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ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Electronic Structure and Optoelectronic Properties of Bismuth Oxyiodide Robust against Percent-Level Iodine-, Oxygen-, and Bismuth-Related Surface Defects

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Supporting Information

Electronic Structure and Optoelectronic Properties of Bismuth Oxyiodide Robust Against Percent-Level Iodine-, Oxygen- and Bismuth-Related Surface Defects

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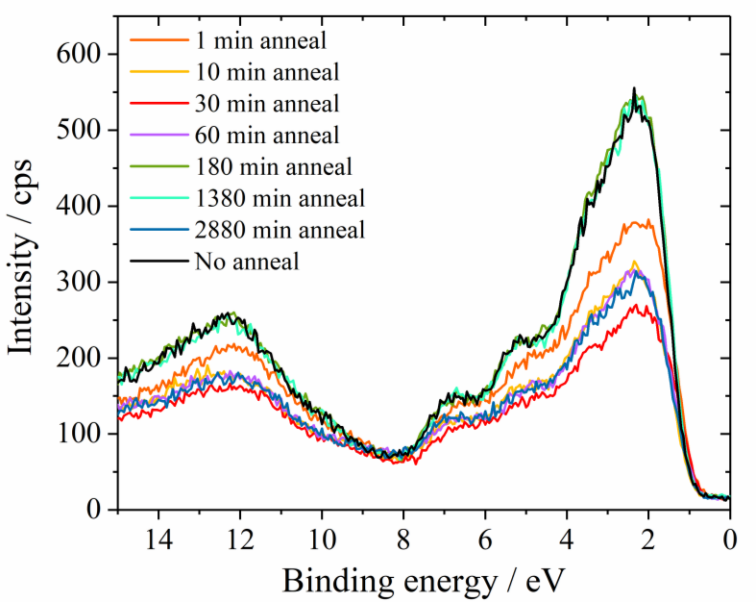

Figure S1. Valence band spectra of BiOI without annealing and with vacuum annealing for different periods of time

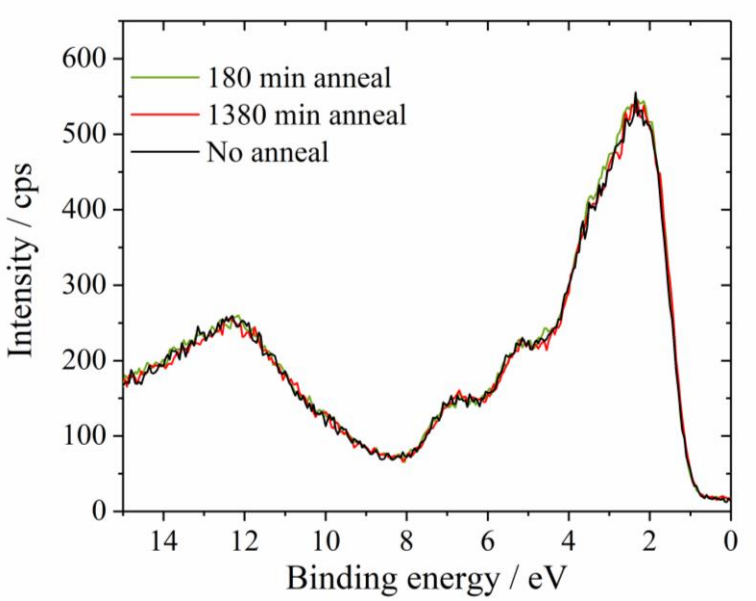

Figure S2. Comparison of the normalized valence band spectra of BiOI without annealing and after 3 h (180 min) and 23 h (1380 min) vacuum annealing.

Table S1. Composition of BiOI thin films without vacuum and annealing *vs.* with 10 min vacuum annealing measured by energy dispersive X-ray spectrophotometry (EDX). Note that only the Bi and I content are shown due to the difficulty in accurately measuring the O content by EDX.

