Solution-Processed BiI₃ Films with 1.1 eV Quasi-Fermi Level Splitting: The Role of Water, Temperature, and Solvent during Processing

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ABSTRACT: We present a mechanistic explanation of the BiI₃ film formation process and an analysis of the critical factors in preparing high-quality solution-processed BiI₃ films. We find that complexation with Lewis bases, relative humidity, and temperature are important factors during solvent vapor annealing (SVA) of films. During SVA, water vapor and higher temperatures limit the formation of the BiI₃−dimethylformamide coordination complex. SVA with an optimized water content and temperature produces films with 300−500 nm grains. Films that formed after solvent removal at lower temperatures showed preferential crystal orientation and, we elucidate its implications for carrier transport. Addition of dimethyl sulfoxide to highly concentrated tetrahydrofuran−BiI₃ inks prevents film cracking after spin-coating. We have measured a quasi-Fermi level splitting of 1.1 eV and a diffusion length of 70 nm from films processed with optimal temperature and humidity. The best device produced by optimized SVA has a power conversion efficiency of 0.5%, $I_{SC}$ of $\sim$4 mA/cm², and $V_{OC}$ of $\sim$400 mV. The low photocurrent and voltage we attribute to the low diffusion length and the unfavorable band alignment between the absorber and the adjacent transport layers. The deep understanding of the relationship between morphology/crystal structure and optoelectronic properties gained from this work paves the way for future optimization of BiI₃-based solar cells.

INTRODUCTION

Photovoltaic (PV) materials such as copper zinc tin sulfoselenide (CZTS), copper indium gallium sulfoselenide (CIGS), and, more recently, hybrid perovskites (HPs) are all solution-processable. Solution-processed materials are exciting because they can be spray-coated, blade-coated, or slot die-coated onto large substrates, often at low temperatures, and thus may reduce the upfront capital expenditure (CAPEX) to begin manufacturing. The CAPEX of roll-to-roll processing may be as low as 0.06$/W_{DCap}$ versus 0.68 to 1.01$/W_{DCap}$ for CdTe and polysilicon processes ($S/W_{DCap}$ is $S$ per annual production capacity in watts). However, materials such as CZTS are not yet commercializable as device efficiencies are still less than 15%, mainly because of low minority carrier diffusion lengths and low open-circuit voltages. However, CIGS cells are commercial and have demonstrated module efficiencies of 16.5% for vacuum-deposited absorbers. Solution-processed CIGS is also being developed with laboratory-scale efficiencies of 14.7%. The process still requires a high-temperature step, and indium (used in CIGS) is considered by some to add financial risk because of indium price volatility or constraints on the manufacturing growth rate. Solution-processed HP materials have increased rapidly and are over 20% with the added benefit of requiring no high-temperature steps. As promising as these material are, they possess several shortcomings. All high-efficiency HP materials contain lead, which has environmental health risk. HP materials also have limited lifespans owing to low thermodynamic stability of the compound, degradation in the presence of light and moisture, or light-induced phase segregation. However, these materials have remarkable properties and defect tolerance. The origin of this defect tolerance is believed to come from a partial oxidation of the Pb²⁺ cation, withholding its 6s² electrons. These 6s² electrons give rise to a valence band maximum consisting of antibonding orbitals. In addition, relativistic spin−orbit effects increase the width of the conduction band considerably. As a result, dangling bonds from vacancy formation appear as resonances within the bands, rather than as trap states in the band gap. BiI₃ likewise possesses this beneficial electronic structure, and it is expected to possess a similar defect tolerance. BiI₃ is composed of layers of edge-sharing BiI₆ octahedra held together in part by van der Waals interactions. Lehner et al. have found that BiI₃ has a large static dielectric constant with principal components of the static dielectric tensor of $\varepsilon_{xx}^{\infty} = 18.9$ and $\varepsilon_{zz}^{\infty} = 15.0$, which may indicate effective screening of

Supporting Information

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charged point defects, thus improving transport.\textsuperscript{22} BiI\textsubscript{3} has also shown lifetimes of over 7 ns.\textsuperscript{19} Materials with lifetimes of at least 1 ns (such as CZTS, InP, and CIGS) have achieved device efficiencies of greater than 10%.\textsuperscript{19} Furthermore, materials such as BiI\textsubscript{3} are well-investigated materials for room-temperature gamma-ray detectors\textsuperscript{23} owing to the high interaction cross section. One of the biggest advantages of Bi\textsuperscript{3+} over Pb\textsuperscript{2+} is that it is less toxic. For instance, bismuth is already in use as a component of lead-free solders. Compared to lead, mercury, and arsenic, bismuth is the least toxic because of its low water solubility.\textsuperscript{24} While the World Health Organization (WHO) has set a standard of 10 ppb for lead in drinking water,\textsuperscript{25} in contrast, no limits have been imposed for bismuth. Finally, BiI\textsubscript{3} has a 1.8 eV band gap and high absorption coefficient.\textsuperscript{21} Using the absorption coefficient data presented by Brandt et al.,\textsuperscript{22} a 500 nm thick film would be sufficient to absorb 95\% of incident above-band gap photons. A 1.8 eV-band gap BiI\textsubscript{3} top cell would be well-matched with a 1.12 eV Si bottom cell, which would give a maximum theoretical efficiency of 45.3\% in a four-terminal tandem configuration.\textsuperscript{26}

