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Post-processing techniques of temperature annealed $MAPbI_3$-perovskite

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Teemu Uusi-Rantala

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Author: Teemu Uusi-Rantala

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The world is at the turning point between green and fossil energy. New and innovative ways to generate electricity are needed. Perovskite solar cells have proved to be efficient and cost effective in the energy sector. The challenges with perovskite cells are their stability and finding efficient fabrication methods. Post-processing is a critical step in the fabrication process, and it can improve perovskite films crystallinity and grain size noticeably. Bigger and more uniform grains result in less grain boundaries and defects in the structure. Less reacting surface due to smaller grain boundary area affects the stability of the cell. In addition to grain size, internal stress can affect the stability. The changes in crystallinity improve the absorption coefficient and result in higher maximum photocurrent generated by the cell and lower internal stress. There are many possible post-processing techniques of which temperature, microwave, laser, UVA and electrode annealing are discussed in this literature review. The best stability was achieved with laser and microwave annealing because internal stress was relieved and there were less point defects. The biggest grain size was achieved by specific temperature annealing technique. The best techniques for large-scale production are microwave, UVA and electrode annealing because they can be easily modified to continuous processing with good film stability.

Keywords: perovskite, post-processing, annealing, $MAPbI_3$

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Maailma on käännekohdassa vihreän ja fossiilisen energian välillä. Tarvitaan uusia ja innovatiivisia tapoja tuottaa sähköä. Perovskiittiaurinkokennot ovat osoittautuneet tehokkaiksi ja kustannustehokkaiksi energiasektorilla. Perovskiittikennojen haasteina ovat niiden vakaus ja tehokkaiden valmistusmenetelmien löytäminen. Jälkikäsittely on kriittinen vaihe valmistusprosessissa, ja se voi parantaa perovskiittikalvojen kiteisyyttä ja raekokoa huomattavasti. Suurempien ja tasaisempien rakeiden vuoksi kalvoissa on vähemmän raerajapintaa ja rakenteessa olevia virheitä. Pienemmän raerajan pinta-alan vuoksi pienempi reagoiva pinta vaikuttaa kennon vakauteen positiivisesti. Kidekoon lisäksi sisäinen jännitys vaikuttaa paljon vakauteen. Kiteisyyden muutokset parantavat absorptiokerrointa, mikä johtaa kennon tuottamaan suurempaan maksimivalovirtaan. Mahdollisia jälkikäsittelytekniikoita on monia, joista tässä työssä on käsitelty lämpö-, mikroaalto-, laser-, UVA- sekä johdinkäsittely. Paras vakaus saavutettiin laser- ja mikroaaltokäsittelyllä, koska näissä sisäinen jännitys on paljon pienempi ja niissä on vähemmän pistevirheitä. Suurin kidekoko on edelleen tiettyjen lämpökäsittelytekniikoiden hallussa. Parhaat tekniikat teolliseen tuotantoon ovat mikroaalto-, UVA- sekä johdinkäsittely niiden liukuhihnatuotannon mahdollisuuksien ja kalvon hyvän vakauden vuoksi.

Avainsanat: perovskiitti, jälkikäsittely, hehkutus, $MAPbI_3$

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1 Introduction

At the moment world is experiencing a leap from using fossil energy to producing renewable energy from various sources. The global target of generating renewable electricity is set to 11.2 TW in 2030. [1] This target is not reached with the current annual proceedings. [1] Solar panels are contributing their bit in this challenge. Solar panel prices are getting lower due to increase in supply. However, manufacturing of the silicon solar cells needs huge amounts of energy. Efficiency of the silicon panels could also be improved. Perovskites could solve the problems in manufacturing energy consumption and efficiency. Now perovskites face challenges in stability and durability which make the commercialization harder. [2] These challenges are very important to overcome to make perovskite solar cells (PSC) suitable for large scale energy production.