Non-annealed BiOI							
	Region 1 (at%)	Region 2 (at%)	Region 3 (at%)	Region 4 (at%)	Region 5 (at%)	Average (at%)	Uncertainty
Bi (M-series)	43.590	43.790	43.890	43.050	43.400	43.544	0.299
I (L-series)	42.740	42.400	42.030	41.840	42.890	42.38	0.401
Ratio (I:Bi): 0.973					Uncertainty in ratio: 0.011		

10 min annealed BiOI							
	Region 1 (at%)	Region 2 (at%)	Region 3 (at%)	Region 4 (at%)	Region 5 (at%)	Average (at%)	Uncertainty
Bi (M-series)	43.370	41.970	43.640	44.590	43.280	43.370	0.840
I (L-series)	41.940	43.550	41.530	40.820	42.750	42.118	0.950
Ratio (I:Bi) : 0.971					Uncertainty in ratio: 0.029		

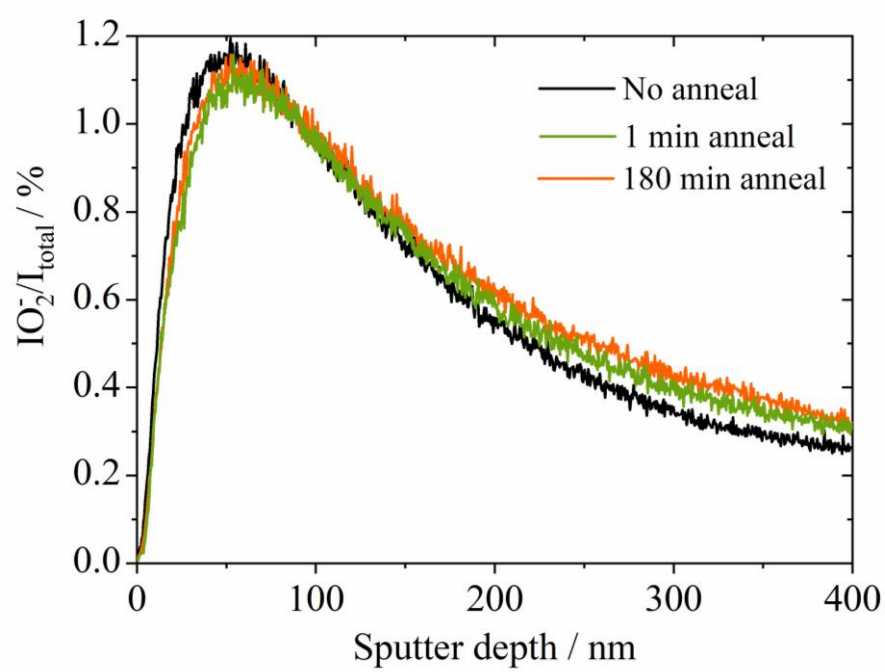

Figure S3. Normalised IO_2^- profiles measured with ToF-SIMS of the unannealed, 1 min annealed and 180 min annealed samples.

