

SUPPORTING INFORMATION

High sensitivity of fluorine gas-assisted FIB-TOF-SIMS for chemical characterization of buried sublayers in thin films

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Table S1. PVD deposition parameters of Al₂O₃/Ni/Al₂O₃/Au/Al₂O₃/Cu/Al₂O₃ multilayer sample.

Layer	Power mode	Plasma power [W]	Plasma current [mA]	Deposition time [s]	Base pressure [mbar]	Process pressure [mbar]	Argon flow [sccm]
Cu	DC	90	200	240	8×10^{-7}	5×10^{-3}	15
Au	DC	53	100	360			
Ni	RF	150	N/A	830			

Table S2: ALD deposition parameters of Al₂O₃/Ni/Al₂O₃/Au/Al₂O₃/Cu/Al₂O₃ multilayer sample.

Precursor				Substrate temperature [°C]	Argon flow [sccm]
H ₂ O		Al(CH ₃) ₃			
Precursor temperature [°C]	Pulse time [ms]	Precursor temperature [°C]	Pulse time [ms]		
100	50	100	50	120	50

Table S3. PVD deposition parameters of ZrMoAg/Al₂O₃/Mo/Al₂O₃/Ag/Al₂O₃/Zr multilayer sample.

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	1385	1.8×10^{-7}	5.0×10^{-3}	35		
Ag		104		700	2.3×10^{-7}				
Mo		67		1760	4.7×10^{-7}				
ZrMoAg		94	250	446	2.4×10^{-7}				
Zr		74	220						
Mo		33	80						

Table S4: ALD deposition parameters of ZrMoAg/Al₂O₃/Mo/Al₂O₃/Ag/Al₂O₃/Zr multilayer sample.

Precursor				Substrate temperature [°C]	Argon flow [sccm]
H ₂ O		Al(CH ₃) ₃			
Pulse time [ms]		Pulse time [ms]			
0.05		0.05		90	50

Table S5. PVD deposition parameters of Al/Al₂O₃/.../Al/Al₂O₃/... multilayer sample. The cycle was repeated 11 times.

Layer	Power mode	Plasma power [W]	Plasma current [mA]	Deposition time [s]	Base pressure [mbar]	Process pressure [mbar]	Argon flow [sccm]
Al	DC	131	300	4324	4×10 ⁻⁸	4×10 ⁻³	13

Table S6: ALD deposition parameters of Al/Al₂O₃/.../Al/Al₂O₃/... multilayer sample. One cycle of H₂O+Al(CH₃)₃ provided an Al₂O₃ layer with approximately 1.2 Å thickness meaning that in order to obtain 1 nm thick ALD layer 8 cycles were needed. Therefore, subsequent layers were deposited within 8, 16, ..., 80 cycles to provide layer thicknesses of 1 nm, 2 nm, ..., 10 nm, respectively.

Precursor				Substrate temperature [°C]	Argon flow [sccm]
H ₂ O		Al(CH ₃) ₃			
Precursor temperature [°C]	Pulse time [ms]	Precursor temperature [°C]	Pulse time [ms]		
100	50	100	50	120	50

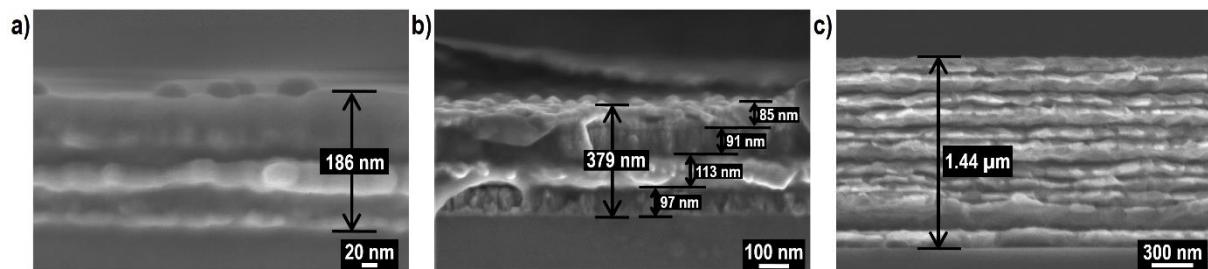


Figure S1. The SEM images of mechanically cleaved cross-sections. Multilayer materials are presented from top to bottom: a) Al₂O₃/Ni/Al₂O₃/Au/Al₂O₃/Cu/Al₂O₃/Si, b) ZrMoAg/Al₂O₃/Mo/Al₂O₃/Ag/Al₂O₃/Zr/Si and c) Al/Al₂O₃/Al/Al₂O₃/.../Al/Si.

