Residual Film Stresses in Perovskite Solar Cells: Origins, Effects, and Mitigation Strategies

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ABSTRACT: Metal halide perovskites are an emerging class of materials that are promising for low-cost and high-quality next-generation optoelectronic devices. Despite this potential, perovskites suffer from poor thermomechanical and chemical stability that must be overcome before the technology is commercially viable. Key sources of the instabilities in perovskites are ion migration and defects that can be tied to high residual stresses accumulated in the perovskite thin films during processing. This Mini-Review serves as a general overview of residual thin-film stresses, specifically in perovskite solar cells. A brief introduction to the origin of residual stresses in thin films is followed by the effects of these stresses in perovskite films. Mitigation strategies for these stresses are then highlighted, followed by potential avenues of further exploration of residual stresses in perovskite films.

INTRODUCTION

Metal halide perovskites are solution-processable semiconductors with highly desirable optoelectronic properties including direct and tunable band gaps, long carrier diffusion lengths, high charge-carrier mobilities, and strong light absorbance.\(^1,2\) Perovskite-based thin-film photovoltaic devices exhibit power conversion efficiencies (PCEs) over 25%, comparable to mature technologies like crystalline silicon solar cells but at only a fraction of the material use.\(^3\) Furthermore, perovskite solar cells (PSCs) can be fabricated via high-throughput and low-cost roll-to-roll printing on flexible substrates, enabling applications that are not accessible with traditional rigid photovoltaic technologies, e.g., portable or wearable power harvesting.

Although perovskites are potentially disruptive materials in the optoelectronic technology space given their promise for high efficiency at a low cost, these materials are riddled with stability issues—degrading with exposure to moisture, heat, mechanical stresses, and electric fields—which currently limit the commercial viability of perovskite-based technologies.\(^4\) A primary cause of these instabilities is a high density of defects that arise during perovskite film growth, which can be attributed to the generally uncontrolled nature of solution-processed deposition.\(^5\) Defects in perovskite cause deleterious ion migration and trap states,\(^6\) ingress and egress of moisture,\(^7\) or nonradiative charge recombination,\(^8\) which act in concert to produce poor device performance and mechanical instability.

Addressing the chemical instabilities has been at the forefront of perovskite research since the discovery of the technology, while mechanical instabilities have only begun to be studied in recent years. These mechanical instabilities are particularly important for devices on the module scale, where shear stresses scale with device size and small impurities or defects can result in catastrophic failure of the devices through cracking and decohesion.\(^9,10\) The ability of a film to resist fracture propagation—i.e., its fracture resistance, \(K_c\)—and the critical stresses in the film (residual and applied), \(\sigma_c\), are related to each other by eq 1

\[
\sigma_c = \frac{K_c}{\Omega_s \sqrt{h_f}}
\]

where \(h_f\) is the film thickness and \(\Omega_s\) is the critical decohesion number. The critical decohesion number is a dimensionless quantity which depends on the ratio of the tensile modulus of the film (\(E_f\)) to the tensile modulus of the substrate (\(E_s\)) and the ratio of the film thickness (\(h_f\)) to the substrate thickness (\(h_s\)). In brittle films such as perovskite, cracking parallel to the substrate (i.e., decohesion of the film) occurs to relieve elastic energy stored in the film once tensile stresses within the film are greater than \(\sigma_c\).\(^11,12\) Conversely, relaxation of compressive stresses can result in buckling and delamination.\(^12,13\) In context of these potential failure mechanisms, residual stress formation in perovskite thin films and their effects on layer stability and behavior must be understood. While it is apparent that large...
residual stresses greater than $\sigma_c$ can lead directly to layer failure or delamination, smaller stresses also affect the film stability (Figure 1).

![Figure 1. Residual stresses in perovskite thin films form through differences in volume changes between the film and underlying substrate. These stresses can be tensile or compressive in nature, with effects being dependent on how large they are relative to the critical stress, $\sigma_c$.](image1.png)

In this Mini-Review, we will focus on residual stresses in perovskite thin films. First, we will give a brief overview of the characterization of thin-film stresses, followed by a discussion on the origin of the formation of residual stresses in thin films. Next, we will show how residual stresses affect perovskite properties and stabilities as well as strategies for addressing these stresses. Finally, we will discuss opportunities for further research in this area.

**CHARACTERIZATION OF THIN-FILM STRESSES**

Characterization of film stresses can be performed by nondestructive methods such as X-ray diffraction (XRD) or thin-film stress measurements by substrate curvature, or by destructive methods, such as focused ion beam milling with digital image correlation (FIB-DIC).$^{14-16}$ In studies on stresses in perovskites, the nondestructive methods are the most commonly utilized; however, FIB-DIC can provide useful complementary information, so we will briefly discuss all three of these approaches to measuring thin-film stresses.

