Electronic Supplementary Information

Controlling the preferred orientation of layered BiOI thin films

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S1. Experimental setup and growth process

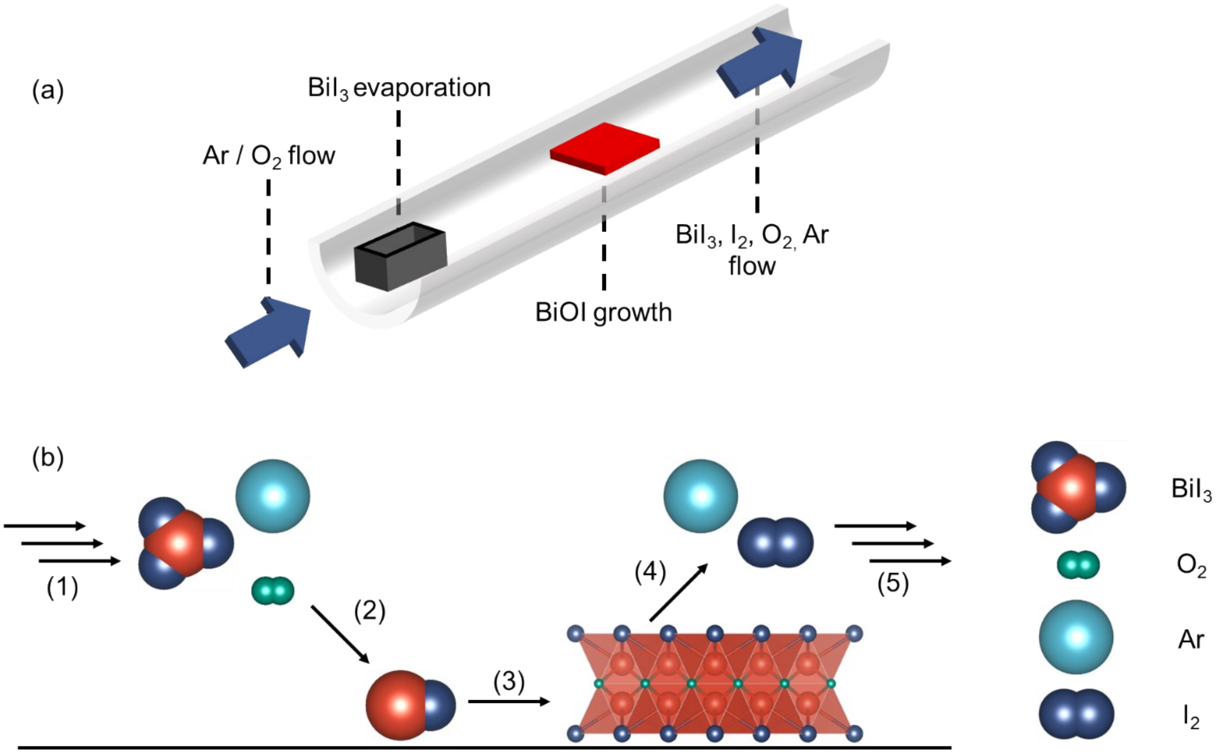

Figure S1. (a) Schematic representation of the experimental setup used to grow BiOI by chemical vapor deposition (CVD) inside a tube furnace. BiI_3 was used as a precursor, along with an Ar/O_2 gas mixture as oxidant/carrier gas. (b) Mechanism of BiOI growth by CVD. (1) A gas mixture of BiI_3, O_2 and Ar are transported towards the substrate. (2) The gaseous species are transported towards the surface through the boundary layer. (3) The species diffuse on the substrate and react to form BiOI. (4) The gaseous by-products diffuse away from the surface and (5) are transported away from the substrate. We note that reactions could occur instead in the gas phase rather than on the surface, and reaction products could diffuse over the surface instead. We found that increasing the temperature in the substrate zone resulted in large agglomerates forming and depositing, which suggests that gas-phase reactions and the deposition of BiOI to the substrate is possible. On the other hand, a combination of gas-phase and surface reactions is also possible. Further work is needed to elucidate this detail.