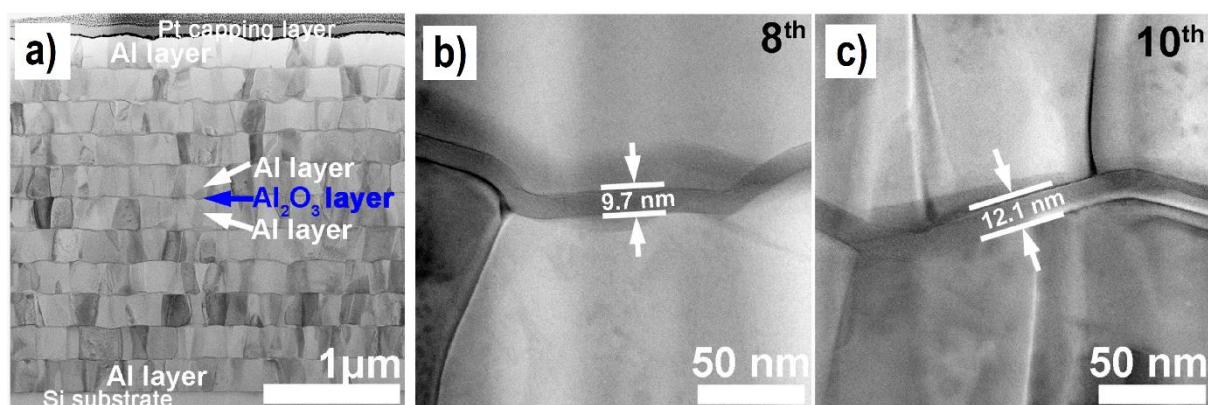


Figure S2. TEM results of Al/Al₂O₃/.../Al/Al₂O₃/.../Al multilayer: a cross-section of TEM lamella (a) and lift-out interfacial images of the 8th (b) and 10th (c) interfaces. Reprinted from *Thin Solid Films*, Vol. 711, Tianle Xie et al, "Synthesis of model Al-Al₂O₃ multilayer systems with monolayer oxide thickness control by circumventing native oxidation", Pages No. 138287, Copyright (2020), with permission from Elsevier.

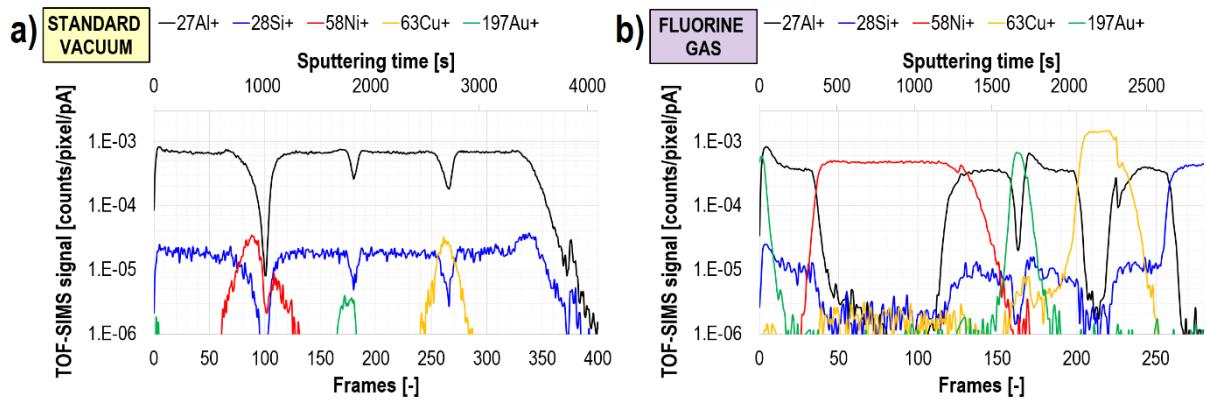


Figure S3. The depth profiles of $\text{Al}_2\text{O}_3/\text{Ni}/\text{Al}_2\text{O}_3/\text{Au}/\text{Al}_2\text{O}_3/\text{Cu}/\text{Al}_2\text{O}_3$ multilayer sample obtained under standard vacuum conditions (a) and during the fluorine gas-assisted TOF-SIMS measurements (b).