Processing variables such as substrate temperature during physical vapor deposition or choice of solvent for solution processing\textsuperscript{21} greatly impact the morphology of the BiI\textsubscript{3} film. Bridgman growth\textsuperscript{27} and vacuum-based methods\textsuperscript{27} are well-developed techniques for making BiI\textsubscript{3} films. Solution-processing routes are less well-developed. BiI\textsubscript{3} has been solution-deposited from dimethylformamide (DMF),\textsuperscript{21,27} tetrahydrofuran (THF),\textsuperscript{27} and dimethyl sulfoxide (DMSO).\textsuperscript{28} In fact, bismuth trihalides are known to form coordination compounds with all of these solvents.\textsuperscript{28,29} These solvents are similar in that they possess Lewis base sites, which result in the formation of solvent and BiI\textsubscript{3} forming Lewis acid-base adducts. Hamdeh et al. have applied DMF solvent vapor annealing (SVA) on a spin-coated BiI\textsubscript{3} film from THF solution to grow large grains, and by this, they have achieved the highest power conversion efficiency (PCE) to date for a BiI\textsubscript{3}-based solar cell of 1.0\%.\textsuperscript{27} In SVA, films are heated in the presence of solvent vapor using solvents that have affinity for BiI\textsubscript{3}. The presence of solvent vapor increases the mobility of molecular species in the film and allows the film to reorganize and achieve larger grains. DMF SVA has been used previously in the hybrid perovskite to grow grains of 1 \(\mu\)m in diameter.\textsuperscript{30,31} However, SVA is sensitive to the environment, which causes severe reproducibility issues, and the key parameters, which have an impact on the morphology, are neither known nor understood. Furthermore, the key parameters, which have an impact on the morphology, are neither known nor understood. Further, state-of-the-art BiI\textsubscript{3} solar cells with a PCE of around 1\% suffer from significant current and voltage losses. The materials chemistry reasons for these deficiencies are not known to date.

Here, we address both issues. We present an investigation of important variables affecting SVA of BiI\textsubscript{3} films, such as temperature and water concentration. We used DMF as the SVA solvent as it forms a mildly stable BiI\textsubscript{3}–DMF complex,\textsuperscript{28} which plays a role in growing good morphologies. We show that tuning of water vapor concentration and temperature is crucial to grow large-grained, void-free solution-processed BiI\textsubscript{3} films and that the presence of ambient oxygen is less crucial. We present a mechanism for the action of both water and temperature. Through this understanding, we present an optimized SVA process for growing continuous BiI\textsubscript{3} films on TiO\textsubscript{2} substrates. For the first time, we apply absolute intensity photoluminescence (AIPL) measurements on BiI\textsubscript{3} films to assess the maximum possible open-circuit voltage and lateral dc photoconductivity measurements to assess the carrier transport. These measurements give us access to the two key parameters for solar cell operation, the quasi-Fermi level splitting (QFLS) and the average electron–hole diffusion length. By correlating different SVA processes with these material property measurements and PV device performance, we reveal the limiting factors for the low device performance.

\section*{RESULTS AND DISCUSSION}

\subsection*{Effect of Water, Temperature, and Solvent on Morphology}

Pre-SVA films are dense but small-grained (Figure 1a). SVA grows the grains (Figure 1b–c), but the morphologies are not always the same. We noticed that films prepared in the fume hood with SVA at 100 °C on different days have very different morphologies. These films were prepared under the exact same conditions, with the only difference being the humidities on these days. Indeed, it is known that relative humidity (RH) can have a significant influence on SVA.\textsuperscript{36} We see disconnected disk-shaped grains (Figure 1b), whereas films prepared at a different day showed large, uniform, and dense grains (Figure 1c). To better understand this, we treated BiI\textsubscript{3} films with SVA at different temperatures and RHs.