Measuring stresses by XRD is also known as the XRD-$\sin^2 \psi$ method, where $\psi$ describes the tilt angle of the substrate. The XRD-$\sin^2 \psi$ method can be used with 1D or 2D measurements from either a standard or $\mu$XRD. In this method, the XRD scans are measured at varying tilt angles, and the $2\theta$ of the same diffraction peak as a function of tilt angle is determined. Assuming stresses are present, the diffraction peaks will shift with $\psi$, and $2\theta$ will be defined by the point of maximum X-ray intensity, the midpoint of the width at half-maximum intensity, the geometric center of the entire peak, or mathematical approaches.$^{14}$ Stresses are extrapolated from eq 2 by linear regression

$$d_{\psi\theta} = \left[ \frac{1 + \nu}{E_f} \right] \sin^2 \psi - \left( \frac{2\nu}{E_f} \right) \sigma_l d_0 + d_0$$

(2)

where $d_{\psi\theta}$ is the $d$-spacing of the lattice plane measured; $E_f$ is the Young modulus of the film; $\nu$ is the Poisson ratio of the film; $\sigma_l$ is the stress in the film; and $d_0$ is the $d$-spacing in the condition where the lattice is unstrained. A key benefit of the XRD-$\sin^2 \psi$ method is that it can provide information on the directionality of the stresses if measurements are taken both in-plane and out-of-plane relative to the substrate (Figure 2b). However, there are drawbacks, including a high degree of uncertainty in films that are highly granular and rough like polycrystalline perovskite films.$^{14}$

![Figure 2. Mismatch of coefficients of thermal expansion can result in residual stresses. (a) Schematic showing the two possible cases of coefficient of thermal expansion (CTE) mismatch between the film and substrate. Top: If the film has a higher CTE than the substrate, the film undergoes tensile strain upon cooling. Bottom: If the film has a lower CTE than the substrate, the film undergoes compressive strain upon cooling. Reprinted with permission from ref 6. Copyright 2020 Crown. (b) Schematic showing out-of-plane and in-plane XRD measurements and (c) the resultant XRD spectra showing that the perovskite films annealed on a substrate (AF) have lattice expansion normal to the surface and contraction parallel to the surface relative to free-standing single-crystalline perovskite (SCP). Reprinted with permission from ref 19. Copyright 2017 The Authors.](image2.png)

Global film stresses can be determined by thin-film stress measurement tools, which measure the curvature of a substrate due to stresses in thin films deposited on top. Typically, an array of laser spots is deflected off of a substrate, and the distance between these spots is measured; after thin-film deposition, the distance between these deflecting laser spots is again measured, and the differential in distance before and after thin-film deposition arises from film stresses curving the
substrate.\textsuperscript{10,15,17} These stresses can be approximated using Stoney’s equation\textsuperscript{10,15}

\[ \sigma_f = \frac{E_f t_f^2}{6t_h(1 - \nu)} \left( \frac{1}{R} - \frac{1}{R_0} \right) \]

where \( E_f \) is the Young modulus of the substrate; \( t_h \) is the Poisson ratio of the substrate; \( t_f \) is the thickness of the substrate; \( t_l \) is the thickness of the film; \( R \) is the radius of curvature of the substrate after film deposition; and \( R_0 \) is the radius of curvature of the substrate before film deposition. While this method is rather straightforward, the key shortcoming is that it is typically used to measure the average macrostrain over an entire sample and does not have the resolution to measure localized stresses grain-by-grain. If strain is heterogeneous in the film, like it often is in polycrystalline perovskites, the localized effects of stresses on densities of defects and trap states are immeasurable.\textsuperscript{18}

Focused ion beam milling with digital image correlation is a destructive stress measurement method that can provide information about localized stresses, and stresses as a function of material depth. Initially, a unique surface pattern is deposited on top of the region of interest. When using the ring-core method, this pattern comprises small spherical particles (e.g., 50 nm platinum nanoparticles), surrounded by a ring to prevent redeposition or damage during milling.\textsuperscript{16} Using the FIB, a trench is milled around the outside of the ring, and SEM micrographs are taken intermittently throughout the process. The stress at each of these increments can then be determined using DIC, which can correlate the positional movement of the spherical particles with stress/strain relaxation. While FIB-DIC can provide information about localized stresses, global film stresses cannot be measured by this technique. Furthermore, even with the use of the ring to prevent redeposition during milling, some redeposition occurs, and increasing noise in the data can occur as the milling depth increases.\textsuperscript{16}

While these measurement techniques have their relative strengths and weaknesses, together they provide a complementary suite of tools to fully characterize thin-film stresses. Combining these tools gives information about global and localized film stresses, with an understanding of directionality (i.e., in-plane versus out-of-plane stresses) and how stresses can change with depth.