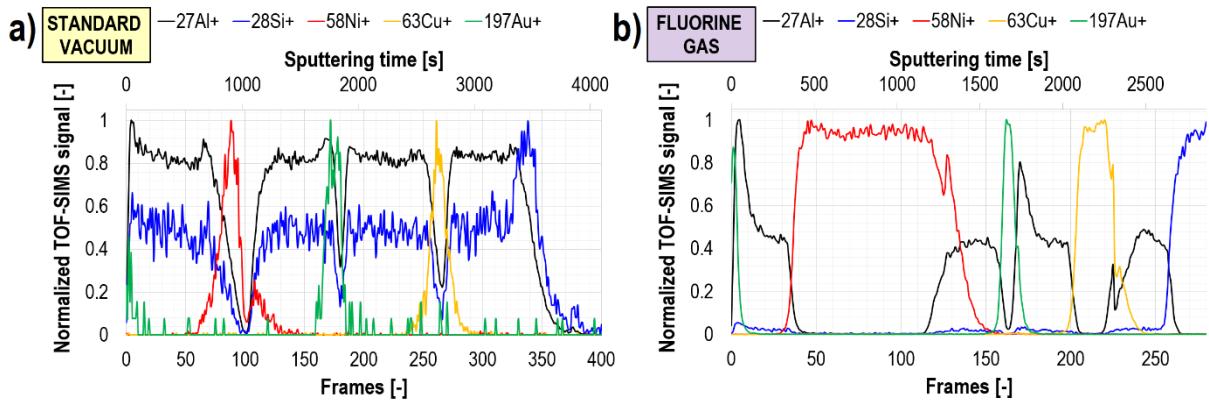


Figure S4. Normalized to 1 TOF-SIMS depth profiles of $\text{Al}_2\text{O}_3/\text{Ni}/\text{Al}_2\text{O}_3/\text{Au}/\text{Al}_2\text{O}_3/\text{Cu}/\text{Al}_2\text{O}_3$ multilayer acquired under standard vacuum conditions (a) and in the presence of fluorine gas.

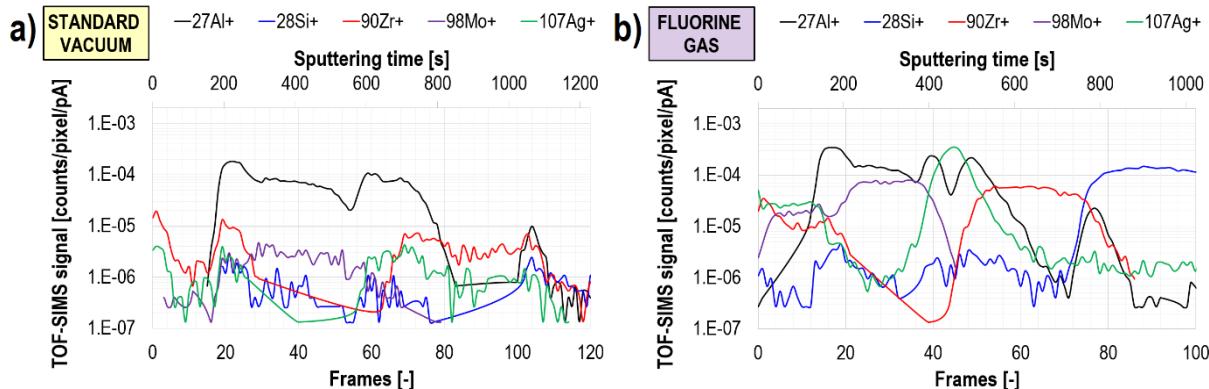


Figure S5. TOF-SIMS depth profiles of the $\text{ZrMoAg}/\text{Al}_2\text{O}_3/\text{Mo}/\text{Al}_2\text{O}_3/\text{Ag}/\text{Al}_2\text{O}_3/\text{Zr}$ multilayer obtained under standard vacuum conditions (a) and with the presence of fluorine gas (b).