We prepared films treated with SVA at 0, 35, and 70% RH at 80, 100, and 120 °C both in a fume hood but also inside a glovebox to investigate the effect of ambient atmosphere. The relevant parameter behind RH is the activity of water, which is proportional to the vapor phase mole fraction. The vapor phase mole fraction is related to the water concentration, assuming that all water introduced during the start of SVA goes into the vapor phase. Water concentrations for a RH/T combination are given in Table S1. Multiplying this number by the SVA inner volume gives the total mass of water needed for SVA. It is this mass of water that was mixed with DMF to create the water–DMF SVA solvent mixtures. We observe that the SVA solvent is completely evaporated throughout the SVA process. Some minor solvent and water loss is expected as the SVA Petri dish volume gives the total mass of water needed for SVA. It is this mass of water that was mixed with DMF to create the water–DMF SVA solvent mixtures. We observe that the SVA solvent is completely evaporated throughout the SVA process.

Figure 1. Scanning electron microscopy (SEM) images of BiI\textsubscript{3} films grown on FTO/TiO\textsubscript{2} substrates (a) after spin-coating and before SVA; post DMF SVA on days with (b) lower RH and (c) higher RH.
rapidly evaporates. We developed a modified ink to prohibit cracking. Addition of 1–2 vol % DMSO to the THF inks prevented cracking and resulted in smooth films (Figure S2b). The colors of the pure THF and THF + DMSO films are different. The pure THF films are black after spin-coating owing to the rapid THF evaporation leaving a pure BiI₃ phase behind. The THF + DMSO films are dark red after spin-coating. This red color indicates the presence of a BiI₃−DMSO complex in the film. Within 20 min of exposure to ambient air, these films gradually turn black, indicating that the BiI₃−DMSO complex is not stable at room temperature and thus decomposes to leave behind the pure BiI₃ phase. This slow decomposition process accompanied by the evaporation of DMSO helps in obtaining uniform BiI₃ films and 0% RH (Figure 2a) remained orange until it was uncovered. This indicates that even though the Petri dishes are not sealed, they retain SVA solvent for the duration of SVA.

All films prepared with SVA at 80 °C and 0% RH (Figure 2a) remained orange until it was uncovered. This indicates that even though the Petri dishes are not sealed, they retain SVA solvent for the duration of SVA.

All films prepared with SVA at 80 °C turned orange during step 2 (solvent exposure) of the SVA process, independent of RH. However, the time it took the films to turn orange increases with RH. The film prepared at 80 °C and 0% RH (Figure 2a) turned completely orange within 30 s of solvent addition. For the same temperature, films prepared at 35% RH (Figure S5b) and 70% RH (Figure 2d) turned completely orange 7 and 9 min into SVA, respectively. The film prepared at 100 °C and 0% RH showed a nonuniform behavior: part of the film turned orange 60 s into SVA and part remained black (Figure S6a). The SEM images of the orange part of this film are shown in Figures 2b and S6b. This is in good agreement to our initial findings where we observed morphological differences with films treated with 100 °C SVA under different ambient humidities. The partial color change indicates that the portion of the substrate that turned orange experienced a higher DMF partial pressure than the portion that stayed black. The region that turned orange was the side of the substrate closest to the evaporator. During the final step of SVA, where the lid is opened so that the solvent could escape, all of the films that had turned orange during SVA immediately turned black again. No color change was observed for 100 °C + 35% RH (Figure S5e), 100 °C + 70% RH (Figure 2e), or any of the films made at 120 °C (Figure 2f). Visually, there is a difference between films that turned orange during SVA and those that stayed black: films that turned orange are hazy, whereas those that did not change color remain relatively shiny. The haziness of the films that turned orange during SVA comes from light scattering at larger domains (1–20 μm) that developed in the film (Figures 2a,b,d and S6b).

The films that changed color during SVA at 80 °C (Figures 2a,d and S5) have larger domains sitting on top of the films. Looking at the higher magnification images, we see that the film is primarily made of clusters of small (<100 nm diameter) grains. The film that experienced the plume of DMF (Figure 2b) consists of large platelets (~15 μm diameter). The differences between this case and the 80 °C cases are attributable to the high DMF concentration in the plume. All of the films that did not change color are similar (Figure 2c–f), consisting of apparent grain sizes of 300–500 nm diameter, as determined by SEM. This means that as long as the films do not change color during SVA, dense, large-grained films can be grown.
Films made inside and outside of a glovebox with the same SVA condition have similar morphologies. For instance, films made with SVA at 120 °C and 70% RH inside (Figure S7a) and outside (Figure S7b) a glovebox show similar SEM grain size (300–500 nm) and polydispersity. This shows that the ambient environment does not have a big impact on morphology. We will focus on films prepared outside a glovebox for the rest of our discussion. Full comparison of glovebox and air films is given in the Supporting Information (Figures S4 and S5).