\section*{ORIGINS OF RESIDUAL FILM STRESSES}

Residual stresses form in thin films during growth and/or deposition processes, with stresses originating from the differences in the relative volume change of the thin film and the underlying substrate after removal from processing conditions.\textsuperscript{9} Key driving forces for these differences in volume change include the coefficient of thermal expansion (CTE) mismatch and elimination of defects such as dislocations or grain boundaries.\textsuperscript{7} In the typical thin-film case, where the lateral dimensions of the film are much greater than its thickness, the stresses are predominantly biaxial (parallel to the substrate).\textsuperscript{9} At the film edges, interfacial shear and normal stresses play a larger role, which can result in decohesion that acts in concert with the biaxial stresses to propagate delamination of the film.\textsuperscript{9}

Residual stress development in thin films is most often linked to a mismatch of the coefficients of thermal expansion of the film and substrate.\textsuperscript{10,13,17} Film growth processes frequently occur at temperatures outside of the range of normal operating temperatures; after deposition, as the substrate and film reach their storage or operating temperature, the CTE mismatch drives differences in the relative volume change of the film and substrate. Despite these differences in relative volume change, the film and substrate have strong interfacial adhesion that pins them together and initiates stresses in the film. If the CTE of a film is greater than that of the substrate it is adhered to, the substrate will shrink less in the lateral dimensions upon cooling than the film would if it were free-standing, resulting in a tensile stress on the film (Figure 2a).\textsuperscript{6,10} Conversely, if the CTE of the film is less than that of the substrate, upon cooling, the substrate will shrink more than the film would if it were free-standing, and the stress will be compressive.\textsuperscript{6,10} The strains in these examples occur in-plane, while the strain out-of-plane is in the opposite direction (e.g., if the in-plane strain is compressive, the out-of-plane strain is tensile) to alleviate the inhibited in-plane strain (Figure 2b,c).\textsuperscript{19}

Another mechanism that leads to residual stress formation during thin-film growth is densification of the film by atomic diffusion to fill in defects, cavities, and grain boundaries.\textsuperscript{7} As atoms diffuse and fill previously unoccupied spaces, the thin film undergoes volume contraction relative to the substrate, applying a tensile stress to the film.\textsuperscript{1} Conversely, in two-step processes like those frequently used in ABX\textsubscript{3} perovskites, the opposite effect can happen. In the first step, a film comprising the B-site metal and X-site halide (but not A-site cation) is deposited, which is then converted to perovskite by a second step in which the A-site cation diffuses into this film. In the first step, strong interfacial interactions bond the film to the substrate. When the A-site cation diffuses into the film in the second step, volume expansion occurs in the film, but not the substrate, inducing a compressive stress in the film.\textsuperscript{20}

While the mechanisms leading to residual stresses described above are different, a generalizable rule is that if the relative volume changes of the film and substrate—particularly in the lateral dimension—are different, stresses will form within the film. These differences in relative volumetric changes distort the lattice of the films due to it being anchored to the substrate, which removes two degrees of freedom from which the film can expand/contract as it would if it were free-standing.

\section*{FILM STRESSES IN PEROVSKITES}

The underlying causes of residual stress formation in perovskite thin films are similar to those of other thin films and depend on film growth kinetics, substrate of growth, and deposition technique.\textsuperscript{10,13,20} In perovskites, the predominant driver of the formation of these stresses appears to be large CTE mismatches between the high-CTE perovskites and lower-CTE substrates.\textsuperscript{6,10,19}

During a one-step perovskite film growth process, the deposited film is initially wet and saturated with solvent. These wet films (i.e., not yet annealed or subjected to antisolvent treatment) will have no internal stresses because chemical interactions with the substrate are minimal and the film is still liquid-like enough to release stress through molecular motion.\textsuperscript{14} In this wet state, an intermediate phase complex is formed between the perovskite precursors and the solvent or other species present in the solution (e.g., additives to control crystallization kinetics); upon removal of the solvent, the intermediate is converted to perovskite, forming a polycrystalline film with strong interfacial interactions with the underlying
substrate that prevent free expansion and contraction of the film.\textsuperscript{10,13}

In a two-step process, the growth of a BX\textsubscript{2} film occurs in the first step; this film undergoes the same residual stress development as perovskite in a one-step process. During the second step, BX\textsubscript{2} is converted to the ABX\textsubscript{3} perovskite by the insertion of A-site cations. In these processes, the addition of the A-site cation after formation of the initial prefilm leads to a large lattice volume expansion; Tang and co-workers observed an expansion of nearly 218\% when converting PbBr\textsubscript{2} to CsPbBr\textsubscript{3}, resulting in large residual compressive stresses within the film, measured as high as \(-208.7 \pm 14.5\) MPa.\textsuperscript{20} In these cases, the properties of the BX\textsubscript{2} film strongly influence the final ABX\textsubscript{3} perovskite morphology; therefore, tuning the morphology of the BX\textsubscript{2} through the film crystallization temperature (i.e., changing the rate at which the solvent is driven out of the film) will change the residual stresses in the ABX\textsubscript{3} film.\textsuperscript{10}

