Origin of annealing-atmosphere-dependent defect formation and photocathodic behaviour in $BiFeO_3$ thin films

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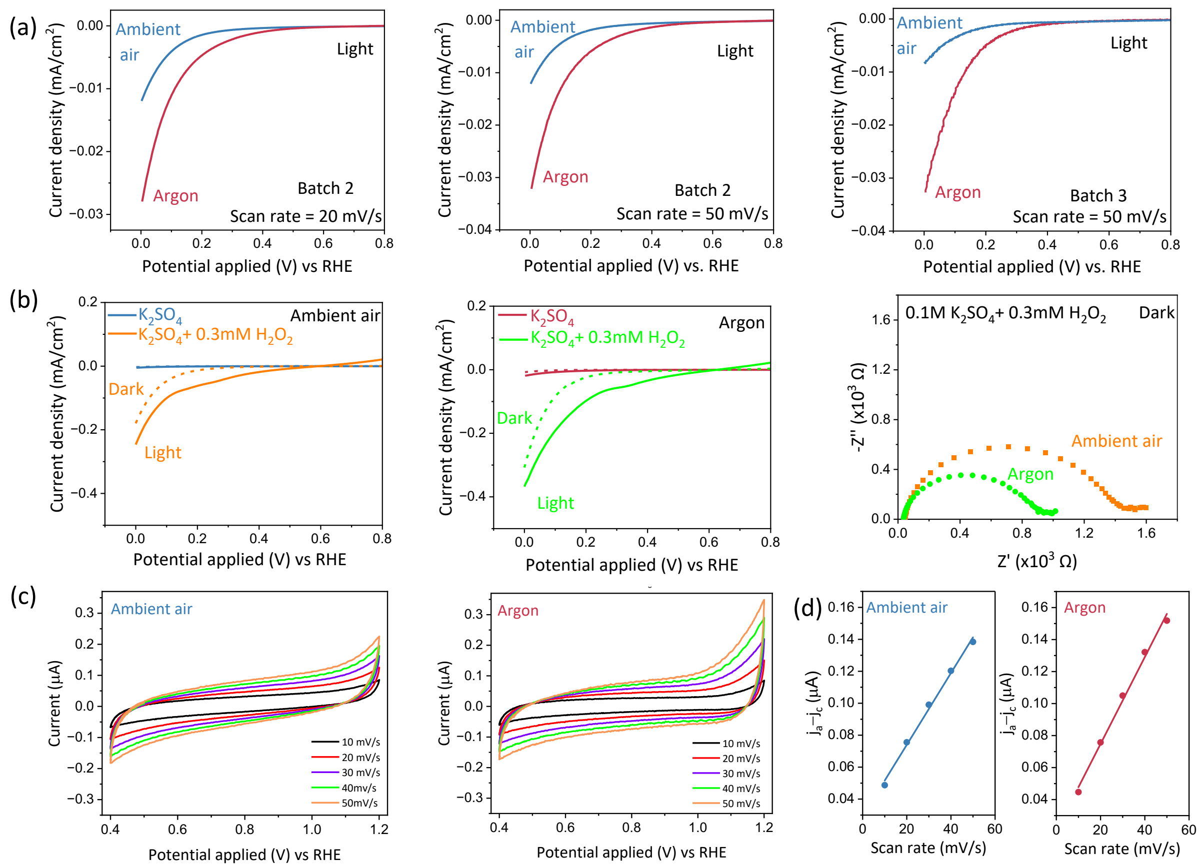

Figure S1. (a) LSV data of different batches of samples at different scan rates showing consistent effect of annealing atmosphere on the photocathodic behaviour. (b) LSV and EIS data of ambient air and argon annealed BFO thin films in the presence of H_2O_2, an electron acceptor. Reaction conditions: AM 1.5G; power density= 1000 W/m^2; electrolyte employed is 0.1M K_2SO_4; pH=5.6. (c) CV of thin films annealed in argon and ambient air at different scan rates to determine ECSA. (d) Plots of current and scan rate to determine the C_{dl} value.