**Mechanism behind the Effects of Water, Temperature, and Solvent.** We explain the role of SVA temperature and water concentration by considering the Bi$_3$I$_6$–DMF complexation chemistry. Norby et al.\textsuperscript{28} have determined via allowing the DMF to readily complex with the Bi$^{3+}$ center. The ionic character of the Bi$^+$ is a hard base, and the iodide anion is a soft base.\textsuperscript{40} As a result, Bi(DMF)$_8$ solvent complex is made with the Bi$^{3+}$ center to give a solvent complex crystal with a unit cell of Bi(DMF)$_8$–Bi$_3$I$_{12}$. Octahedral complexes such as Bi$_3$I$_4$ typically undergo ligand exchange via a dissociative interchange mechanism ($I_d$).\textsuperscript{39} In an $I_d$ mechanism, the bond with the incoming group is formed at the same time the bond with the leaving group is broken. In our case, the incoming group is the carbonyl on the DMF and the leaving group is an iodide anion. Bi$^{3+}$ is a Lewis acid of intermediate hardness. The oxygen in the DMF carbonyl group is a hard base, and the iodide anion is a soft base.\textsuperscript{40} As a result, Bi$^{3+}$ is expected to have a similar ability to complex with the carbonyl oxygen in DMF and the iodide. Furthermore, as has been shown by Sanderson et al., the bond dissociation enthalpy of the Bi–I bond is the smallest for the Bi–halides (i.e., the Bi–I bond is easier to break than other Bi–halide bonds).\textsuperscript{41} The character of the bond is largely ionic, and the large ionic radius of the iodide anion means it is held less strongly by the Bi$^{3+}$ center because of electron–electron repulsion between Bi and I. The ionic character of the Bi–I bond is critical for facile DMF complexation. The $I_d$ mechanism requires a good leaving group. Because the Bi–I bond is more ionic than covalent and thus more easily broken, the iodide makes a good leaving group, allowing the DMF to readily complex with the Bi$^{3+}$ center.

We first consider the water-free (DMF vapor only) 80 °C case. The spin-coated crystalline Bi$_3$I$_6$ film is made up of Bi$_3$I$_6$ octahedra arranged in two-dimensional (2D) sheets.\textsuperscript{21} Consider a single Bi$_3$I$_6$ octahedron exposed to DMF vapor. The DMF approaches the Bi$^{3+}$ center and begins to form a Bi–OR complex with the DMF carbonyl oxygen. At the same time, the Bi–I bond is being broken and the I$^-$ leaves. This reaction continues to take place until the Bi center is coordinated to eight DMF molecules [Bi(DMF)$_8$],\textsuperscript{39} which is charge-balanced by a [Bi$_3$I$_{12}$]$^{3–}$ group. If enough DMF is present, the entire film is transformed to a DMF–Bi$_3$I$_6$ coordination compound. This compound may crystallize with a unit cell composed of four Bi(DMF)$_8$–Bi$_3$I$_{12}$ pairs, as shown by Norby et al.\textsuperscript{28} We note that Bi$_3$I$_6$ also coordinates with DMSO and THF, the solvent system for our inks (a more detailed discussion about this can be found in the Supporting Information).

The Bi$_3$I$_6$–DMF coordination compound is the orange phase witnessed under low RH and low T. The solvent complex film is thicker than the Bi$_3$I$_6$ film because of DMF uptake. The unit cell volume of the Bi$_3$I$_6$–DMF solvent crystal is 6507.2 Å$^3$, and it contains four Bi(DMF)$_8$–Bi$_3$I$_{12}$ moieties, that is, a volume of 406.7 Å$^3$ per Bi$_3$I$_6$.\textsuperscript{28} Pure Bi$_3$I$_6$, in contrast, has a unit cell volume of 1016.7 Å$^3$ with six Bi$_3$I$_6$ moieties per unit cell,\textsuperscript{42} that is, a volume of 169 Å$^3$ per Bi$_3$I$_6$. This means that there is a volume increase and, concomitantly, a thickness increase of the orange phase of a factor of 2.4 compared with the Bi$_3$I$_6$ film. Upon drying, this film collapses back to the Bi$_3$I$_6$ film, which results in a different morphology relative to the initial (pre-SVA) Bi$_3$I$_6$ film. This can lead to very rough films with large Bi$_3$I$_6$ clusters, as shown in Figure 2a,d or to films with large disconnected platelets, as shown in Figure S6b. If a Bi$_3$I$_6$ film is exposed to DMF vapor for a much longer time than 9 min in our SVA process, then macroscopic morphologies can form, as shown in Figure S9.