Regardless of the number of growth steps, in films that have been annealed and then cooled, the extent of expansion/contraction inhibition in a film on the substrate relative to a free-standing film is related to the CTE mismatch between the film and substrate. The conversion of the wet precursor films into perovskite typically occurs at annealing temperatures of at least 100 °C, and in typical device architectures, large CTE mismatches induce large residual tensile stresses upon cooling to room temperature. These residual stresses are linearly related to the CTE mismatch and difference between the processing temperature and temperature at which the stress is measured, as described by the following relationship\textsuperscript{10}

$$\sigma_{\Delta T} = \frac{E_f}{1 - \nu_f} (\alpha_f - \alpha) \Delta T$$

(4)

where $\sigma_{\Delta T}$ is the stress that develops due to the temperature change; $E_f$ is the Young modulus of the film; $\nu_f$ is the Poisson ratio of the film; $\alpha_f$ is the CTE of the film; $\alpha$ is the CTE of the substrate; and $\Delta T$ is the change in temperature from the film annealing temperature. CTEs for a selection of common materials utilized in perovskite solar cells are shown in Table 1, demonstrating the large range of CTEs in different device layers. This table is not an exhaustive list and is meant to simply give orders of magnitude of various device layers. The CTE of glass—frequently used as a substrate for devices—is more than an order of magnitude lower than the CTE of perovskites, typically leading to large tensile stresses in the perovskite. Alternatively, polymer-based substrates exhibit CTEs closer to that of the perovskites, which should minimize stresses that form due to CTE mismatch during annealing of the perovskite films.

If residual stresses within a film are tensile, stress relaxation can occur through cracking; however, when residual stresses are compressive, the primary mechanism for stress release is through wrinkling of the film.\textsuperscript{12} While it is somewhat obvious why cracking is destructive to device performance, wrinkling can also cause device failure. With large enough compressive stresses, wrinkling can result in decohesion from the substrate, severing the charge transport pathway.\textsuperscript{12,13} Wrinkling has been observed in Cs\textsubscript{0.17}FA\textsubscript{0.83}Pb(Br\textsubscript{0.17}I\textsubscript{0.83})\textsubscript{3} perovskite grown by the antisolvent method, where thin-film stresses manifest as wrinkles with a periodicity of micrometers.\textsuperscript{13,36} In the antisolvent method, a secondary solvent in which the primary solvent is soluble but the perovskite is not is dripped onto the film during formation. This process extracts the primary solvent quickly, forming an intermediate which is constrained to the substrate and resulting in the formation of a compressive stress which causes wrinkling in the perovskite films. Bush et al. measured the residual stresses of the film in this state to be compressive at \(-21.6 \pm 3.0\) MPa.\textsuperscript{13} This compressive stress was attributed to the volume change, resulting from the removal of the DMSO by the antisolvent and conversion of the DMSO-PbI\textsubscript{2} intermediate to perovskite. The wrinkling was found to be controllable by the rate of film formation through tuning the solvent and perovskite compositions, with slower perovskite formation decreasing the wrinkling (and compressive stress). After annealing the perovskite at 100 °C for 30 min, the substrate constraint led to an in-plane compressive stress which is partially released by the formation of wrinkles. This annealing step drove the stress from compressive to tensile, with a measured tensile stress of 35.7 ± 4.2 MPa. Despite the transition from compressive to tensile stresses after annealing, the wrinkling of the perovskite remained. This observation was confirmed in a follow-up study where residual stresses were again found to be independent of the antisolvent used for film formation, with the conclusion reached that once the perovskite forms it essentially "freezes" in the stresses.\textsuperscript{10} It is possible that using rapid solvent extraction to intentionally induce large compressive stresses in the intermediate form of the perovskite could possibly limit the tensile stresses once full perovskite conversion occurs. However, it is unclear how much "memory", if any, the fully converted perovskite film has of the stresses in the intermediate state. Furthermore, ever higher compressive stresses could potentially result in delamination of the perovskite layer and catastrophic device failure.