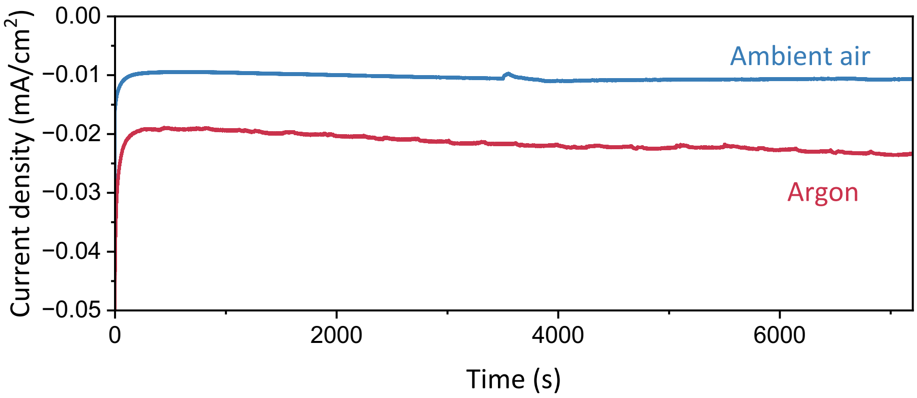

Figure S2. Chronoamperometry measurements at –0.1 V vs RHE, to test the stability of BFO thin films annealed in ambient air and argon.

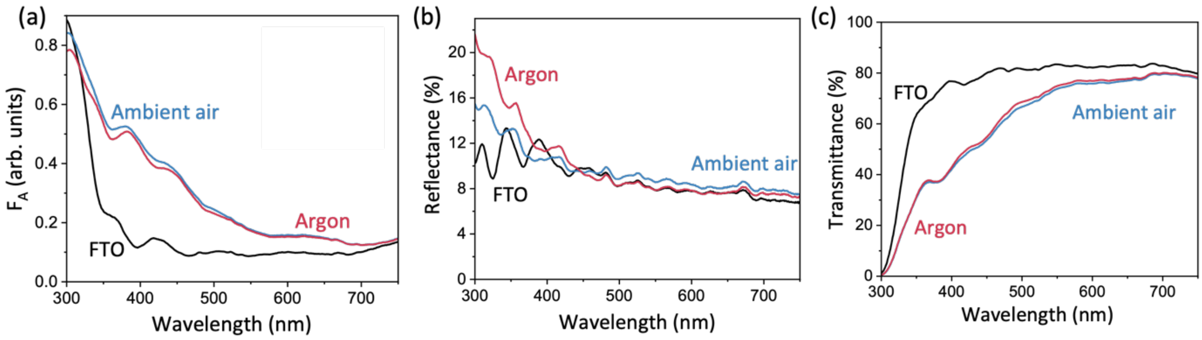

Figure S3. Comparing (a) the F_A (b) percent reflectance, and (c) percent transmittance of BFO thin films annealed in ambient air and argon. All data is compared with the FTO substrate.