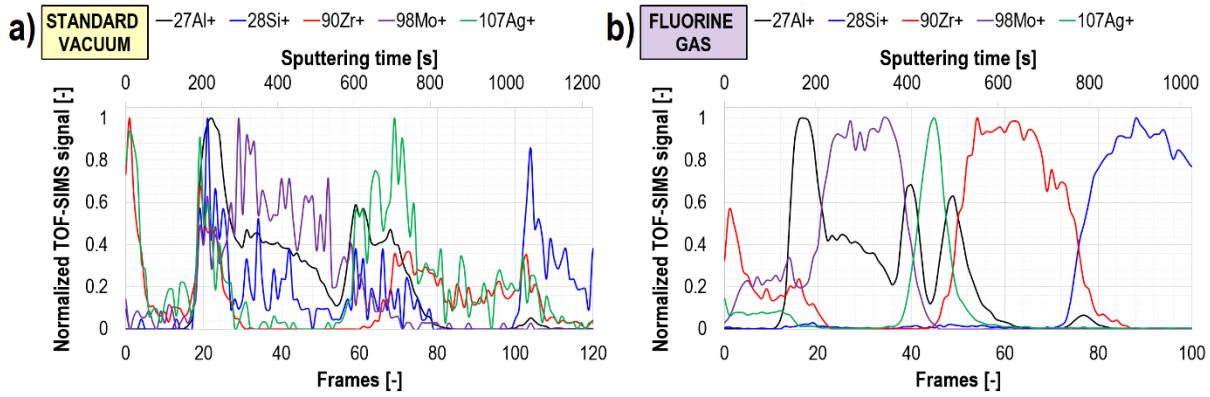


Figure S6. The normalized to 1 TOF-SIMS depth profiles of the ZrMoAg/Al₂O₃/Mo/Al₂O₃/Ag/Al₂O₃/Zr sample. The data were acquired without (a) and with (b) the presence of supplementary gas. The exact signal values are provided in Figure S5.

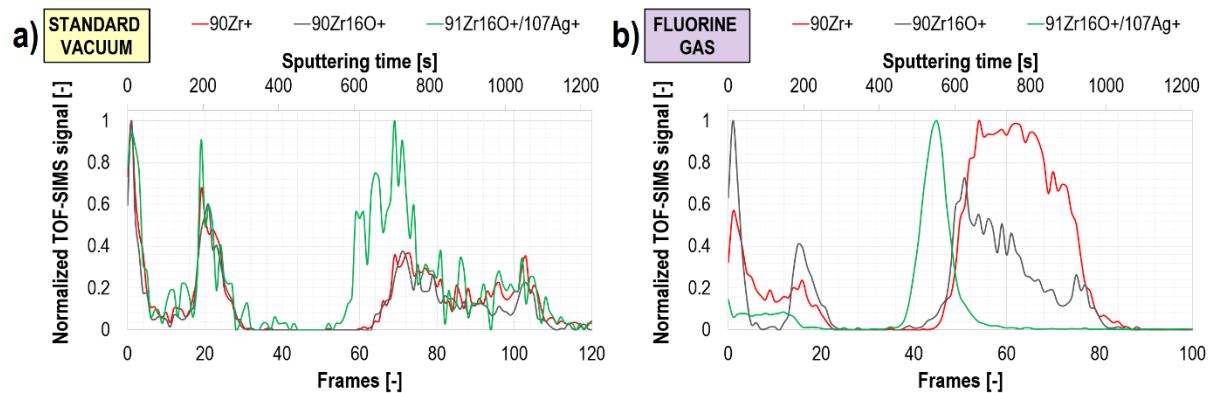


Figure S7. The normalized to 1 TOF-SIMS depth profiles of signals acquired at masses 90, 106 and 107 (corresponding to ${}^{90}\text{Zr}^+$ signal, ${}^{90}\text{Zr}^{16}\text{O}^+$ signal as well as ${}^{91}\text{Zr}^{16}\text{O}^+$ and/or ${}^{107}\text{Ag}^+$ signals): ZrMoAg/Al₂O₃/Mo/Al₂O₃/Ag/Al₂O₃/Zr sample. The data were obtained without (a) and with (b) the presence of supplementary gas.