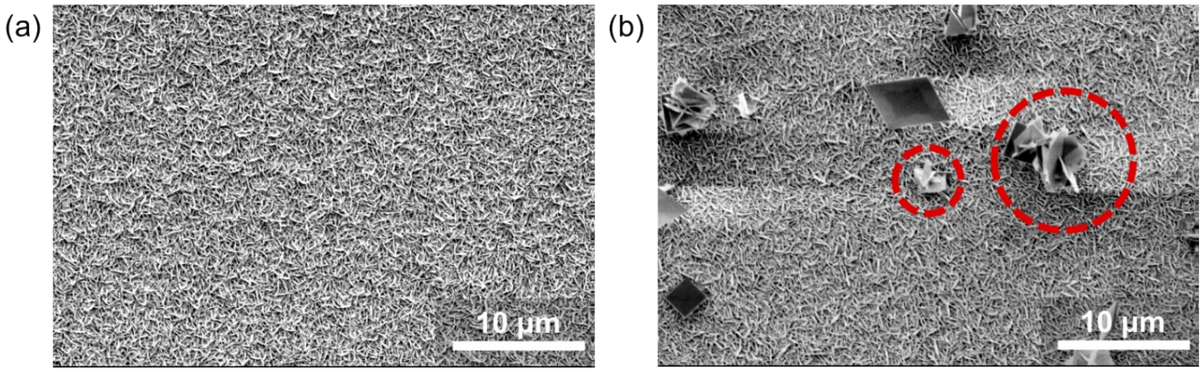

Figure S2. Evidence for gas phase reactions forming BiOI, which deposits onto the surface. Scanning electron microscopy image of BiOI grown by CVD at a substrate temperature of (a) 325 ^{o}C and (b) 450 ^{o}C. In both cases the precursor temperature was approximately 25 ^{o}C below the substrate temperature. The red dashed circles indicate an example of BiOI agglomerates which reacted in the gas phase before depositing onto the substrate.

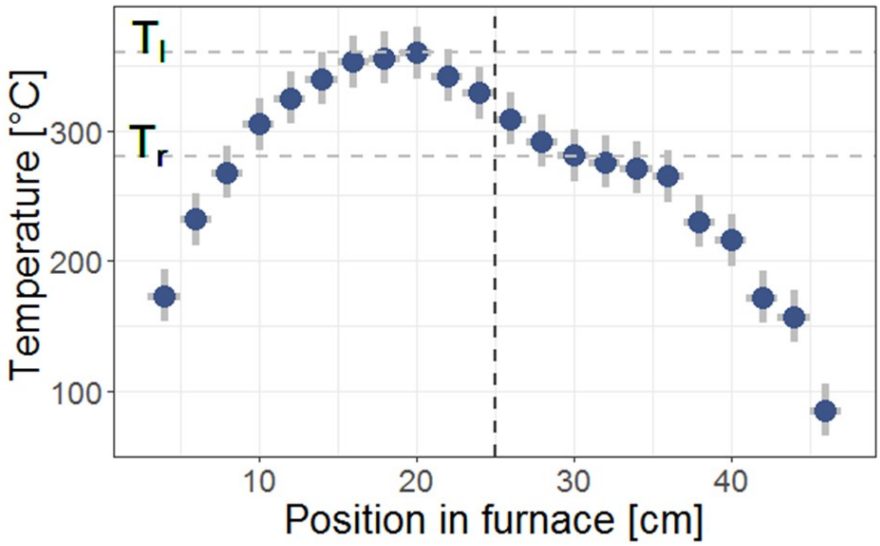

Figure S3. Measured temperature profile inside the two zone furnace as function of position. The region from 0 – 25 cm indicates the left zone of the furnace, which was set to temperature T_l = 360 ^{o}C. The region from 25 – 50 cm indicates the right zone of the furnace, which was set to T_r = 280 ^{o}C.

S2. Calculating the radiative limit

The open circuit voltage (V_{oc}) is given by

$$V_{oc} = \frac{nkT}{q} ln\left(\frac{I_L}{I_0} + 1\right),$$ (S1)

where n is the diode ideality factor (unity for an ideal diode), I_0 is the dark saturation current, q is the elementary charge, I_L is the ilumination current, k is the Boltzmann constant and T the absolute temperature.

