

XPS study in BiFeO₃ surface modified by argon etching

Supplementary information

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1. Adventitious carbon C 1s (AdC)

Figure S1 shows the behavior of C 1s peaks of adventitious carbon with argon etching until 80 s when the film is carbon-free. The table S1 shows the evolution of the peak parameters over-etching time, the data at 80 s are missing because the statistic is too low for quantification.

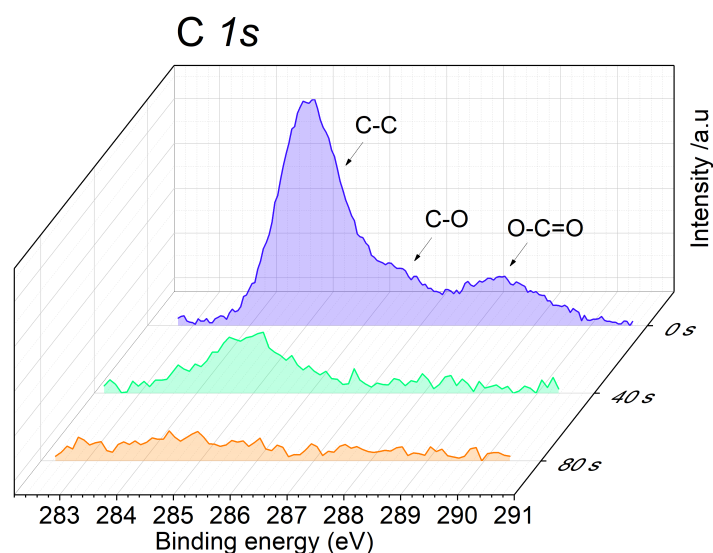


Figure S1. C 1s XPS spectra evolution with Ar⁺ etching time at 0 s, 40 s and 80 seconds.

Table S1. C 1s peaks parameters evolution with Ar⁺ etching time. R.S.F= 1.0

Etching time (s)	C 1s peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area (%)
0	C-C	285.0	1.2	11836.2	65.1
	C-O	286.4	1.2	2342.5	12.9
	O-C=O	288.2	2.1	4003.1	22.0
40	C-C	284.7	1.6	2517.7	65.0
	C-O	286.0	1.7	755.3	19.5
	O-C=O	287.9	1.8	602.9	15.5

2. O 1s core level

Figure S2 shows the evolution of O 1s peaks with argon etching. The table S2 exhibits the development of peak parameters with etching time. The adventitious carbon disappears at 80 s already.

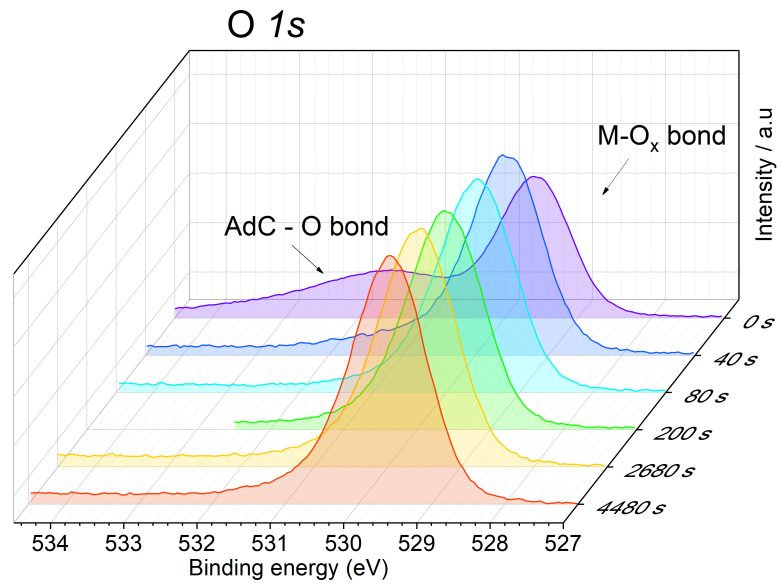


Figure S2. O 1s XPS spectra evolution with Ar⁺ etching time.