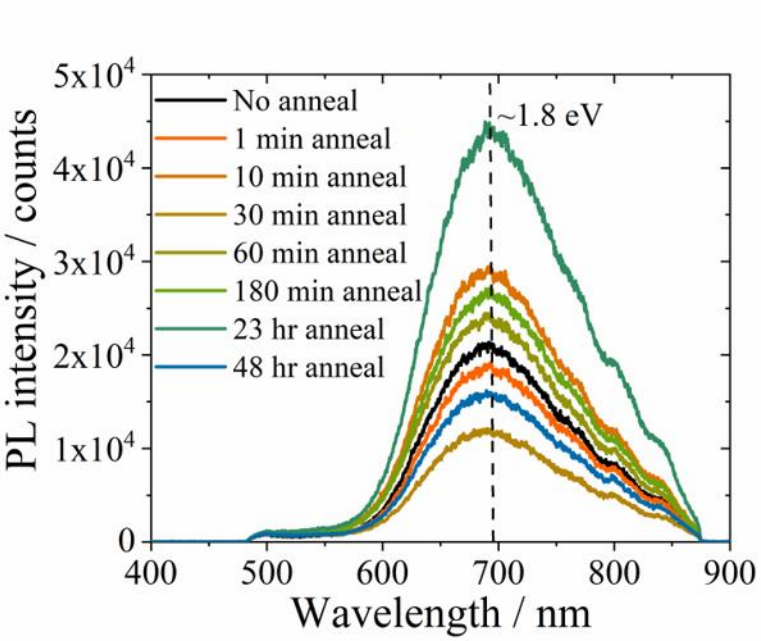

Figure S4. Photoluminescence spectra of unannealed and vacuum-annealed BiOI films

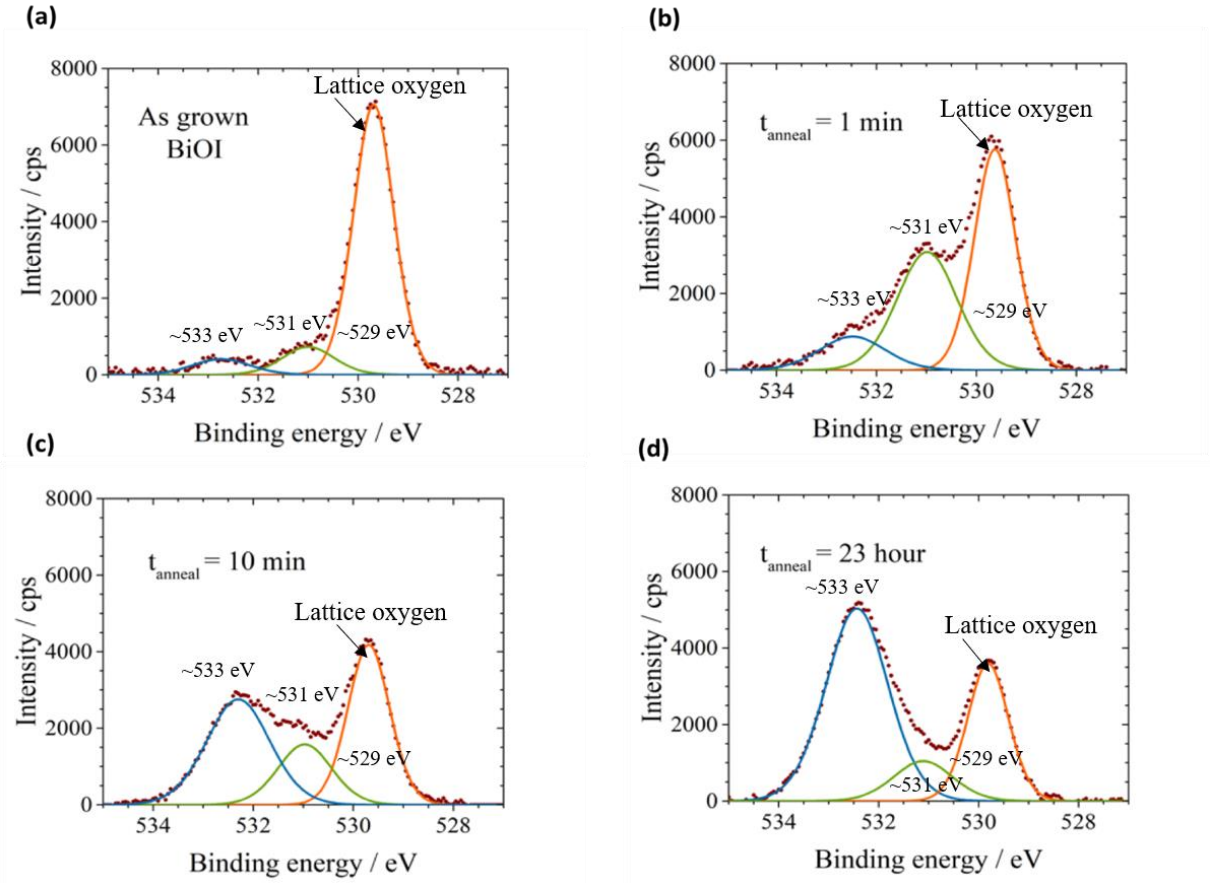

Figure S5. O1*s* core spectra of (a) as grown BiOI, (b) BiOI vacuum annealed for 1 minute, (c) BiOI vacuum annealed for 10 min and (d) BiOI vacuum annealed for 23 h at 100 ºC, 25 Pa.