The illumination and dark current can be written by

$$I_L = \int_0^\infty EQE(E)\theta^{SUN}(E)dE,$$ (S2)

and

$$I_0 = \int_0^\infty EQE(E)\theta^{T}(E)dE,$$ (S3)

where the EQE stands for the external quantum efficiency of the solar cell (see Figure S4), E is the energy of photons, θ^{SUN} is the radiation flux corresponding to the AM1.5G spectrum and θ^{T} is the radiation flux corresponding to a blackbody at the operational temperature of the solar cell (in this case at 298.15 K). The radiation flux of a black body radiator from a thermal emitter at temperature T can be written as

$$\theta^T(E) = \frac{2\pi}{h^3c^2}\frac{E^2}{e^{\left(\frac{E}{kT}\right)} - 1}$$ (S4)

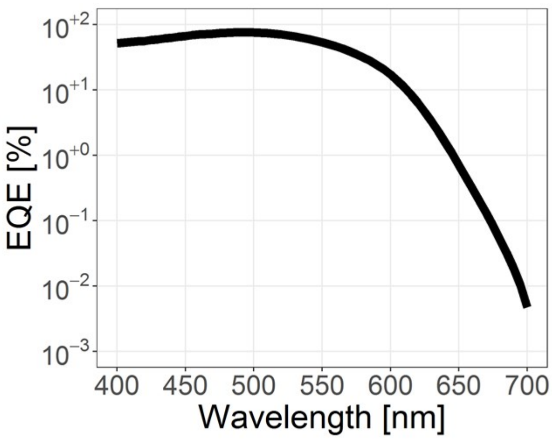

Figure S4. Measured external quantum efficiency (EQE) of the BiOI solar cells as a function of the wavelength.