Table S2. O 1s peaks parameters evolution with Ar⁺ etching time. R.S.F= 2.93

Etching time (s)	O 1s peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area (%)
0	M-O _x	529.6	1.1	49486.4	56.5
	AdC-O	531.5	2.6	38096.7	43.5
40	M-O _x	529.6	1.2	54689.4	87.8
	AdC-O	530.9	1.6	7609.3	12.2
80	M-O _x	529.5	1.2	89565.3	100
200	M-O _x	529.6	1.2	87284.1	100
2680	M-O _x	529.5	1.2	81339.5	100
4480	M-O _x	529.5	1.2	79750.0	100

3. Bi 5d core level

Figure S3 shows the behaviour of Bi 5d peaks with argon etching and Table S3 summarizes the evolution of the peak parameters. The oxidation state of Bi^{3+} decreases visibly with argon etching time, unlike the bismuth metal $\text{Bi}^{(0)}$, which appears at 40 s.

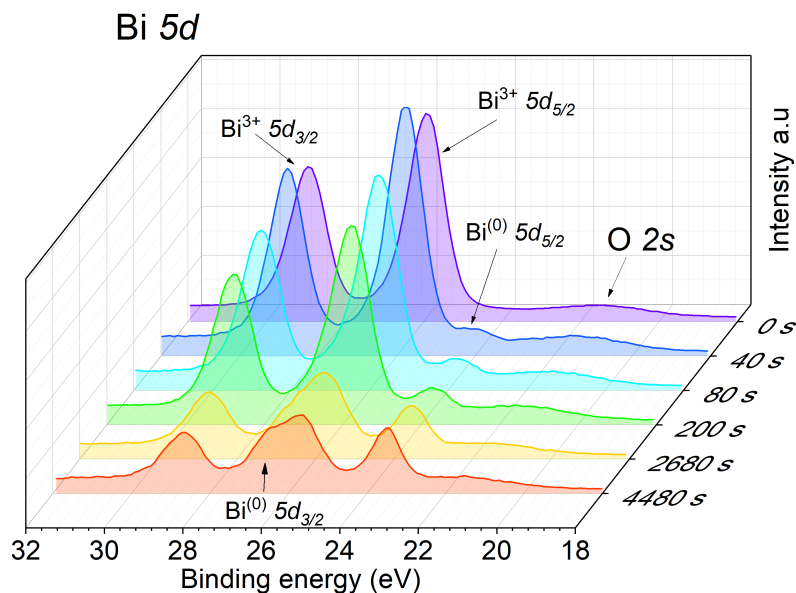


Figure S3. Bi 5d XPS spectra evolution with Ar^+ etching time.

Table S3. Bi 5d peaks parameters evolution with Ar^+ etching time. R.S.F = 3.0

Etching time (s)	Bi 5d peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area (%)
0	$\text{Bi}^{3+} 5d_{5/2}$	25.8	1.1	35580.5	59.9
	$\text{Bi}^{3+} 5d_{3/2}$	28.8	1.1	23838.9	40.1
40	$\text{Bi}^{3+} 5d_{5/2}$	25.8	1.1	28964.2	57.1
	$\text{Bi}^{3+} 5d_{3/2}$	28.8	1.1	19406.0	38.2
	$\text{Bi}^{(0)} 5d_{5/2}$	24.0	1.0	1478.6	2.9
	$\text{Bi}^{(0)} 5d_{3/2}$	27.1	0.9	916.8	1.8
80	$\text{Bi}^{3+} 5d_{5/2}$	25.8	1.1	38155.1	55.5
	$\text{Bi}^{3+} 5d_{3/2}$	28.8	1.1	25182.4	36.6
	$\text{Bi}^{(0)} 5d_{5/2}$	23.7	1.1	3271.2	4.8
	$\text{Bi}^{(0)} 5d_{3/2}$	26.8	0.8	2178.6	3.1
200	$\text{Bi}^{3+} 5d_{5/2}$	25.8	1.1	35562.6	54.0
	$\text{Bi}^{3+} 5d_{3/2}$	28.8	1.1	23826.9	36.2
	$\text{Bi}^{(0)} 5d_{5/2}$	23.7	1.1	3858.4	5.9
	$\text{Bi}^{(0)} 5d_{3/2}$	26.8	0.8	2569.7	3.9

Etching time (s)	Bi 5d peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area (%)
2680	Bi ³⁺ 5d _{5/2}	25.7	1.2	15235.0	38.8
	Bi ³⁺ 5d _{3/2}	28.7	1.2	10207.5	26.0
	Bi ⁽⁰⁾ 5d _{5/2}	23.7	1.0	8271.4	21.1
	Bi ⁽⁰⁾ 5d _{3/2}	26.6	1.1	5508.7	14.1
4480	Bi ³⁺ 5d _{5/2}	25.7	1.2	12576.8	33.4
	Bi ³⁺ 5d _{3/2}	28.7	1.2	8426.5	22.4
	Bi ⁽⁰⁾ 5d _{5/2}	23.5	0.9	10029.5	26.6
	Bi ⁽⁰⁾ 5d _{3/2}	26.6	0.8	6679.7	17.6