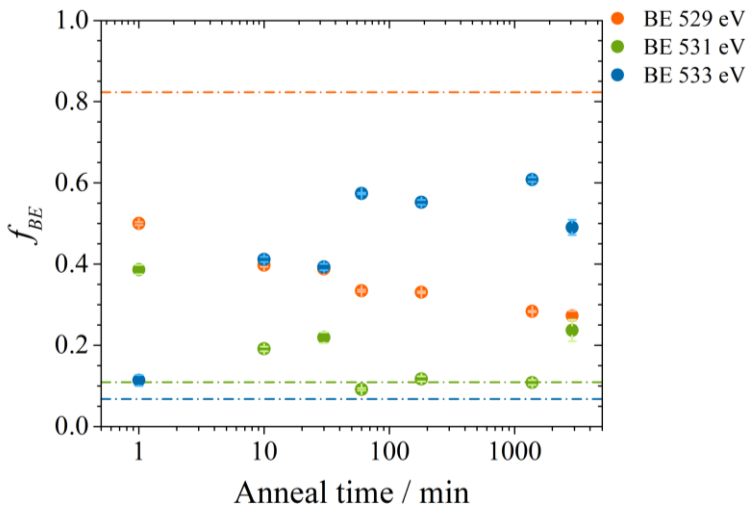

Figure S6. Plot shows the change in fractional contribution (f_{BE}) of the peaks at binding energies 529 eV, 531 eV and 533 eV to the O 1*s* spectra as vacuum annealing time increased. The dashed lines show the fractional contribution of the peaks at binding energy 529 eV (orange), 531 eV (green) and 533 eV (blue) to the O 1*s* spectrum for an as grown BiOI sample.

Table S2. The conditions used to grow mixed phase samples **A, B** and **C**, the color of the film and the phases present as determined by XRD. Powder Diffraction Files (PDF) were used to identify BiOI (00-010-0445), Bi_5O_7I (00-038-0669), BiO_9I_3 (00-058-0583) and $Bi_2O_{2.33}$ (00-027-0051) and β-Bi_2O_3 (00-001-0709).

Sample ID	Conditions		Film color	Phases present
	Temperature / ºC	O_2 flow / %		
A	450	5	Red	BiOI, Bi_5O_7I
B	450	50	Red	BiOI, Bi_5O_7I, $Bi_2O_{2.33}$
C	400	50	Yellow	BiOI, BiO_9I_3, Bi_5O_7I, β-Bi_2O_3

Table S3. The estimated Fermi level (E_F) to valence band (VB) offset of mixed phase samples A, B, and C, as predicted from the XPS valence band spectra.