To improve PSC's power conversion efficiency, the improvement of the PSC films crystal structure and grain size is important. Chemicals like lead and iodide are affordable and suitable chemicals to be used in perovskite solar technology. This is why perovskite is a cost-effective material to process [3], [4] with a wide range of usable applications. Perovskite is being studied because of its lower price and because it has many suitable material properties. Optimized PSCs have high potential in efficiency, semi-transparency, flexibility, recyclability, sustainability, low weight and a wide bandgap. [4] Perovskites are cheaper than silicon and with their help the price of the solar panels could be reduced. [2]

This literature review focuses on different post-processing techniques to improve perovskite thin films grain size, crystallization and optical properties. Perovskite acts as an active light absorbance layer in the solar cells. [2] The problem with perovskite technology is the challenge in large scale post-processing crystallization. Temperature annealing works well with small area films. Larger areas fabricated with temperature annealing techniques result in poor crystallization and large amount of grain boundaries that challenge charge carrier lifetime. [2] In addition temperature annealing is not energy efficient.

2 Perovskite structure

Natural perovskite is a mineral originally found in the Ural Mountains and later named after Russian geologist Lev Perovski. [4] The mineral consists of titanium, calcium and oxygen in the structure named perovskite structure. [4] Nowadays any material that has a perovskite structure is called a perovskite. [3] This means that the name perovskite does not refer to original mineral found in Ural Mountains but the crystal structure of the chemical.

PSCs are mostly fabricated of organic ions, metals and halogens. These metal-halide perovskites have advantages like high absorption coefficient, low binding energy for excitons, high mobility of electrons, and long diffusion length. [5] A thin perovskite film acts as an active layer and absorbs visible light. Absorbed energy excites electrons, which generates electricity. [3], [5] Perovskite requires a thinner active layer than silicon [3] and the crystallization energy barrier (56,6-97,3 kJ/mol) is much lower for perovskite. [6] The lower energy need means that also lower energy annealing methods can be used to improve the crystal structure. PSCs are made of different atoms regarding the wanted properties. Methylammonium lead iodide is one of the most common ones. However, lead is not safe to humans, environment or animals, so researchers are trying to find an environmentally friendly and non-toxic solution. [7]

Perovskite structures are usually described as having one anion and two cations. The lattice is named ABX_3.[5], [8] A is a monovalent cation, B is a divalent cation, and X is a monovalent anion. [5] This is a structure for all perovskites. In the studied perovskite $MAPbI_3$ (MAPI) the methylammonium CH_3NH_3 (MA) is the A cation, lead Pb is the B cation and iodide I is the X anion. Perovskite has different structural phases in different temperatures. In the highest temperature phase, the MAPI has cubic structure. [9] By lowering the temperature, the structure changes first from high temperature cubic (α-phase) to tetragonal (β-phase) and further orthorhombic (γ-phase). [9], [10]

The structures cannot be seen with eyes or sometimes even with microscope so there are different ways to study them. X-ray diffraction (XRD) and transmission electron microscopy are used to reveal atomic scale crystallography and strains. [11] Scanning electron microscopy (SEM) is used to gain information of the grains size and grain boundaries. [12] MAPI-perovskite β-phase has multiple peaks in XRD (Figure 1). The highest peaks can be seen commonly at (110), (220) and (310). [13] The peaks are a result of the constructed interference of X-rays from the crystal structure. [14]