S3. Full XRD patterns of BiOI thin films for Figure 2

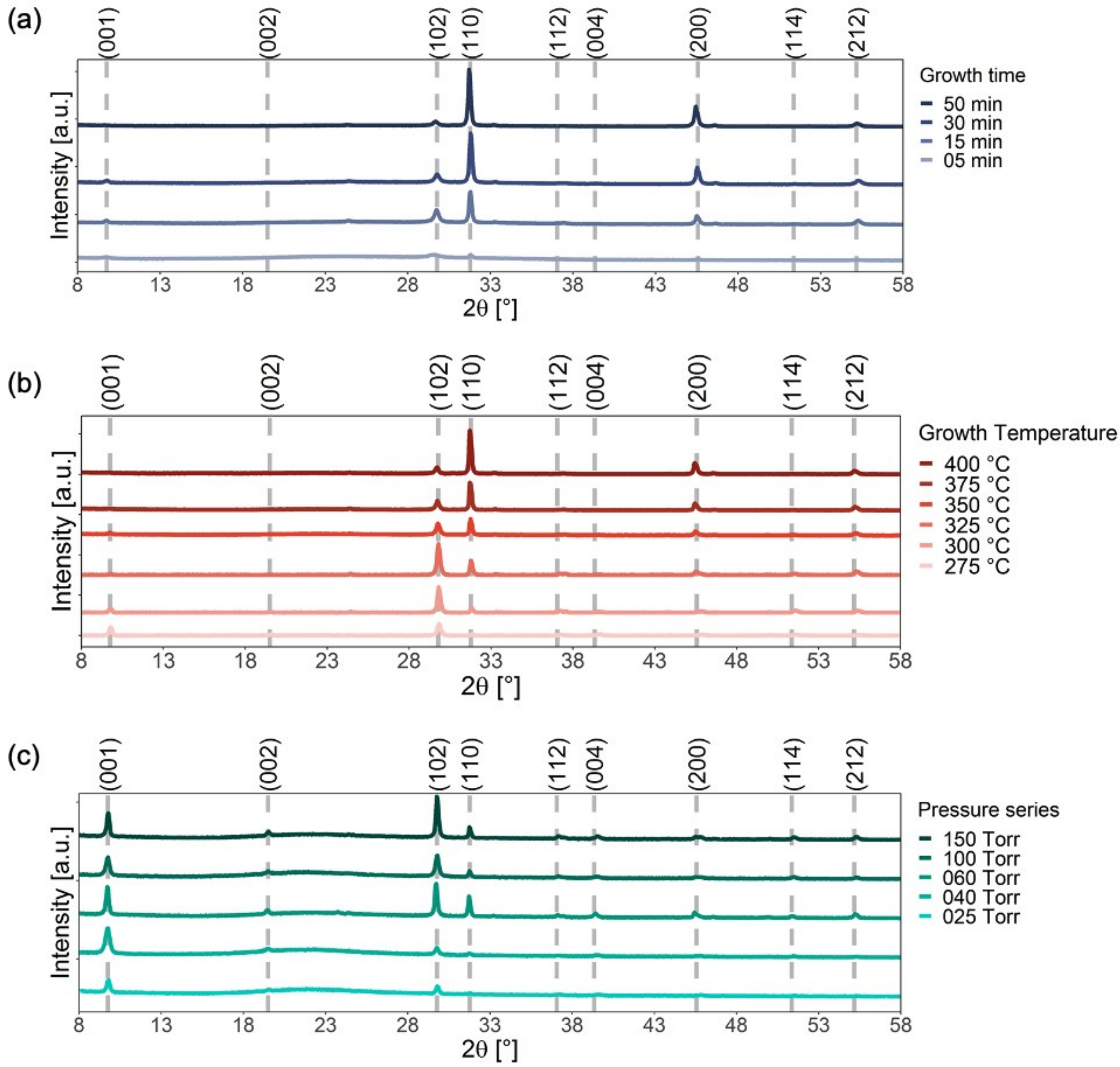

Figure S5. X-ray diffraction pattern of bismuth oxyiodide grown by chemical vapor deposition (a) for different growth times, (b) at different temperatures and (c) at different pressures. In (a), the precursor temperature was 325 °C, substrate temperature 360 °C and pressure atmospheric. In (b), the substrate temperature was kept 30 °C above the precursor temperature and the growth time was adjusted to account for the changes in growth rate to keep the film thickness to approximately 700 nm. In (c) the precursor temperature was 325 °C, substrate temeprature 360 °C and growth time 30 min.

S4. Summary of device parameters

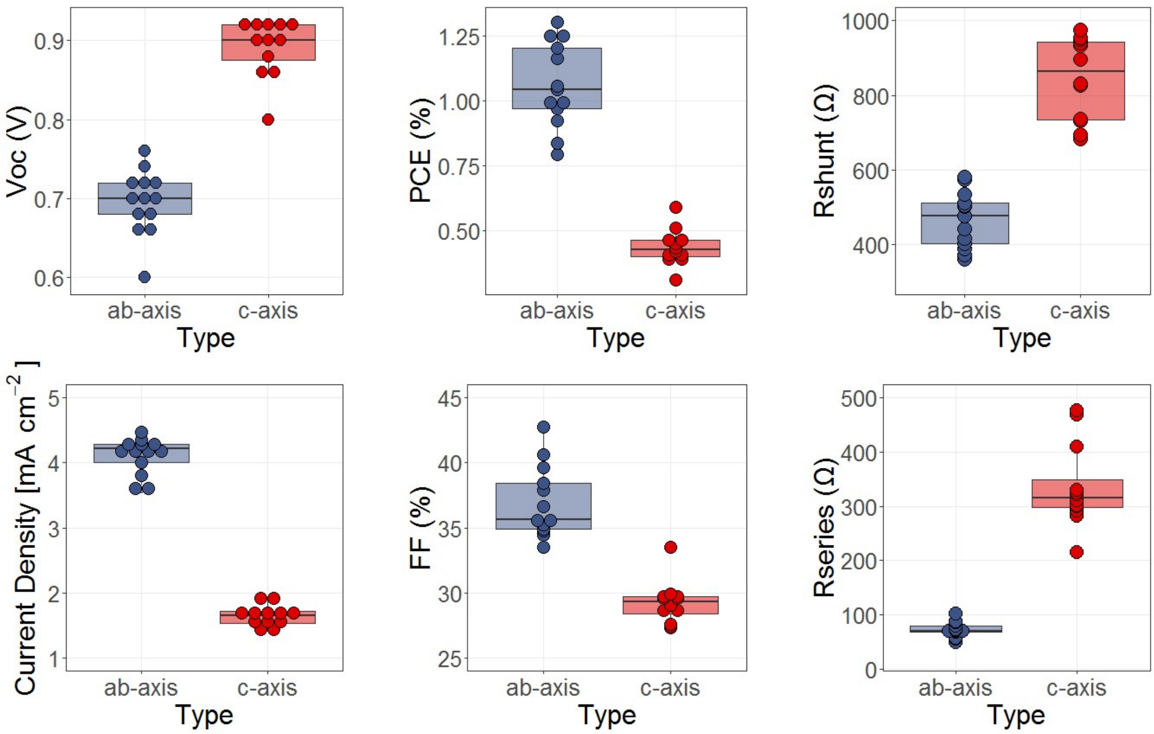

Figure S6. Boxplots of the measured open circuit voltage (V_{oc}), power conversion efficiency (PCE), shunt resistance (R_{shunt}), short circuit current density, fill factor (FF) and series resistance (R_{series}) for devices with predomenantly a/b-axis oriented films (dark blue) and c-axis oriented films (red).