Now, consider the case of SVA at higher temperatures ($T \approx 120$ °C). We did not observe the orange phase formation during SVA at this temperature with the DMF concentrations considered. To better understand this, we collected data to perform a van’t Hoff analysis (details in the Supporting Information). The reaction considered is 4Bi$_3$I$_6$ + 8DMF $\rightarrow$ [Bi(DMF)$_8$]$^{4+}$[Bi$_3$I$_{12}$]$^{3–}$. Bi$_3$I$_6$ films were placed in sealed vials with different DMF dosings. The Bi$_3$I$_6$ films were allowed to complex with the DMF at room temperature until the orange solvent complex formed. The vials were then heated in a box oven, slowly increasing the temperature until the films turned black again. From these temperatures, we get the equilibrium constant for the Bi$_3$I$_6$–DMF complexation. By plotting ln($K_a$) versus $1/T$, we can extract Δ$H_{\text{rxn}}$ and Δ$S_{\text{rxn}}$ for the system. On the basis of the stoichiometry of the above reaction, this yielded values of Δ$H_{\text{rxn}}$ of $\approx$ 3 ± 1 eV and Δ$S_{\text{rxn}}$ of $\approx$0.006 ± 0.003 eV/K per molecular of the coordination compound. If one assumes that each successive DMF addition has similar thermodynamics, the enthalpy and entropy are Δ$H_{\text{rxn}}$ of $\approx$0.4 eV and Δ$S_{\text{rxn}}$ of $\approx$0.0007 eV/K per DMF, respectively. This means that this reaction is enthalpically favorable up to 140 °C, at which point the entropic term begins to dominate. At temperatures exceeding 140 °C, no concentration of DMF would result in the films turning orange. The important point here is that at elevated temperatures, it is more favorable for the DMF to be in the vapor phase rather than to be complexed with Bi$_3$I$_6$. It is this effect that prevents the orange solvent complex from forming at higher SVA temperatures, independent of RH. For an efficient crystal growth during SVA, the maximum DMF concentration below the level which leads to the orange phase is desirable. Thus, our DMF concentration (10 ppm) during SVA is chosen so that the orange solvent complex forms up to a concentration below the level which leads to the orange phase. Therefore, we see between films prepared at 100 °C with 0 and 70% RH.

**Effect of Substrates on Film Morphology.** We spin-coated 200 mg/mL Bi$_3$I$_6$ in THF + 1–2 vol % DMSO onto FTO/TiO$_2$, FTO/ZnO, and ITO/Cu/ITO substrates. We observe significantly different film morphologies with the
different substrates. Films grown on TiO₂ (Figure 3a) are made of 300–500 nm densely packed grains. Films grown on ZnO (Figure 3b) are more polydisperse and contain small and large platelets with sharp edges. Films prepared on copper-doped nickel oxide (Cu/NiO₂) (Figure 3c) are also more polydisperse than the films grown on TiO₂ but also contain large (1 μm dia.) platelets. We rationalize these observations by noting that film−substrate surface energy differences can influence growth. In the cases where substrate surface energy is smaller than film + interface surface energies, island growth is expected. Other factors such as deposition temperature also can impact crystal growth. This means that by optimizing parameters such as deposition temperature also can impact crystal growth. In the cases where substrate surface energy is smaller than film + interface surface energies, island growth is expected. Other factors such as deposition temperature also can impact crystal growth. This means that by optimizing parameters such as deposition temperature also can impact crystal growth. In the cases where substrate surface energy is smaller than film + interface surface energies, island growth is expected. Other factors such as deposition temperature also can impact crystal growth.

Crystallographic Orientation. XRD spectra for BiI₃ films grown at different SVA temperatures and water vapor concentrations are shown in Figure 4a). The films that turned orange during SVA, that is, those grown at 80 °C (0% RH and 70% RH) and 100 °C (0% RH) show a pattern significantly different from the black ones. The most pronounced XRD peaks for those films are due to reflections at the (003), (006), and (009) planes, which belong to the same family of (001) planes. This indicates a texturing of those films. In contrast, the films that did not change color during SVA show much smaller peaks for the (001) planes. We observe pronounced reflections at (113) and (300) in these films, indicating less texturing.