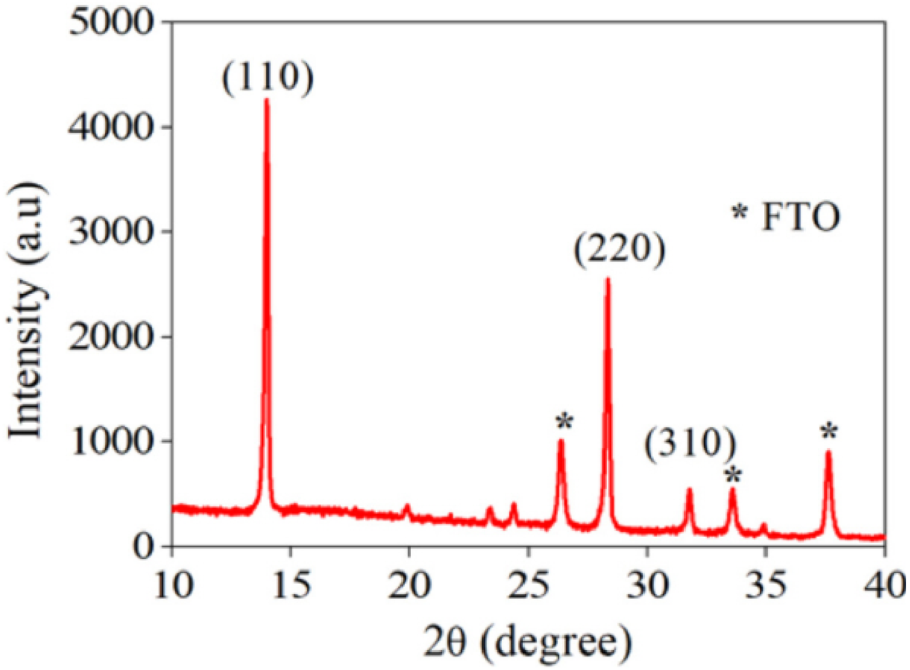

Figure 1 XRD-peaks of the tetragonal MAPbI3 (Image reproduced with permission from Nur'aini [15], Copyright (CC-BY-NC 4.0) 2021, Journal of Electrochemical Science and Technology)

Crystal structures begin to form when supersaturated solution nucleates. [16] First there is a seed crystal which starts to grow by taking material from the surrounding solution. [8] If the seed crystal grows independently the crystal is called single crystal. [8] The single crystals are hard to produce because the environments temperature, humidity and pressure need to be optimal. [8] If there are multiple seed crystals the crystal is called polycrystalline. [8] Perovskite structures are mostly polycrystalline. [8] If the seed crystal is lower than the critical radius, the seed crystal re-dissolves into the surrounding solution. [16] To make efficient perovskite films the nucleation must be rapid and crystal growth needs to be slow. [16]

3 Perovskite performance indicators

The parameters that are most compared in literature are open circuit voltage, short-circuit current density, peak power and fill factor. [17] Power conversion efficiency is also important, but it is calculated with these parameters. Open circuit voltage means that no current is flowing through the system. This is the maximum measurable voltage. After the circuit is closed (short circuit) with solar cell electrodes the current is flowing at maximum rate, and voltage has dropped to zero. By dividing the maximum current with the cell area, we get maximum current density. [17] Current density is more universal unit than just current. Current can vary depending on the surface area.

Fill factor is an important parameter to investigate when researching solar cells. Fill factor gives a value which compares maximum realistic power to theoretical maximum power. Low fill factor can indicate current leakage through pinholes or defects in the structure. [18] Power can be lower due to shunt resistance. Shunt resistance is mostly dependent in manufacturing defects. [19]

The most seen parameter is power conversion efficiency (PCE). This parameter gives information how effectively the cell uses incident power. [17] The value is a good indicator of perovskite solar cells overall efficiency and is an easy value to compare with other solar cells PCE values.

The efficiency of the PSCs varies depending on grain size, grain boundaries, defects, impurities, panel area and used materials. In 2025 highest PCE of the PSC was 27 % [20], which is a huge improvement to first PSCs in 2009. This PCE is coming closer to the theoretical PCE limit of a single junction solar cell, so called Shockley–Queiser limit. The limit was calculated in 1961 to be 33,7 % with a p-n-junction band gap of 1,4 eV. [21]

The indicators in addition that are important in PSC efficiency are grain size, XRD intensity and the peak width and the panels voltage. High voltage is related to uniform crystal growth and low values for nonradiative recombination. Grain size is one of the main factors when researching perovskites post-processing. High XRD-peak in specific areas can indicate high level of crystallization and low defect density. Bigger grains have larger structures where the X-ray can scatter coherently and cancel unwanted diffractions incoherently. [14] However, the peaks can be affected by the options and quality in XRD-equipment. [14] The broadened peak can be informative about grain size because smaller grains contribute peak broadening. [14] The form of the peak cannot be the only indicator of grain size because also strains broaden the peak. [14]

There are several methods to improve panels photocurrent output by controlling nucleation and universal grain growth. Nucleation rate (J) can be calculated with equation 1

$$J = K\, exp\frac{-\Delta G}{k_B T}, \tag{1}$$

where K=pre-exponential factor, ΔG=Gibbs free energy for critical radius of the nucleus, kB = Boltzmann’s constant and T = nucleation temperature. [20]

Nucleation rate is highly affected by the level of the solution supersaturation. Nucleation rate could be more effective with higher level of supersaturation, smaller surface free energy and higher temperature. [16]

4 Post-processing of perovskites

During manufacturing the films can experience changes in the perovskite structure. Unwanted changes, defects and vacancies, affect the performance of the cells. [5] To improve the crystal structures uniformity in the solar cells different annealing methods are under estimation. Annealing is executed after the precursor solution is already spin coated and treated with antisolvent or some other technique and the crystallization has begun. [22]

Post processing can significantly improve PSCs crystallization and grain size. Bigger grain size and more uniform crystal structure improves the charge carrier movements. Bigger grainsize results in less grain boundaries, vacancies and nonradiative recombination.