4. Bi 4f core level

Figure S4 shows the behavior of Bi 4f peaks with argon etching and the table S4 summarizes the evolution of peak parameters. Bi³⁺ oxidation state is visible decreasing with argon etching time as opposed to bismuth metallic, Bi⁽⁰⁾, that appears at 40 s.

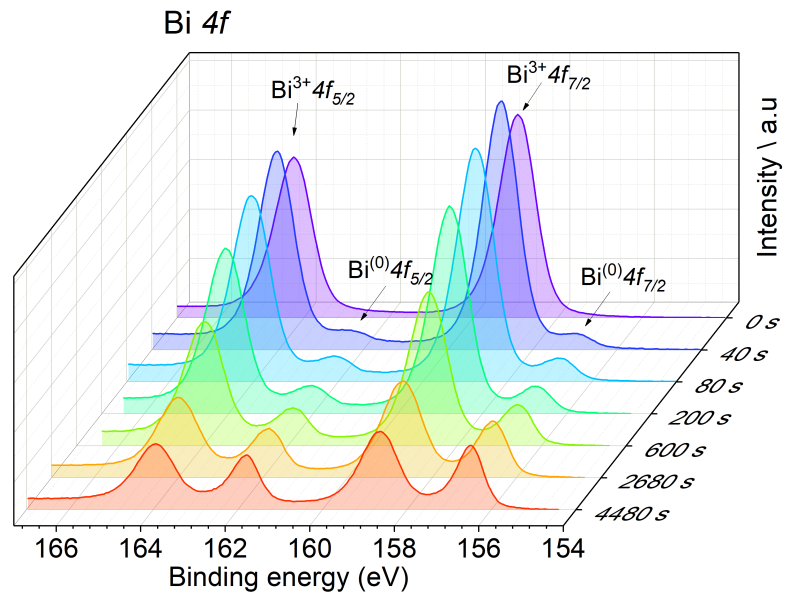


Figure S4. Evolution of Bi 4f doublet peak with Ar⁺ etching time. The metallic bismuth doublet peak appears as a function of etching time, indicating a progressive increase in oxygen loss in the BFO surface.

Table S4. Bi 4*f* peaks parameters evolution with Ar⁺ etching time. R.S.F = 24.8

Etching time (s)	Bi 4 <i>f</i> peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area relative(%)
0	Bi ³⁺ 4 <i>f</i> _{7/2}	158.7	1.0	184552.6	56.6
	Bi ³⁺ 4 <i>f</i> _{5/2}	164.2	1.0	141551.7	43.4
40	Bi ³⁺ 4 <i>f</i> _{7/2}	158.7	1.0	153674.5	53.6
	Bi ³⁺ 4 <i>f</i> _{5/2}	164.0	1.0	115255.8	40.2
	Bi ⁽⁰⁾ 4 <i>f</i> _{7/2}	157.0	1.1	9971.6	3.5
	Bi ⁽⁰⁾ 4 <i>f</i> _{5/2}	162.3	1.1	7777.8	2.7
80	Bi ³⁺ 4 <i>f</i> _{7/2}	158.7	1.0	212134.4	52.1
	Bi ³⁺ 4 <i>f</i> _{5/2}	164.0	1.0	159100.8	39.1
	Bi ⁽⁰⁾ 4 <i>f</i> _{7/2}	156.8	0.9	20059.2	4.9
	Bi ⁽⁰⁾ 4 <i>f</i> _{5/2}	162.1	1.0	15646.2	3.9
200	Bi ³⁺ 4 <i>f</i> _{7/2}	158.8	1.0	194516.5	51.7
	Bi ³⁺ 4 <i>f</i> _{5/2}	164.1	1.0	145887.4	38.8
	Bi ⁽⁰⁾ 4 <i>f</i> _{7/2}	156.7	0.9	20251.7	5.4
	Bi ⁽⁰⁾ 4 <i>f</i> _{5/2}	162.0	0.9	15796.3	4.1
600	Bi ³⁺ 4 <i>f</i> _{7/2}	158.7	1.1	151455.5	47.2
	Bi ³⁺ 4 <i>f</i> _{5/2}	164.0	1.1	113591.6	35.4
	Bi ⁽⁰⁾ 4 <i>f</i> _{7/2}	156.6	0.8	31331.1	9.8
	Bi ⁽⁰⁾ 4 <i>f</i> _{5/2}	161.7	0.9	24438.3	7.6
2680	Bi ³⁺ 4 <i>f</i> _{7/2}	158.7	1.1	81766.5	38.5
	Bi ³⁺ 4 <i>f</i> _{5/2}	164.0	1.1	61324.8	28.9
	Bi ⁽⁰⁾ 4 <i>f</i> _{7/2}	156.5	0.8	39337.0	18.5
	Bi ⁽⁰⁾ 4 <i>f</i> _{5/2}	161.8	0.9	29896.2	14.1
4480	Bi ³⁺ 4 <i>f</i> _{7/2}	158.6	1.1	67157.1	35.2
	Bi ³⁺ 4 <i>f</i> _{5/2}	163.9	1.1	50703.6	26.6
	Bi ⁽⁰⁾ 4 <i>f</i> _{7/2}	156.5	0.8	41866.2	21.9
	Bi ⁽⁰⁾ 4 <i>f</i> _{5/2}	161.8	0.8	31232.2	16.3