Sample	E_F – VB / eV
A	0.55
B	0.87
C	1.24

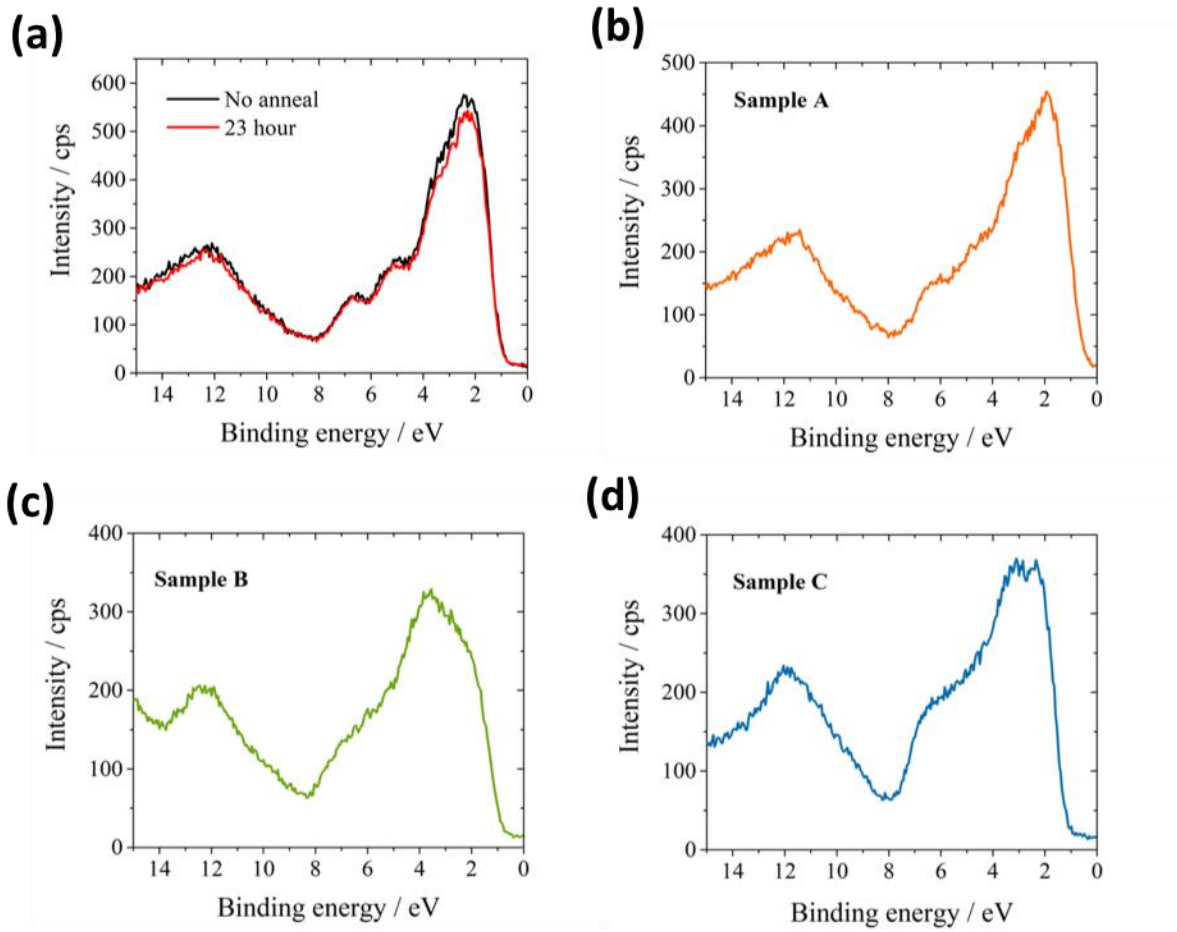

Figure S7. The valence band spectra for a) as-deposited BiOI (black line) and BiOI vacuum annealed for 23 hours at 100 ºC, 25 Pa (red line), b) sample A, a mixed phase sample containing BiOI and Bi_5O_7I, c) sample B, a mixed phase sample containing BiOI, Bi_5O_7I and $Bi_2O_{2.33}$, and d) sample C, a mixed phase sample containing BiOI, BiO_9I_3, Bi_5O_7I and β-Bi_2O_3.