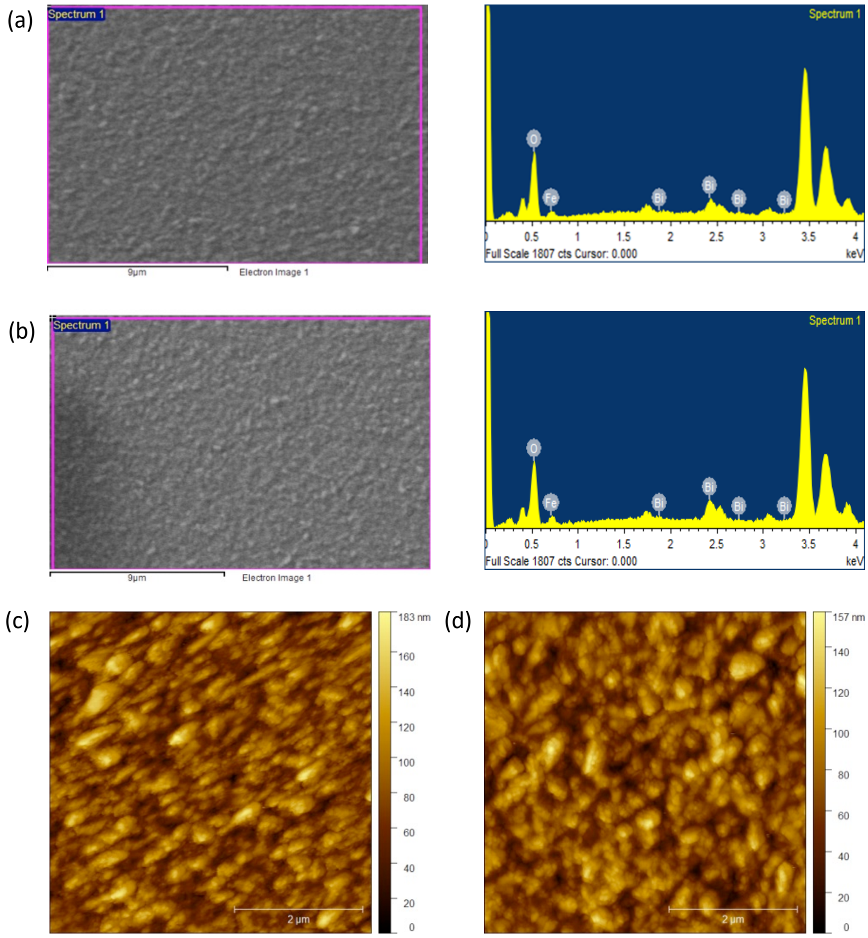

Figure S4. EDS images of BFO thin films annealed in (a) ambient air, (b) argon atmosphere. Note that, a greater >1 Bi:Fe ratio in argon-annealed BFO can be attributed to the excess of Bi precursor added during the synthesis of the samples. AFM images of the BFO thin films annealed in (c) ambient air and (d) argon.

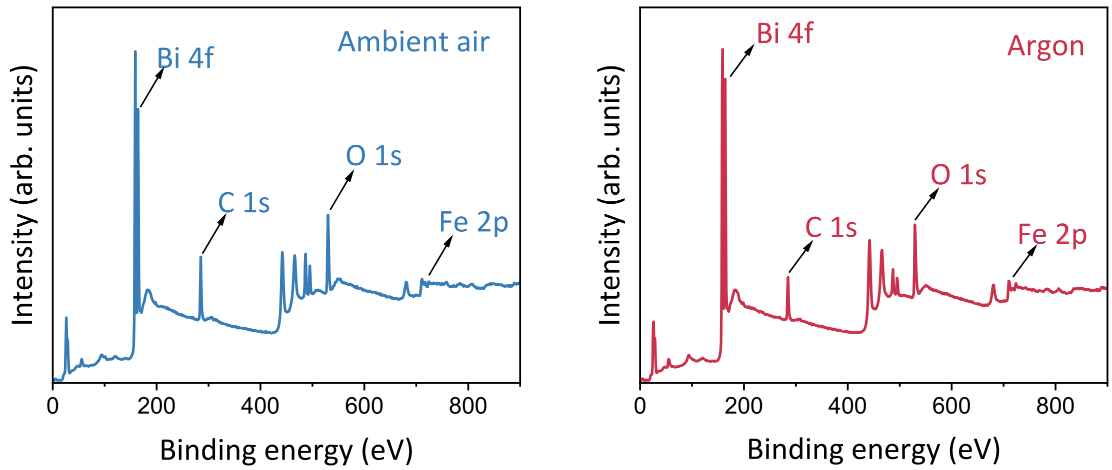

Figure S5. XPS survey spectra of BFO thin films annealed in two different atmospheres.

Table S1. Peak parameters and percentage contribution of the deconvoluted peaks of XPS core level Bi 4f spectra.

a. Bi 4f spectrum of ambient air annealed BFO thin films.

Peak	Position (eV)	FWHM (eV)	Percentage composition (%)
Bi^{3+} $4f_{7/2}$	158.67	1.08	86.32
Bi^{3+} $4f_{5/2}$	163.97	1.08	
$Bi^{(3-x)+}$ $4f_{7/2}$	157.67	1.08	13.68
$Bi^{(3-x)+}$ $4f_{5/2}$	163.02	1.08	

b. Bi 4f spectrum of argon annealed BFO thin films.

Peak	Position (eV)	FWHM (eV)	Percentage composition (%)
Bi^{3+} $4f_{7/2}$	158.69	1.08	91.24
Bi^{3+} $4f_{5/2}$	163.99	1.08	
$Bi^{(3-x)+}$ $4f_{7/2}$	157.57	1.08	8.76
$Bi^{(3-x)+}$ $4f_{5/2}$	162.95	1.08	

Table S2. Peak parameters and percentage contribution of the deconvoluted peaks of XPS core level O 1s spectra.

a. O 1s spectrum of ambient air annealed BFO thin films.

Peak	Position (eV)	FWHM (eV)	Percentage composition (%)
O_i	529.29	1.18	41
O_{ii}	529.90	1.18	36
O_{iii}	531.12	1.18	23

b. O 1s spectrum of argon annealed BFO thin films.