5. Fe 2p core level

Figure S5 shows the behavior of Fe 2p peaks with argon etching and the table S5 summarizes the evolution of peak parameters. A deconvolution model describes the presence of Fe^{2+} in the film and the appearance of metallic $\text{Fe}^{(0)}$ certainly at 40 s.

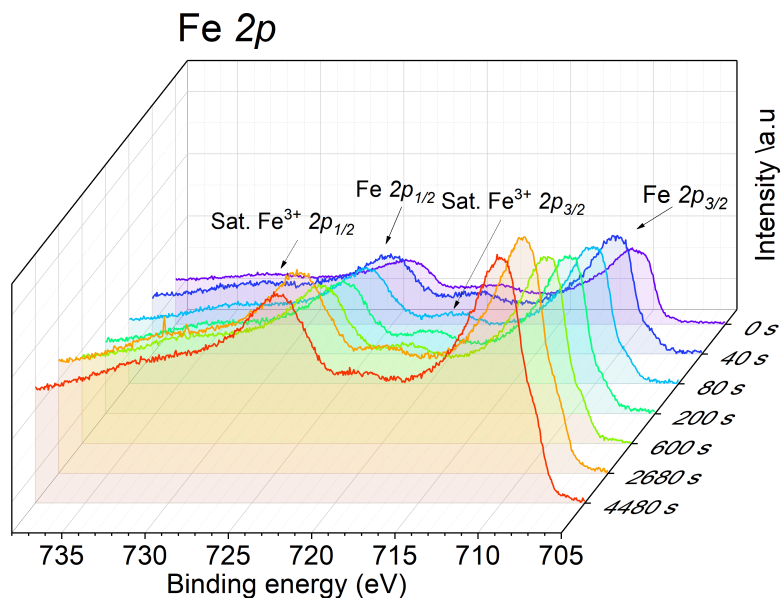


Figure S5. Fe 2p evolution with Ar^+ etching time.

Table S5. Fe 2p peaks parameters evolution with Ar^+ etching time. R.S.F= 16.4

Etching time (s)	Fe 2p peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area (%)
0	$\text{Fe}^{2+} 2p_{3/2}$	709.6	1.1	8470.3	8.4
	$\text{Fe}^{2+} 2p_{1/2}$	723.1	1.8	4658.7	4.5
	$\text{Fe}_{\text{Sat.}}^{2+} 2p_{3/2}$	713.9	2.5	2541.1	2.5
	$\text{Fe}_{\text{Sat.}}^{2+} 2p_{1/2}$	727.8	2.9	1164.7	1.2
	$\text{Fe}_{\text{Sat.}}^{3+} 2p_{3/2}$	718.6	3.7	10896.2	10.7
	$\text{Fe}_{\text{Sat.}}^{3+} 2p_{1/2}$	731.6	3.9	5992.9	6.0
	$\text{Fe}^{3+} 2p_{3/2}$	710.1	2.5	43584.7	43.0
	$\text{Fe}^{3+} 2p_{1/2}$	723.6	3.3	23971.6	23.7