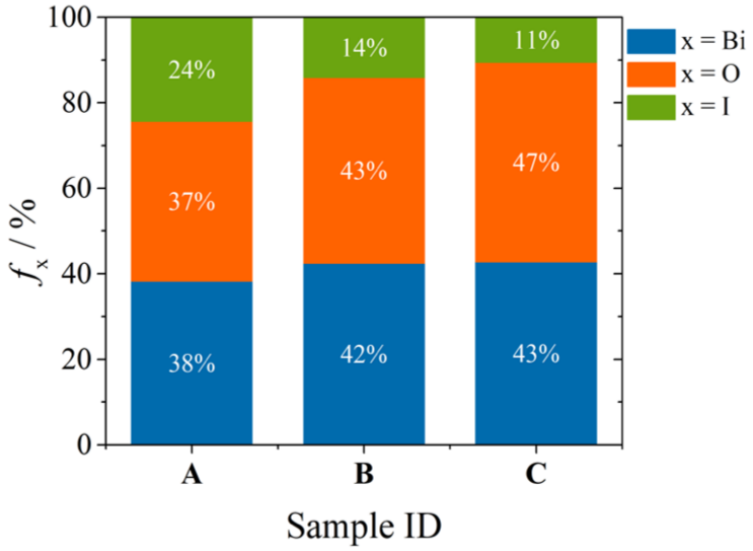

Figure S8. The composition of samples A, B and C determined using the areas of the XPS core level spectra, accounting for the relative sensitivity factor for each orbital.