Vacancies cause nonradiative recombination and degradation of the perovskite film stability. [6] Nonradiative recombination occurs when the carriers (electron or hole) recombine and generate structural vibration and heat. [23] Radiative recombination is another reaction where electron reacts with hole and disposes the excess energy as a photon. [23] Radiative recombination is desirable reaction with LEDs [23] but weaken the efficiency of solar panels.

4.1 Temperature annealing

Temperature annealing (TA) means a technique where heat is used to improve the grain size and crystal structure of PSC. [22], [24] During temperature annealing the perovskite precursor solution with seed grains is heated to specific temperature for a predetermined time. The heat vaporizes most of the liquids in the thin film’s leftover precursor. [22] During this process the solution concentration increases, and the crystallization process continues in the film. [22] High or low temperatures can be used with some limitations depending on the goal of the annealing. [20], [24], [25], [26]

On the negative side TA can lead to vaporization of the solution ions and generate vacancies in the perovskite structure. [6] Furthermore, too long-lasting TA with high temperatures can lead to deformation of the perovskite. [22]

Usage of the high temperature (350 °C) requires high temperature tolerance of the substrate. [24] If evaporating is made on a silicon substrate to make hybrid cells, the silicon has a chance to degrade its performance. TA in open environment causes rapid volume shrinkage which leads to cracks and voids in the perovskite films. [6] To reduce this there are several ways to control evaporation rate and crystal growth speed.

Bar coating of MAPI means reduced evaporation in temperature annealing using moving cover plate. [26] Reduced evaporation has given positive results. [26] Constant sweep speed needs to be optimal to grow the biggest grains in the direction of the sweep. [26] With bar coating method the biggest grains grown have been approximately 300 µm. [26] This grain size is large. The sweeping helps to grow oval-like grains which results in more single grain area in the film. Higher sweeping speeds result in faster nucleation. [26] With faster nucleation the grain growth is not as symmetrical as it could be with optimal speeds. Uniform temperature evaporation of the film precursor without reduced evaporation resulted in smaller grains and lower crystallinity. [26] Open-circuit voltage of the sweep-controlled film is higher when compared to open environment films. [26] The slight increase in voltage means more uniform crystal structure and smaller defect density. XRD-peaks at (110) and (220) reveal tetragonal [9], [26] perovskite structure.

Step annealing means that the precursor solution is heated to two different temperatures. First at lower temperatures and after the first step at higher temperatures. First step slows the crystal growth and improves the grain size. [27] Pre annealing temperatures of 20-30 °C lower to step temperature have shown the best results in film’s absorbance intensity of UV-visible spectra. [27] Higher absorbance is a result of better crystallinity and lower defect density in the film. Lower pre-temperatures than previous values are not sufficient, so the precursor has not fully transformed into perovskite. If the precursor has not fully transformed the absorbance is also much lower. [27] Too low temperature can evaporate part of the reacting components. Due to reagent evaporation perovskite cannot form even in 100 °C. [27] Optimal pre-temperature is noted at 90 °C. [27] At this pre-temperature the hole mobility is higher compared to 100 °C. [27] 30 minutes longer pre-annealing time improves hole mobility drastically. [27] This information tells that even minutes longer pre-annealing can have a huge impact on the material properties.