Etching time (s)	Fe 2p peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area (%)
40	Fe ⁽⁰⁾ 2p _{3/2}	707.9	1.1	1333.8	0.9
	Fe ⁽⁰⁾ 2p _{1/2}	720.9	1.2	746.9	0.5
	Fe ²⁺ 2p _{3/2}	709.6	1.4	12815.2	8.4
	Fe ²⁺ 2p _{1/2}	723.1	2.2	7176.5	4.7
	Fe ²⁺ _{Sat.} 2p _{3/2}	714.1	2.7	4869.8	3.2
	Fe ²⁺ _{Sat.} 2p _{1/2}	727.8	3.0	2434.9	1.6
	Fe ³⁺ 2p _{3/2}	709.9	3.3	56392.8	36.8
	Fe ³⁺ 2p _{1/2}	723.4	3.8	31579.9	20.7
	Fe ³⁺ _{Sat.} 2p _{3/2}	718.4	4.7	21429.3	14.0
	Fe ³⁺ _{Sat.} 2p _{1/2}	730.9	5.9	14098.2	9.2
80	Fe ⁽⁰⁾ 2p _{3/2}	707.9	0.9	1402.9	0.5
	Fe ⁽⁰⁾ 2p _{1/2}	720.9	1.2	785.9	0.3
	Fe ²⁺ 2p _{3/2}	709.6	1.6	28696.5	11.0
	Fe ²⁺ 2p _{1/2}	723.1	2.8	16357.0	6.3
	Fe ²⁺ _{Sat.} 2p _{3/2}	714.4	3.7	10904.7	4.2
	Fe ²⁺ _{Sat.} 2p _{1/2}	727.8	3.9	5739.3	2.2
	Fe ³⁺ 2p _{3/2}	710.0	3.6	91355.5	34.9
	Fe ³⁺ 2p _{1/2}	724.0	3.9	51159.1	19.6
	Fe ³⁺ _{Sat.} 2p _{3/2}	718.4	4.2	34715.1	13.3
	Fe ³⁺ _{Sat.} 2p _{1/2}	730.8	5.4	20098.2	7.7
200	Fe ⁽⁰⁾ 2p _{3/2}	707.9	0.9	2205.3	0.8
	Fe ⁽⁰⁾ 2p _{1/2}	720.9	1.2	1234.9	0.4
	Fe ²⁺ 2p _{3/2}	709.6	1.7	33483.3	11.4
	Fe ²⁺ 2p _{1/2}	723.1	2.8	18750.6	6.4
	Fe ²⁺ _{Sat.} 2p _{3/2}	714.4	3.4	12723.6	4.3
	Fe ²⁺ _{Sat.} 2p _{1/2}	727.6	3.6	6361.8	2.2
	Fe ³⁺ 2p _{3/2}	710.0	3.6	100283.6	34.0
	Fe ³⁺ 2p _{1/2}	723.5	3.9	56158.8	19.1
	Fe ³⁺ _{Sat.} 2p _{3/2}	718.4	4.2	38107.7	12.9
	Fe ³⁺ _{Sat.} 2p _{1/2}	731.0	6.0	25070.9	8.5
600	Fe ⁽⁰⁾ 2p _{3/2}	707.8	1.1	4314.2	1.2
	Fe ⁽⁰⁾ 2p _{1/2}	720.9	1.2	2416.0	0.6
	Fe ²⁺ 2p _{3/2}	709.5	1.8	40189.5	11.0
	Fe ²⁺ 2p _{1/2}	722.9	2.9	22506.1	6.2
	Fe ²⁺ _{Sat.} 2p _{3/2}	714.3	4.6	15272.0	4.2
	Fe ²⁺ _{Sat.} 2p _{1/2}	727.5	3.4	7636.0	2.1
	Fe ³⁺ 2p _{3/2}	709.8	3.4	124271.7	34.1
	Fe ³⁺ 2p _{1/2}	723.3	4.2	69592.1	19.2
	Fe ³⁺ _{Sat.} 2p _{3/2}	718.2	4.1	47223.2	13.0
	Fe ³⁺ _{Sat.} 2p _{1/2}	730.9	6.0	29825.2	8.4