Peak	Position (eV)	FWHM (eV)	Percentage composition (%)
O_i	529.36	1.14	67.6
O_{ii}	530.92	1.18	31
O_{iii}	533.38	1.18	1.4

Table S3. Peak parameters and percentage contribution of the deconvoluted peaks of XPS core level Fe 2p spectra.

a. Fe 2p spectrum of ambient air annealed BFO thin films.

Peak	Position (eV)	FWHM (eV)	Percentage composition (%)	Fe^{3+}/Fe^{2+} ratio
Fe^{3+} $2p_{3/2}$	710.79	1.4	55.67	1.25
Fe^{3+} $2p_{1/2}$	724.00	1.4		
Fe^{2+} $2p_{3/2}$	709.55	1.4	44.32	
Fe^{2+} $2p_{1/2}$	722.91	1.4		

b. Fe 2p spectrum of argon annealed BFO thin films.

Peak	Position (eV)	FWHM (eV)	Percentage composition (%)	Fe^{3+}/Fe^{2+} ratio
Fe^{3+} $2p_{3/2}$	710.89	1.4	71.73	2.54
Fe^{3+} $2p_{1/2}$	724.20	1.4		
Fe^{2+} $2p_{3/2}$	709.57	1.4	28.27	
Fe^{2+} $2p_{1/2}$	722.97	1.4		

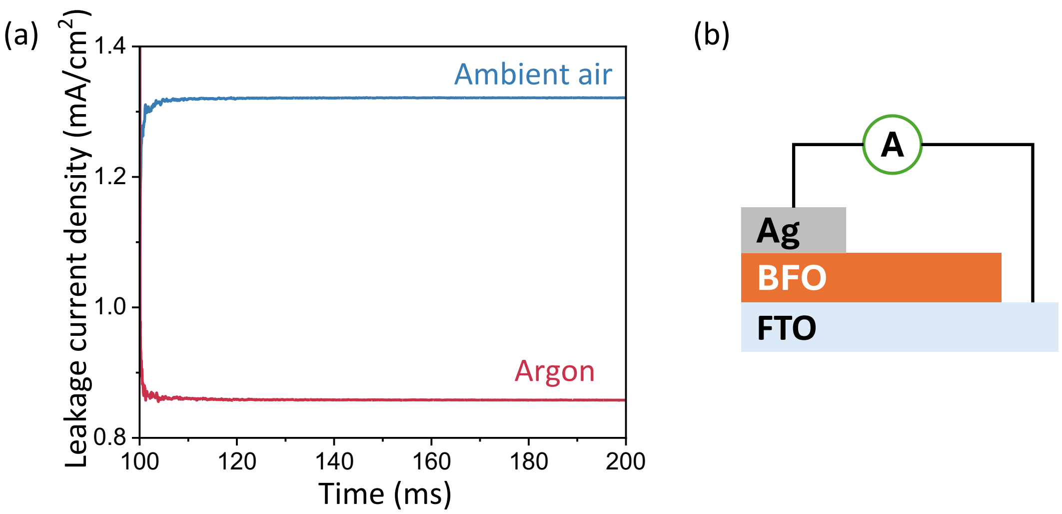

Figure S6. (a) Leakage current density of BFO thin films annealed in air and argon atmosphere with respect to time. (b) Graphical representation of the device configuration utilized for leakage current measurements, where 0.1 V was applied with 0.1 s soak time, followed by measuring the current for next 0.1 s.