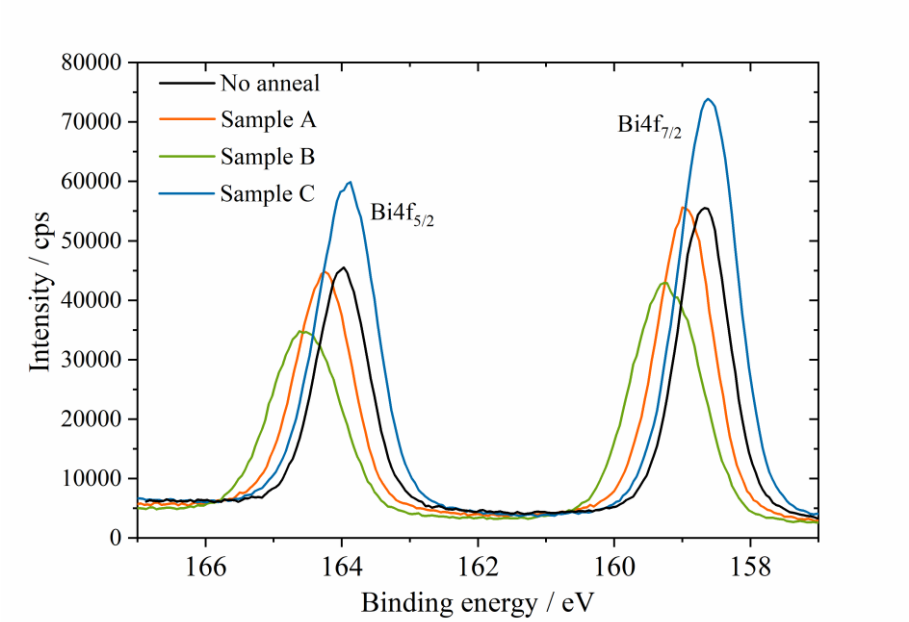

Figure S9. Bi 4*f* core level spectra of non-annealed and mixed phase samples

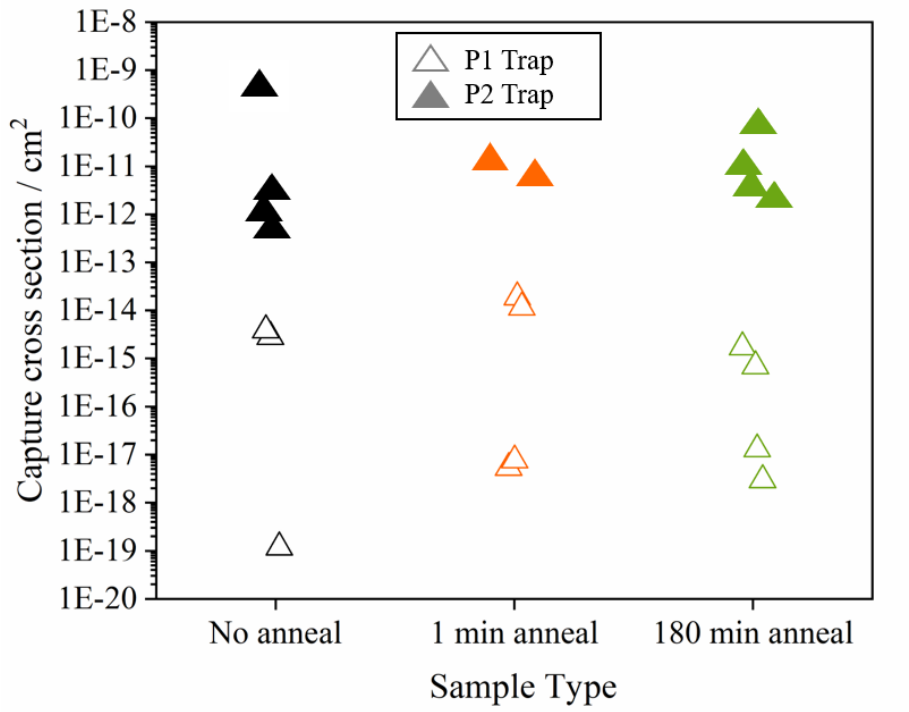

Figure S10. PICTS data of the capture cross-section for vacuum annealed samples. Two deep levels were found in the PICTS spectra (see Figure S11) and these are labelled P1 and P2. The open points are for the P1 trap found in each sample, while the closed points are for the P2 trap in each sample