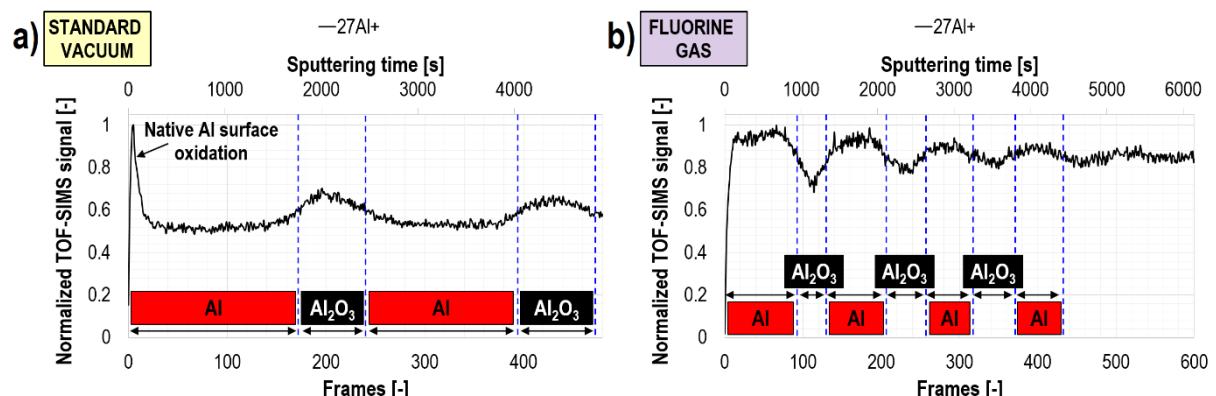


Figure S8. The normalized to 1 depth profile of the ${}^{27}\text{Al}^+$ secondary ion signal measured in Al/Al₂O₃/Al/Al₂O₃/.../Al multilayer. The TOF-SIMS data acquired at standard vacuum conditions (a) and in the presence of fluorine gas (b). The blue dashed lines roughly indicate the location of the interfaces (estimated at a half of ascending/descending signal slopes). The absolute signal values are given in Figure S9.

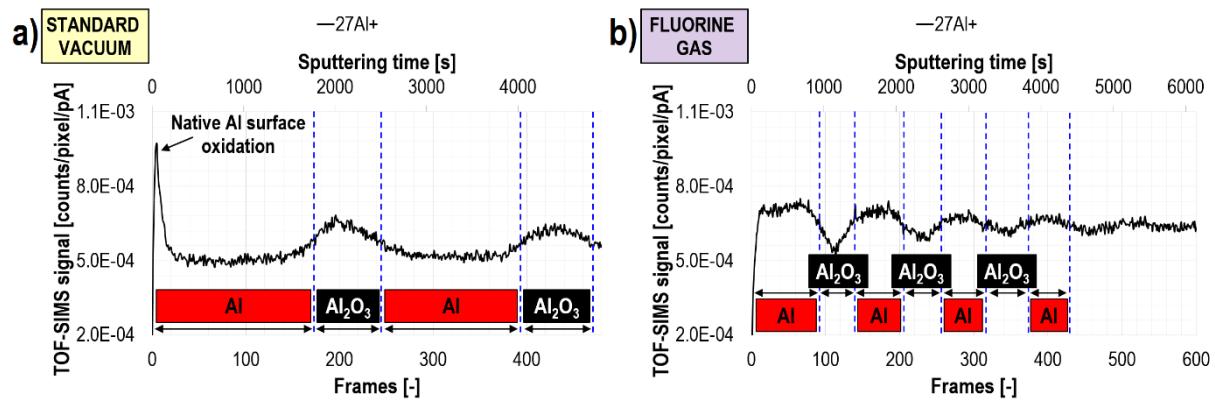


Figure S9. The depth profile of Al/Al₂O₃/.../Al/Al₂O₃/.../Al multilayer sample acquired using TOF-SIMS under standard vacuum conditions (a) and in the presence of fluorine gas (b).