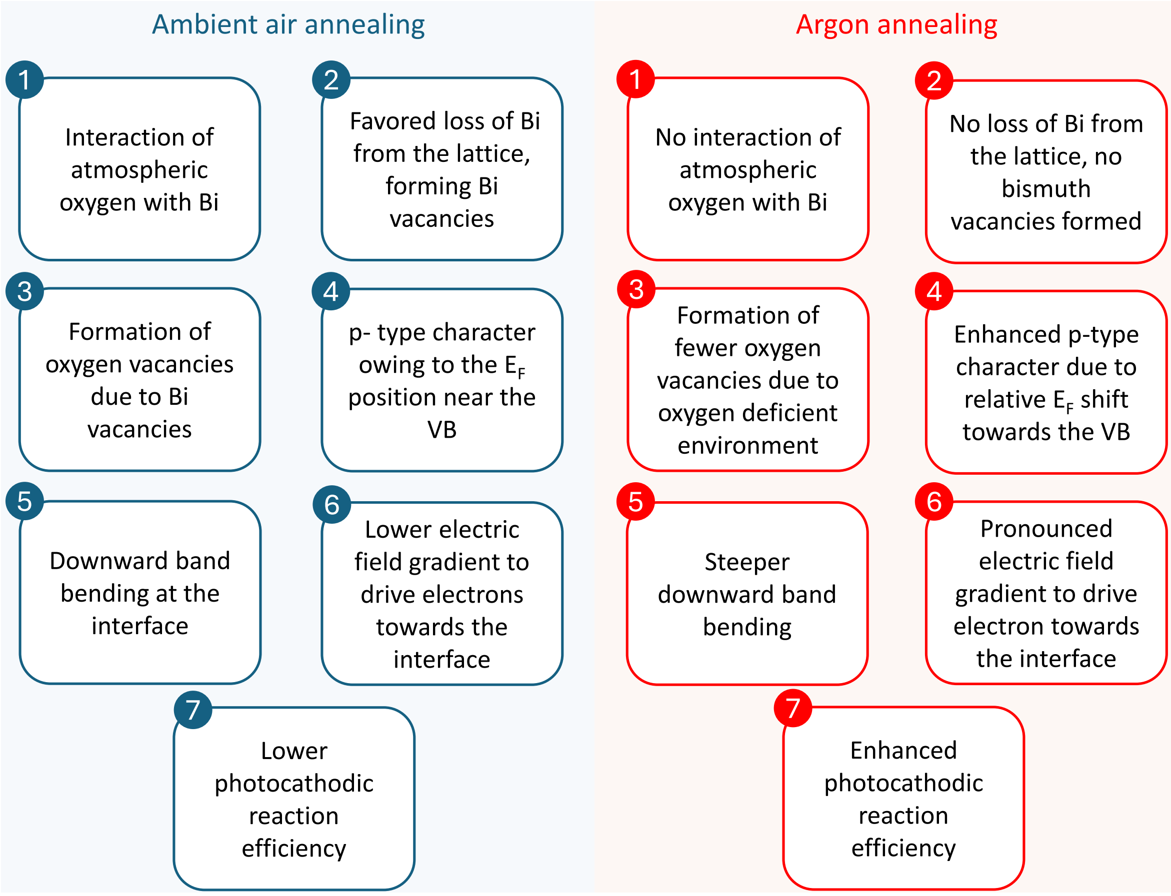

Figure S7. Summary of the annealing atmosphere dependent processes and optoelectronic properties that determine the PEC performance.

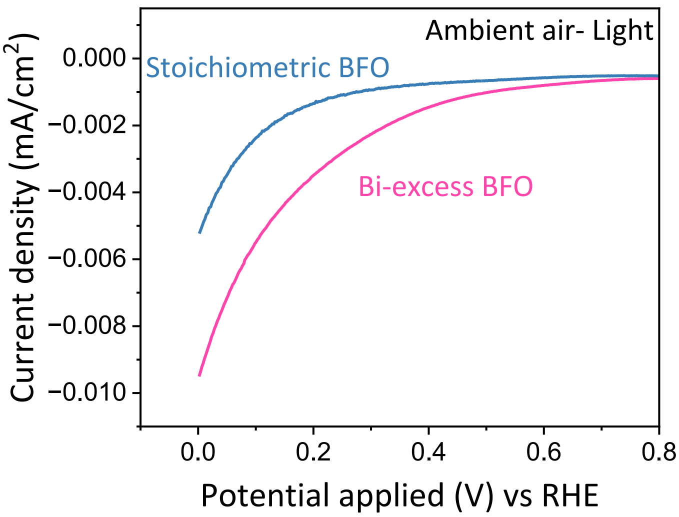

Figure S8. LSV data of 20% Bi-excess and stoichiometric BFO (both films annealed in ambient air) under solar simulator illumination. Reaction conditions: AM 1.5G; power density= 1000 W/m^2; electrolyte employed is 0.1M K_2SO_4; pH=5.6; scan rate=50 mV/s, scan direction is from 0.8 V towards 0 V vs RHE.

Table S4. Fitting parameters of the EIS data presented in Figure 7 of the main text.

Sample	Bulk electrolyte/ solution resistance, **R_S** (Ω)	Interfacial charge transfer resistance, **R_{CT}** (Ω)	Constant phase element **CPE** (μMho*s^N)
Ambient air annealed BFO	43.9	5300	10.8 N= 0.835
Argon annealed BFO	43.9	1930	15.5 N= 0.855