To further study this texturing effect, we evaluate the texture coefficient (TC). The TC of a plane (hkl) is defined as

\[ TC(hkl) = \frac{I(hkl)}{I_{\text{powder}}(hkl)} \times \frac{\frac{1}{N}}{\sum \frac{1}{N}} = \frac{I(hkl)}{I_{\text{powder}}(hkl)} \times \frac{1}{N} \]

where \( I(hkl) \) is the measured intensity, \( I_{\text{powder}}(hkl) \) is the intensity of the powder diffraction, and \( N \) is the number of planes considered. A TC equal to 1 indicates no preferred orientation. The TCs for the (300), (113), and (003) planes are shown in Figure 4b for different SVA temperatures and water concentrations. All films that turned orange during SVA, that is, at 80 °C show a TC of around 3 for the (003) plane and of close to 0 for the (113) and (300) planes. We note that the same TCs are also observed for the films that turned orange during SVA at 100 °C, 0% RH (not shown in Figure 4b). This indicates a strong texturing: these films are oriented with their (003) plane predominantly parallel to the substrate; that is, the BiI₃ film is layered in such a way that the planes which contain edge-shared BiI₆ octahedra are parallel to the substrate. The films that did not change color do not show this texturing: TCs for the (003) and (113) planes are between 0.5 and 0.9, whereas the TC for the (300) plane is around 1.5. This indicates a slightly preferred orientation in such a way that the edge-shared BiI₆ planes are perpendicular to the substrate. Similar texturing has been found in BiI₃ films that have formed from BiI₃−DMSO complexes. Because the 2D sheets of edge-shared BiI₆ octahedra are only weakly connected by van der Waals forces, it is expected that in-plane transport should exhibit larger mobility than perpendicular to the 2D sheets. Hence, the films that turned orange during SVA should show a better carrier transport parallel to the substrate and worse transport perpendicular to the substrate plane than the films that did not change color. We will come back to this point later.

Optoelectronic Quality. We performed AIPL measurements at a PV device relevant excitation laser intensity comparable to one sun. PL measurements on BiI₃ films have been carried out previously, however, because the PL quantum yield (PLQY) is very low, those measurements used laser excitation intensities comparable to >100 sun. Here, we were able to measure BiI₃ AIPL at 1 sun effective intensity. This was enabled by both the high quality of the films and a modification to our measurement technique (see the Supporting Information for details).

The AIPL is peaked at 1.78 eV with a full width at half-max of 180 meV (Figure 5a, blue trace). This is very close to the measured band gap of 1.79 eV determined from UV−vis absorption measurements (Figure 5a, red trace). The fact that the PL peak is right at the band edge indicates that sub-band gap states should not cause a significant loss of voltage. From AIPL, we get the PLQY, which we used to calculate the QFLS (Figure 5b) with the method described in Braly and Hillhouse. The QFLS is an indication of the maximum voltage \( V_{oc} \) achievable by a solar cell device. QFLS is proportional to \( kT \ln(1/\text{PLQY}) \). Therefore, what may appear as larger differences in PLQY does not correspond to as large differences in QFLS. In Figure 5b, we also show the ratio of the measured QFLS to the Shockley−Queisser QFLS (QFLS₀) for a material with the same band gap, \( \chi = \text{QFLS}/\text{QFLS}_0 \). \( \chi \) may be considered to be the optoelectronic quality of the material. All films prepared at 80 °C as well as the film prepared at 100 °C with 0% RH have PLQY < 1 × 10⁻⁷. Those were the films that turned orange during SVA. The films prepared at 100 °C with 35 and 70% RH and all 120 °C films have PLQY values of 2 × 10⁻⁷. These films remained black during SVA.

The lower PLQY films were the films that had turned orange during SVA, whereas the higher PLQY values were obtained from the films that did not change color during SVA. PLQY was greater by 2–6 times in the films that did not change color during SVA. This may be understood as an effect of the grain
size. The films that turned orange during SVA have grains with diameters \( \leq 100 \) nm. The films that remained black have grains 300–500 nm in size. The differences in PLQY may be attributed to nonradiative recombination at the grain boundaries. The smaller grained films have a greater number of grain boundaries, meaning that nonradiative recombination would be greater. However, we cannot exclude differences in the bulk. Films that turned orange during SVA may have entrained DMF within the crystalline BiI\(_3\). This may give rise to different point defects and contribute to nonradiative recombination.

Coming back to our discussion on transport, a lateral dc photoconductivity method\(^{34,35}\) was used to estimate the lateral diffusion length to assess the impact of SVA on carrier transport. The diffusion length \( (L_D) \) determined from this technique is an average (root mean square) of the electron and hole diffusion lengths. A slight trend is observed toward higher diffusion lengths with increasing temperature and RH from 40 nm at 80 °C/0% RH to 55 nm at 120 °C/0% RH and 70 nm at 120 °C/70% RH, as shown in Figure 5c. Because these are lateral diffusion lengths, that is, the carriers flow parallel to the substrate, this behavior is contradictory to what we would expect from the above discussion on texturing of the films: carrier transport is expected to be better for films that turned orange during SVA (i.e., at 80 °C/0% RH and 80 °C/70% RH), which is obviously not the case. One likely reason for this is the much lower grain size of the films that changed color during SVA compared to the films that did not change color (see Figure 2), giving rise to significantly more grain boundaries, which reduces the carrier mobility. In addition, the lifetime of photoexcited carriers in the films that turned orange during SVA is significantly lower than that in the films that did not change color because of the higher recombination rate as indicated by the lower PLQY. Because the diffusion length is proportional to the mobility-lifetime product, the latter two effects counterbalance the beneficial texturing effects of the films that turned orange during SVA as compared to the films that did not change color.