The thermomechanical stability of module-scale perovskite photovoltaics in the field is highly dependent on the cohesive fracture energy, or $G_c$ of the perovskite. Critically, Rolston et al. demonstrated that a decreased $G_c$ in perovskites was correlated with increased residual tensile stresses.\textsuperscript{10} It was observed that the fracture energies of perovskites with mixed cations and/or halides decreased monotonically with increasing annealing temperature, which also correlated with increasing residual stresses due to CTE mismatch with the substrate.\textsuperscript{70} As stated above, the fracture behavior of a material is an important consideration when designing module-scale

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**Table 1. Coefficients of Thermal Expansion, $\alpha$, Young’s Modulus, $E$, and Poisson’s Ratio, $\nu$, of Some Materials Commonly Included in Perovskite Photovoltaic Devices**

| Material                        | $\alpha$ (10\textsuperscript{-6} K\textsuperscript{-1}) | $E$ (GPa) | $\nu$ |
|--------------------------------|-----------------|----------|------|
| glass                          | 3.7\textsuperscript{19} | 73\textsuperscript{21} | 0.162\textsuperscript{22} |
| silicon                        | 2.6\textsuperscript{10} | 130\textsuperscript{21} | 0.28\textsuperscript{3} |
| polyethylene terephthalate (PET) | 20\textsuperscript{10} | 4.6\textsuperscript{24} | 0.38\textsuperscript{25} |
| polycarbonate (PC)             | 65\textsuperscript{10} | 2.3\textsuperscript{3} | 0.37\textsuperscript{6} |
| indium tin oxide (ITO)         | 8.5\textsuperscript{19} | 210\textsuperscript{27} | 0.3\textsuperscript{7} |
| methylammonium lead iodide (MAPbI\textsubscript{3}) | 61.19 | 20.5\textsuperscript{28} | 0.33\textsuperscript{9} |
| formamidinium lead iodide (FAPbI\textsubscript{3}) | 203\textsuperscript{30} | 11.1\textsuperscript{31} | 0.3\textsuperscript{2} |
| formamidinium lead bromide (FAPbBr\textsubscript{3}) | 150\textsuperscript{33} | 11.2\textsuperscript{31} | –   |
| cesium lead iodide bromide (CsPbI\textsubscript{3}) | 84\textsuperscript{6} | 23.8\textsuperscript{34} | 0.3\textsuperscript{4} |
| 2D phenylammonium lead iodide (PbA\textsubscript{2}PbI\textsubscript{4}) | 109.4\textsuperscript{35} | – | –   |
| PDCBT                           | 315\textsuperscript{8} | – | –   |

\(\text{“Denotes property reported here is an average of multiple crystallographic orientations reported in the reference.”}\)
devices, and a material with a higher $G_e$ is more likely to survive the demands of in-field operation. Regardless, as the $G_e$ decreases and residual tensile stresses increase with annealing temperature, it can be expected that at some point the residual stresses are higher than the fracture energy, and delamination could occur spontaneously.

Aside from catastrophic failure of charge transport pathways via cohesive or adhesive fracture, residual stress can lead to reduced performance and stability of devices.\(^\text{10,19,35}\) Residual stresses weaken intermolecular bonds through lattice strain, decreasing the activation energy for ion migration—a concept demonstrated by Huang and co-workers in multiple perovskite compositions.\(^\text{19}\) The authors measured the extent of strain in MAPbI\(_3\) perovskite thin films by comparing XRD spectra of films to perovskite powders scraped from these films. Using XRD provided flexibility with the measurement angles, allowing probing of the strain both in-plane and out-of-plane. The XRD peak shifts to higher diffraction angles represent smaller lattice spacing and are therefore due to compressive stresses; likewise, XRD shifts to lower angles are due to tensile stresses. Both in-plane and out-of-plane XRD spectra were taken, and it was determined that the thin film was under tensile strain in-plane of the substrate and under compressive strain out-of-plane of the substrate.\(^\text{19}\) This observation was also found to be composition independent with FA\(_{0.85}\)MA\(_{0.15}\)Pb\(_2\)(I\(_{0.85}\)Br\(_{0.15}\))\(_3\) and Cs\(_{0.05}\)(FA\(_{0.95}\)MA\(_{0.05}\))\(_{0.95}\)Pb(I\(_{0.85}\)Br\(_{0.15}\))\(_3\) perovskites both exhibiting lattice strain. The activation energies of ion migration in MAPbI\(_3\) perovskite under different strains (convex, flat, and concave) with 0.2, 0.47, and 0.62% out-of-plane strain, respectively after 500 h of continuous illumination. (c) XRD spectra showing the development of PbI\(_2\) in the more strained films after illumination. Reprinted with permission from ref 19. Copyright 2017 The Authors.

\[ E_a = \frac{G_e}{\Delta T} - \frac{\gamma}{\rho} \]

\[ \Delta T = T_{	ext{final}} - T_{	ext{initial}} \]

\[ \gamma = \text{fracture energy} \]

\[ \rho = \text{density} \]

\[ G_e = \text{modulus of elasticity} \]

Upon examination of eq 4, it is apparent that strategies to reduce residual tensile stresses in metal halide perovskites should focus on reducing $(\sigma_t - \sigma_c)$ and $\Delta T$, given that the Young’s moduli and Poisson’s ratios of metal halide perovskites do not vary greatly across different compositions (Table 1). To date, four strategies have been demonstrated to successfully mitigate residual stresses within metal halide perovskite thin films: (1) reduction of the perovskite conversion temperature; (2) use of substrates with CTEs that better match the perovskite; (3) use of a buffer layer to mitigate CTE or lattice mismatch between the perovskite and substrate; and (4) postprocess inclusion of organic additives to accommodate stress (Figure 4).