Etching time (s)	Fe 2p peak	Binding energy (eV)	FWHM (eV)	Area (a.u. ²)	Area (%)
2680	Fe ⁽⁰⁾ 2p _{3/2}	707.9	1.0	4867.4	1.1
	Fe ⁽⁰⁾ 2p _{1/2}	720.9	1.2	2677.1	0.6
	Fe ²⁺ 2p _{3/2}	709.6	2.2	59954.1	13.5
	Fe ²⁺ 2p _{1/2}	723.0	2.9	33574.3	7.6
	Fe ²⁺ _{Sat.} 2p _{3/2}	714.4	3.7	21583.5	4.9
	Fe ²⁺ _{Sat.} 2p _{1/2}	727.6	4.5	11391.3	2.3
	Fe ³⁺ 2p _{3/2}	709.8	4.2	142689.6	32.1
	Fe ³⁺ 2p _{1/2}	723.3	4.6	79906.2	18.1
	Fe ³⁺ _{Sat.} 2p _{3/2}	718.3	4.6	52795.2	11.9
	Fe ³⁺ _{Sat.} 2p _{1/2}	731.1	5.5	34245.5	7.9
4480	Fe ⁽⁰⁾ 2p _{3/2}	707.9	1.2	5795.0	1.5
	Fe ⁽⁰⁾ 2p _{1/2}	720.9	1.3	2897.5	0.7
	Fe ²⁺ 2p _{3/2}	709.5	2.4	64262.8	16.3
	Fe ²⁺ 2p _{1/2}	722.9	3.0	35987.2	9.2
	Fe ²⁺ _{Sat.} 2p _{3/2}	714.3	4.0	116610.2	5.9
	Fe ²⁺ _{Sat.} 2p _{1/2}	727.5	4.4	12209.9	3.1
	Fe ³⁺ 2p _{3/2}	709.9	4.1	116610.2	29.6
	Fe ³⁺ 2p _{1/2}	723.4	4.9	65301.7	16.7
	Fe ³⁺ _{Sat.} 2p _{3/2}	718.4	4.4	43145.8	11.1
	Fe ³⁺ _{Sat.} 2p _{1/2}	731.2	4.4	23322.0	5.9

6. Valence Band

Figure S6 and table S6 show the evolution of BiFeO₃ valence band region with argon etching time. Bi 6s peak is noticeable until an etching time of 80 s; over 2680 s is possible that Bi 6s are in new states hybridized with the other elements present in the film. The valence band region, between 2 eV and 8 eV, keeps stable with a reduction of valence band maximum (VBM), also the increase of valence tails representing metallic states from iron and bismuth.

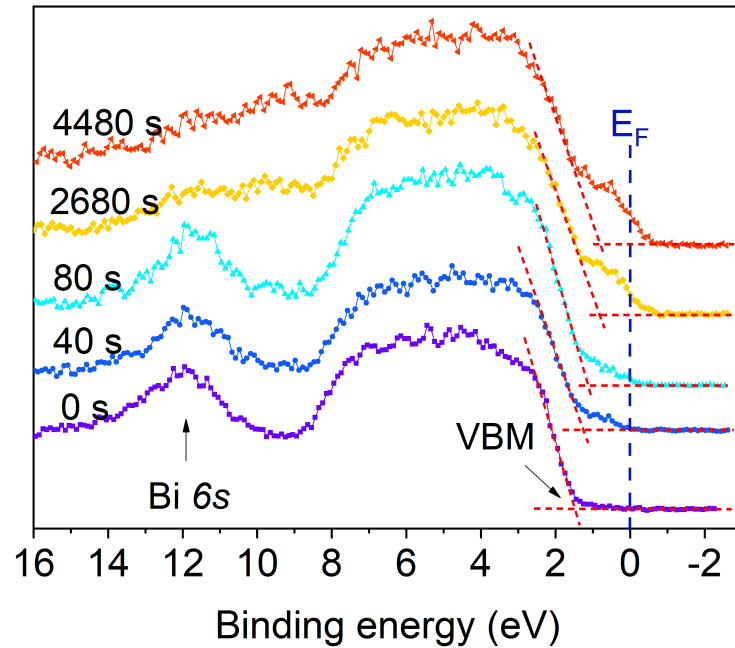


Figure S6. BiFeO₃ valence band behavior with Ar⁺ etching time

Table S6. BiFeO₃ valence band maximum evolution with Ar⁺ etching time.

Etching time (s)	Binding energy (eV) Bi 6s	Valence Band Maximum (eV) (VBM)
0	11.8	1.47
40	11.8	1.19
80	11.6	1.07
2680	-	0.77
4480s	-	0.51