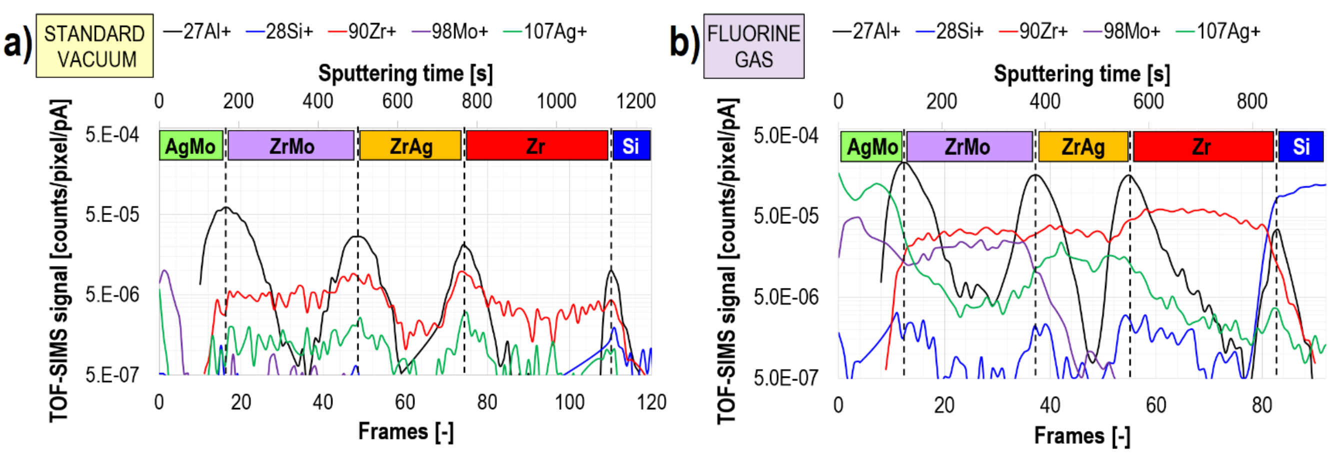

Figure S9. Depth profiles (in logarithmic scale) of $AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr$ multilayer's most prominent isotope signals acquired without (a) and with (b) fluorine gas. Data integration over 5μm×5μm in the x-y plane.

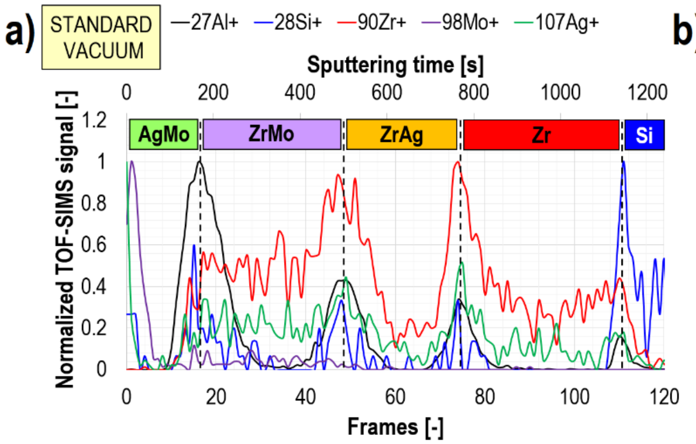

Figure S10. Normalized to 1 depth profiles of AgMo/Al_2O_3/ZrMo/Al_2O_3/ZrAg/Al_2O_3/Zr multilayer's most prominent isotope signals acquired without (a) and with (b) fluorine gas. Data integration over 5μm×5μm in the *x*-*y* plane. Depth profiles with absolute values are given in Figure S9.