The first approach to reduce residual stresses in perovskite films is to decrease the conversion (or annealing) temperature, which typically occurs at or above 100 °C. These high temperatures remove all residual solvent and completely convert the wet intermediate film to perovskite crystals but lead to a large temperature differential between processing and storage of at least 75 °C. For example, the tensile stress of cesium methylammonium formamidinium lead iodide bromide perovskite Cs\(_{0.05}\)(FA\(_{0.95}\)MA\(_{0.05}\))\(_{0.95}\)Pb(I\(_{0.85}\)Br\(_{0.15}\))\(_3\) (CsMAFA) formed in a diethyl ether bath and annealed at 100 °C was measured to be 57.6 ± 4.9 MPa.\(^\text{10}\) However, by eliminating the annealing step and instead allowing the perovskite to form at room temperature over 12 h, the residual stress was reduced to $−10.8 \pm 15.2$ MPa—a compressive rather than tensile stress (Figure 5a). The decrease of tensile stress to compressive stress was shown to improve the phase stability of perovskite (in this case MAPbI\(_3\) on PET) under separate high temperature (85 °C, 25% relative humidity) and high humidity (25 °C, 85% relative humidity) conditions (Figure 5b). The downside to this strategy—at least in this case—is that the conversion to perovskite may not be as complete, and the devices exhibited reduced performance. CsMAFA devices made by annealing at 100 °C had measured PCEs of 16.4 ± 1.4%, while those without the annealing step had substantially lower PCEs of 14.1 ± 0.8%. Another relatively low-temperature process was reported by Hovish et al., that was able to more completely convert the perovskite.\(^\text{17}\) This process, dubbed rapid spray plasma processing (RSPP), utilized atmospheric plasma to rapidly convert the perovskite intermediate that has been spray-coated onto a substrate by

**Figure 3.** Ion migration in MAPbI\(_3\) films under different strain conditions results in poor stability. (a) Activation energy, $E_a$ for ion migration as a function of tensile strain and lighting conditions. Ions are more mobile with increased strain and illumination. (b) Perovskite films under different strains (convex, flat, and concave) with 0.2, 0.47, and 0.62% out-of-plane strain, respectively after 500 h of continuous illumination. (c) XRD spectra showing the development of PbI\(_2\) in the more strained films after illumination. Reprinted with permission from ref 19. Copyright 2017 The Authors.

\[ \sigma_t = \text{tensile stress} \]

\[ \sigma_c = \text{compressive stress} \]

\[ G_e = \text{modulus of elasticity} \]

\[ \Delta T = T_{	ext{final}} - T_{	ext{initial}} \]

\[ \gamma = \text{fracture energy} \]

\[ \rho = \text{density} \]
an ultrasonic spray head. The use of reactive plasma species yielded complete perovskite conversion at lower temperatures and resulted in tensile stresses in \( \text{Cs}_{0.05}\text{FA}_{0.95}\text{Pb/(Br}_{0.17}\text{I}_{0.83})_3 \) as low as \( 4.0 \pm 1.5 \text{ MPa} \), much lower than the \( 49.3 \pm 3.2 \text{ MPa} \) for a sample with identical composition that was spin-coated and annealed at \( 100 \degree \text{C} \). Again, these devices had poorer PCEs than the controls (10% for RSPP compared to 13% for the controls), but greatly improved stability with PCE retention of 125% after 12 h of maximum power point (MPP) tracking in ambient air compared to a PCE retention of less than 75% for the spin-coated control under the same conditions.

Another straightforward approach to reduce residual stresses is minimization of the CTE mismatch between the perovskite and substrate, i.e., reducing the \( \alpha_s - \alpha_f \) term from eq 4. The effectiveness of this strategy was demonstrated by comparing residual stresses in CsMAFA when deposited on different substrates.\(^{10}\) When grown on a silicon substrate (CTE ~ \( 2.6 \times 10^{-6} \text{ K}^{-1} \)) and annealed at \( 100 \degree \text{C} \), a tensile stress of \( 54.0 \pm 8.2 \text{ MPa} \)—high enough to deform copper—was measured in the CsMAFA.\(^{10}\) Polymeric substrates generally have higher CTEs than inorganic substrates due to their weaker intermolecular bonding; replacing the silicon with polycarbonate (CTE ~ \( 65 \times 10^{-6} \text{ K}^{-1} \)) thus resulted in a greatly reduced tensile stress in the CsMAFA of \( 11.8 \pm 2.0 \text{ MPa} \) (Figure 5c). While the residual stresses were not measured in more commonly used substrates such as glass (CTE ~ \( 3.7 \times 10^{-6} \text{ K}^{-1} \)) and polyethylene terephthalate (\( \sim 20 \times 10^{-6} \text{ K}^{-1} \)), it is expected that perovskite on PET would be under less tensile strain than on glass. The trade-off for this approach is that the relatively low glass transition temperatures of these polymeric substrates are not amenable to high-temperature processing and may limit the potential materials used in the device stack. However, a multipronged approach to limit residual stresses using polymeric substrates and reduced perovskite conversion temperatures is likely to be successful, albeit with a modestly reduced device performance.