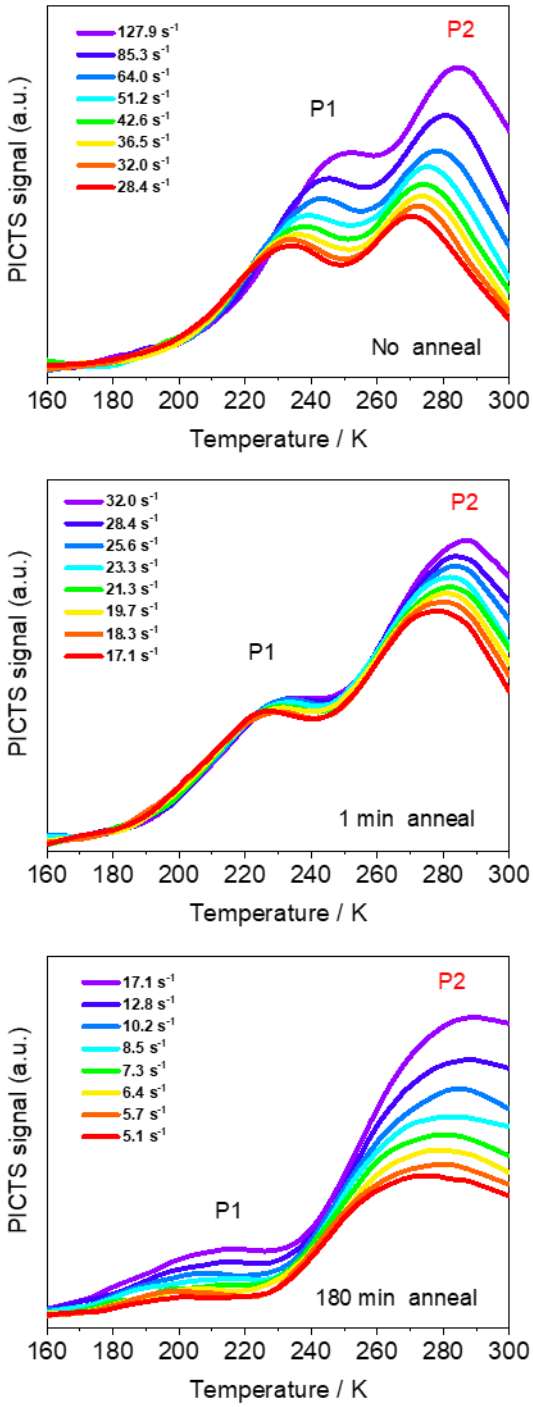

Figure S11. PICTS spectra at various rate window values for unannealed, 1 min annealed, and 180 min annealed BiOI samples. Two thermally-activated peaks, labelled as P1 and P2, are apparent, which can be assigned to two deep levels. These spectra were determined through a boxcar-type scheme from the measured current transients ensuing trap-filling pulses.[1] In brief, the difference between the device current at selected times t_1 and t_2 gives the PICTS signal $\Delta i = i(t_1) - i(t_2)$. The rate window is the defined as $e_n = ln(t_2/t_1)/(t_2 - t_1)$. By plotting the PICTS signal for various rate window values, the PICTS spectra shown here are obtained

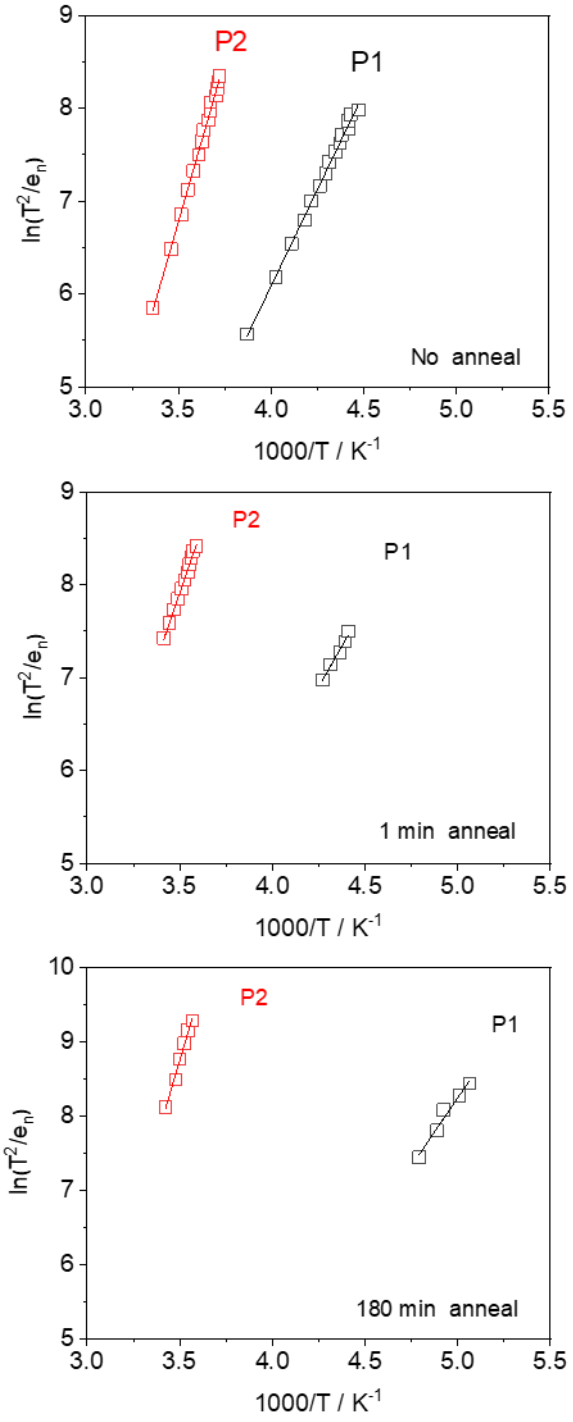

Figure S12. Arrhenius plots extracted from the PICTS spectra shown in Figure S11. In brief, these were derived from the temperature and rate window values of the PICTS spectra peaks in Figure S11, consistently with standard PICTS methodology.[1] The deep level energies for P1 and P2 were determined from the slopes of the traces shown here, while cross-sections were extracted from their intercepts

References

[1] A. Erol, M. Ç. Arıkan, in *Semiconductor Research* (Eds.: A. Patane, N. Balkan), Springer, Berlin, Heidelberg, Germany **2012**, pp. 333–365.