**PV Devices.** We made PV devices to assess the impact of SVA on PV performance. An ideal band diagram (assuming no ion migration, intrinsic BiI\(_3\), no mass transport across the interfaces, and no surface chemistry/interface dipoles) and a device architecture schematic are shown in Figure 6a and the inset of 6b, respectively. We report current density versus voltage (JV) curves and time-dependent PCE (using maximum power-point tracking\(^{32}\)) under continuous simulated AM1.5G illumination. The best solar cell with the optimized SVA process (120 °C + 70% RH) has a stabilized PCE (Figure 6b, blue curve) of 0.51%. A device made from a film that turned orange during SVA (e.g., 80 °C + 70% RH) in the same architecture shows a much lower stabilized PCE of 0.04% (Figure 6b, orange curve).

This more than 1 order of magnitude lower PCE comes mainly from two factors, a significantly lower photocurrent and a much lower fill factor due to the s-shaped JV. We note that the lower photocurrent very likely stems from a much lower carrier diffusion length perpendicular to the substrate for the films that turned orange during SVA. This is expected from the texturing effects discussed above, the lower carrier lifetime due to the s-shaped JV, and the lower mobility due to the increased number of grain boundaries.

While the band alignment shown in Figure 6a suggests that an electric field should be present across the device to assist with carrier collection, if charged iodide vacancies migrate (as in hybrid perovskite solar cells) to screen the internal field, then carrier diffusion would have to be relied on for carrier
The relatively low diffusion lengths measured (70 nm) could then partly explain the low short-circuit current ($J_{sc}$) of 4.14 mA/cm². Another contributing factor to the low photocurrent could be the misalignment of the conduction band edges (CBES) of TiO₂ and BiI₃. An ab initio calculated value for the CB for BiI₃ is 4.1 eV, and the accepted value for TiO₂ is 4.2 eV below vacuum.²² These are very close, and if correct would not yield a barrier for electron extraction. However, if the actual band edge position of BiI₃ is different, it may cause a barrier for electron injection from BiI₃ into TiO₂.

The large differences between the light and dark curves suggest further device issues, such as a light-dependent saturation current, photoexcited carrier screening of electrostatic barriers at the interfaces (not shown in the band diagram), voltage-dependent photocurrent, and light-dependent shunt and series resistances. The table in Figure S10b shows the results of fitting the nonideal diode equation to the light and dark curves for the device made at 120 °C and 70% RH (Figure S10a). The reverse saturation currents ($J_0$), series resistances, and shunt resistances all differ by more than an order of magnitude.

With regard to the low voltage, the low diffusion length may play a role as well, as it signifies significant nonradiative recombination. Furthermore, the band alignment also likely plays an important role. With regard to the hole-extracting contact, the band edge of the spiro-OMeTAD lies 5.1 eV below vacuum,⁴⁷ and the position of the BiI₃ valence band is 6.0 eV below vacuum.²² While one would not expect a barrier for hole extraction, voltage could be lost because of the large offset between the BiI₃ valence band and the spiro-OMeTAD Fermi level.

**CONCLUSIONS**

We have explored the mechanisms behind the BiI₃ film formation process and demonstrated the roles that temperature and water play in the solvent annealing process for BiI₃ layers. We developed a reliable process for growing large-grained, continuous films. Films with small grains and poor morphologies result in reduced device performance and optoelectronic quality. Performing SVA with precise dosing of water and DMF grows uniform films with a SEM-based morphological grain size of 300–500 nm. Water acts to moderate the influence of DMF during the SVA process, allowing more controlled growth to occur. Higher temperatures also moderate the action of DMF.

We used highly concentrated BiI₃−THF inks (200 mg/mL) and observed severe cracking of the films upon spin-coating and drying. Modifying the ink chemistry by addition of 1–2 vol % DMSO, we successfully prevented film cracking and obtained homogeneous and smooth films.

Formation of the orange BiI₃−DMF complex during SVA at low temperatures results in films with a preferred orientation: the planes corresponding to the 2D sheets of BiI₃ octahedra are oriented parallel to the substrate. From diffusion length measurements and device characterization, we obtained clear indication for very poor transport in the direction perpendicular to these planes. The reason is the weak van der Waals interaction of these 2D sheets. This shows that for the structurally two-dimensional material BiI₃, the film texture is an essential parameter for its application in optoelectronic devices.