Residual stresses in perovskites have also been relaxed by introducing buffer layers (or charge transport layers) with high CTEs.\(^{6}\) A key advantage of this approach is that it does not require a reduction in perovskite annealing temperature and thus ensures that the formed perovskite is of high quality and...
that the devices exhibit high efficiencies. Sargent and co-workers employed this approach using a high CTE hole-transport layer (HTL), poly[5,5-bis(2-butyloctyl)-(2,2-bithiophene)-4,4’-dicarboxylate-alt-5,5’-2,2’-bithiophene] (PDCBT), which has a plethora of carbonyl groups that interact strongly with the perovskite and allow strain transfer into the HTL. Using these strong interfacial interactions, the residual strain of the perovskite could be tuned through processing and could actually be driven toward a compressive strain (Figure 5d). This hypothesis was tested by coating PDCBT onto CsPbIBr perovskite—an all-inorganic perovskite that requires annealing temperatures of 160 °C—while the latter was heated at different temperatures ranging from 60 to 120 °C. Film stresses of the CsPbIBr were measured, and it was found that the film stress was tensile if the PDCBT was coated onto perovskite heated below ~80–90 °C and compressive when coated onto perovskite heated higher than 90 °C, showing that the high CTE of the PDCBT could overcome the stresses applied to the perovskite by the low CTE substrate. By driving the residual strain from tensile to compressive, the efficiency increased from 14.8% for devices coated with PDCBT at 60 °C to 16.0% for devices coated with PDCBT at 120 °C. Furthermore, the thermal stability of films under compression was greatly improved relative to those under tension. Films under 1.5% compressive stresses had unchanged PL and absorbance spectra after annealing at 85 °C for 60 h, while films under 1.5% tensile strain presented noticeable shifts in the spectra (Figure 5e,f). Importantly, devices under compressive strain exhibited full PCE retention for 60 h of MPP under continuous 1-sun illumination, while devices under tensile strain degraded to just 50% of the initial PCE after just over 10 h (Figure 5g). These improvements in efficiency and stability were attributed to the increase in the activation energy for ion migration from 0.547 eV for films under 1.5% tensile strain to 0.794 eV for films under 1.5% compressive strain.

Interestingly, the reduction in residual stresses with the addition of PDCBT was contradictory to the findings by Rolston et al., who found that residual stress was independent of the charge transport layer (NiO or PTAA) and instead dominated by the substrate. It is possible that having a high CTE layer above the perovskite contributes to stress reduction more readily than one below it, but further exploration is necessary to understand the differences in the mechanisms.

Aside from reducing the processing temperature or minimizing CTE mismatch between the substrate and perovskite, it is also possible to modulate lattice distortions to reduce the residual stresses within the perovskite thin film. In one example, octylammonium iodide (OAI), a bulky additive comprising eight carbons adjacent to ammonium, was incorporated into A-site vacancies of (FAPbI3)0.85(MAPbBr3)0.15 perovskite films during post-treatment, reducing residual tensile stress at the perovskite surface by over 40% from 77.7 to 45 MPa. This pronounced decrease in tensile stresses was attributed to the more flexible organic cations, accommodating stress to minimize lattice distortion. The reduced stresses were identical at concentrations of OAI between 5 and 20 mM; however, a similar experiment which replaced OAI with phenethylammoniumiodide (PEAI) was found to have a concentration dependence, with the maximum decrease in tensile stresses occurring at a concentration of 20 mM. This difference in behavior with concentration was attributed to OAI being more readily inserted into the perovskite structure than PEAI, meaning that a critical uptake could be achieved at lower concentrations. Devices fabricated with a concentration of 10 mM OAI showed improved device performance (21.48% compared to just 20.02% for the pristine devices) and stability in ambient conditions (95% PCE retention compared to 82% for pristine devices after 1000 h). It should be noted that additives also improve efficiency and stability by passivating defects and adding hydrophobicity to the films, making it challenging to deconvolute the effects of passivation, hydrophobicity, and stress reduction on efficiency and stability; however, this avenue of stress reduction is a potentially interesting area for further exploration.

**OPPORTUNITIES FOR FURTHER WORK**

While residual stresses have been studied in thin films for decades, this area of exploration is relatively new in metal halide perovskites. As such, there are many potential areas of exploration, including a few of which we highlight below.

Stresses can induce phase transitions by reducing the transition energy barrier through lattice deformations. This driving force for phase transition was shown as a positive effect in a nonmetal halide perovskite BaTiO3, where a cubic-to-tetragonal phase transition could be forced at relatively lower annealing temperatures with applied tensile stresses. The tensile stress induced a synergistic shear stress above the critical shear stress, inducing lattice slide and a phase transition at a temperature almost 900 °C lower than it would otherwise occur (575 °C vs 1432 °C). It is possible that this same strategy could be applied to induce a tetragonal-to-cubic phase transition in MAPbI3 at room temperature. Given that this phase transition typically occurs within the operating temperature of perovskite devices (~54 °C), eliminating the mechanical stresses associated with phase change during operational thermal cycling in the field would likely be beneficial to the mechanical stability of the device.

The inclusion of additives directly into the perovskite precursor inks is another approach that could reduce the residual stresses in perovskite films. Additives typically interact with the perovskite precursors in solution through Lewis acid–base interactions, generating coordinated bonds that reduce the free energy of nucleation, forming more uniform films with less defects. The reduction of defects during crystallization can prevent the accumulation of residual stresses, and the relatively compliant organic additives can also potentially relax stresses. As discussed above, this strategy to reduce residual stresses has been successfully demonstrated via post-treatment of (FAPbI3)0.85(MAPbBr3)0.15 perovskite films with OAI and PEAI. In another example, the amino acid 5-aminovaleric acid (5-AVA), was incorporated directly into MAPbI3 precursor ink at a 5 mol% concentration. While the residual stresses were not directly measured, the fracture energy, $G_f$, was found to increase 1200% with the inclusion of 5-AVA from 0.53 ± 0.17 J m$^{-2}$ to 6.04 ± 2.04 J m$^{-2}$. This increased fracture energy was attributed to improved energy dissipation around the grain boundaries by the 5-AVA. There was an observed trade-off in efficiency with the inclusion of 5-AVA in this case, with a decrease from 13.7 ± 1.4% to 12.4 ± 1.0%, but the effect could possibly be mitigated by optimizing the additive and its concentration.

Heterogeneous strain occurs on the microscale within perovskite films and has significant effects on local optoelectronic properties. Stranks and co-workers mapped localized strain using μXRD and then correlated it to optoelectronic
CONCLUSIONS
Residual stresses that develop during the growth of perovskite thin films are typically large and can lead to poor device performance and degradation. So far, there is a dearth of literature on residual stresses and their impacts; however, as perovskite optoelectronic technologies mature toward commercial viability, it is becoming increasingly important to study and develop methods to limit the formation of these destructive stresses. In perovskite, these stresses form predominantly through stress accumulation during annealing as a result of CTE mismatch between the perovskite and substrate, but other pathways such as densification of growing films can also lead to stresses.

In this review, we identified four strategies that have been demonstrated to successfully mitigate large residual stresses in perovskites: (1) reduction of the perovskite conversion temperature; (2) use of substrates with CTEs that better match the perovskite; (3) use of a buffer layer to mitigate CTE or lattice mismatch between the perovskite and substrate; and (4) postprocess inclusion of organic additives to accommodate stress.

Initial studies in the field have laid promising foundations to characterize and address these stresses, but significant areas of note remain unexplored. For example, devices in the field are subjected to thermal fluctuations, which in turn will lead to stress fluctuations given the relative differences in the perovskite and substrate CTEs. How do the perovskite devices handle these stress fluctuations over time? Furthermore, it is apparent that tensile stresses are generally deleterious to perovskite performance and stability, but it is still unclear if compressive stresses are generally beneficial. If compressive stresses are found to be beneficial, it is to be expected that there is a critical amount of compressive stress beyond which the benefit is lost—certainly if the stresses are high enough to delaminate the perovskite from the underlying substrate. Harnessing these stresses to drive desirable behavior, such as a more stable phase transition in MAPbI₃ or tuning band gaps intrinsically, is also of great interest. The above questions just scratch the surface of an area that we believe is ripe for exploration. While this Mini-Review was intended to provide a brief overview of the topic, we hope that it piques interest and sparks new ideas in this emerging research area.

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Notes
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Adam D. Printz earned his PhD in Nanoengineering at the University of California, San Diego. There, he worked in the lab of Prof. Darren Lipomi, focusing on the co-optimization of the mechanical compliance and electronic performance of polymer-based solar cells. He then completed his postdoctoral work at Stanford University in the lab of Prof. Reinhold Dauskardt where he worked on improving the thermomechanical stability of perovskite solar cells. He is now an assistant professor in the Department of Chemical and Environmental Engineering at the University of Arizona, where his research is focused on improving the scalability of printable electronics.

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