From AIP measurements, we determined a QFLS of 1.1 eV at 1 sun, which is a measure for the maximum photovoltage that can be obtained in a solar cell. This is a promising result because an optimized solar cell with BiI₃ as the absorber material only limited by this QFLS could achieve >15% PCE. A QFLS of 1.1 eV is 73% of the Shockley–Queisser limit for BiI₃, which indicates that there is still room for improvements via defect passivation. However, it also indicates that bulk nonradiative recombination is not the main reason for the low voltage of state-of-the-art BiI₃ solar cells. Both the large voltage deficit and current deficit seen in BiI₃ devices are a consequence of low diffusion length and nonoptimal band alignment.

This work reveals the mechanisms behind the film formation process of BiI₃ films, which are potentially also applicable to other metal halide materials. It further expands the understanding of the relationship between the chemistry and physics of BiI₃ films and devices, opening the door for improving device efficiencies. Further development of this material could enable it to become a competitor to PbI₂-based hybrid perovskites while avoiding the toxicity and potentially also the stability issues of the perovskite material.

**EXPERIMENTAL SECTION**

**Materials.** BiI₃ inks (200 mg/mL) were prepared by dissolving BiI₃ (99.999%, Alfa Aesar) in anhydrous THF (99.9%, inhibitor-free, Sigma-Aldrich) inside a N₂-filled glovebox. The inks were sealed and then mixed with an ultrasonicator immediately before use. Fluorine-doped tin oxide (FTO) substrates (14 × 14 mm²) (TEC 7, Sigma-Aldrich) were sequentially cleaned by sonication in a detergent solution, DI water, acetone, and 2-propanol for 10 min. Substrates were cleaned with an Ar plasma immediately before use. TiO₂ solutions were prepared by mixing 10 mL of ethanol (200 proof, Sigma-Aldrich), 69 μL of HCl (37 wt %, MCrion Fine Chemicals), and 0.727 mL of Ti(IV) ethoxide (Aldrich) and sonicating it for 30 min. This solution was spin-coated onto the FTO substrates in air at 2000 rpm for 15 s. Substrates were coated twice, with a 500 °C anneal in a box oven between layers. BiI₃ inks were deposited on the TiO₂-coated substrates by spin-coating at 2000 rpm for 35 s inside a N₂-filled glovebox and in a fume hood. After spin-coating, the films were solvent vapor-annealed for 10 min with DMF−water mixtures. SVA consists of three steps: (1) the as spin-coated BiI₃ film is set inside a Petri dish on a hot plate; (2) after 60 s, the solvent is added to the Petri dish with the film and the lid is closed; and (3) after 9 min, the lid is removed so that the film is exposed to the ambient atmosphere for 60 s to remove residual DMF and water. DMF volume was held constant at 6.4 μL, and water content was varied to achieve 0, 35, or 70% RH at 80, 100, or 120 °C. See Figure S1 and Table S1 in the Supporting Information for details on the SVA setup and water concentrations. Hole transport layers were prepared by spin-coating spiro-OMeTAD, as described elsewhere.⁹ The spiro-OMeTAD was doped with Li and Co and oxidized overnight. Devices were finished by thermal evaporation of 100 nm Au at a base pressure of 1 × 10⁻⁶ Torr.

**Characterization.** SEM images were collected at a 5 kV accelerating voltage with an FEI XL830 Dual Beam SEM/FIB. Crystallographic measurements were collected with a Bruker D8 Discover XRD. AIP measurements were collected at 1 sun photon flux with an apparatus described previously.¹²,³⁵ The 1 sun condition used corresponds to a photon flux of 1.28 × 10²¹ photons/s m² at a laser wavelength of 532 nm. A 150 lines/mm Czerny–Turner monochromator blazed at 500 nm was used to collect the signal. PLQY and the peak position were used to calculate the QFLS and the optoelectronic quality ($χ$).³⁵ PV
devices were tested in air using an AAA solar simulator (Oriel Sol3A) and a Keithley 2400 SMU. A photoconductivity method was used to determine the mean carrier diffusion length, using a bias of +20 V with a 432 nm blue light-emitting diode at 3.66 × 10³ photons/s m² flux, which is 2.8 sun equivalent for a 1.8 eV band gap material. Photoconductivity measurements were made inside a temperature-controlled stage held at 20 °C.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00813.

Additional experimental details, BiI₃ complexation with DMSO and THF, SEM images, and Lambert-W fitting of IV curves (PDF)

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Notes

The authors declare no competing financial interest.

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