4.2 Microwave annealing

To enhance the PSC’s effectiveness and industrial manufacturing potential a great amount of research and new annealing methods is needed. Microwave annealing is a new technique to make crystal structure better in PSCs. Thermal annealing uses extensive range of energy to heat the PSCs to high temperatures [24], and a great deal of energy is wasted. Also, the organic solvents cannot be reclaimed. [28] Microwaves can heat the film more efficiently and focused. Focused radiation affects the evaporation of solvent and enhances crystallization. [13]

Microwave annealing needs a lot of research before it can be used effectively in large scale applications. With microwaves perovskites can be fabricated in room humidity outside of the glovebox and it has given positive results. [28] Annealing time must be optimized to get the best results in material properties. Too short annealing time will lead to unfinished crystallization. Too long annealing time generates too much heat and results in film degradation. [28] Besides the annealing time, annealing power has a key position in optimized grain size. Higher power results in more rapid growth in grains but can locally harm or degrade the film. [28]

In Figure 2 the differences between annealing powers and grain size can be seen. Grain shapes change from needle-like with too low power to degraded grains with too much power. Rapid growth of the selected grains due to microwave radiation causes the formation of voids and cracks in the structure. [28] Cracks lead to lower performance and stability. From the results it is shown that the direction of the radiation field affects in the grain growth. [28]

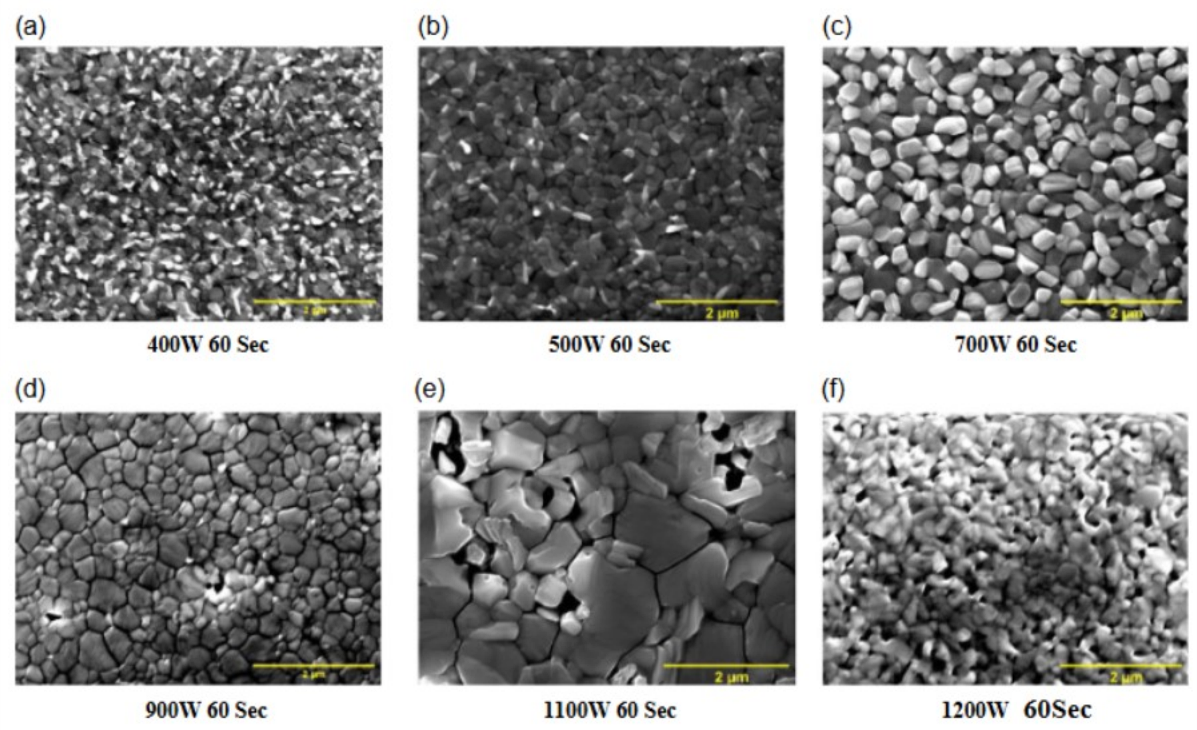

Figure 2 Microwave annealed grain size, a=400W, b=500W, c=700W, d=900W, e=1100W, f=1200W (Image reproduced with permission from Sakib et al, Copyright 2024, John Wiley and Sons)

Microwave annealing generates heat homogenously. FTO-glass does absorb microwaves energy which causes internal eddy currents. [28] Currents generate heat due to internal resistance. [28] In addition, the perovskite solvent's polar particles absorb microwaves and generate heat. With these methods the heating is rapid and uniform throughout the whole sample. [28] Uniform rapid heating transfers to solvent evaporation and supersaturation. Supersaturated solvent starts to nucleate. [28] This reduces point defects and vacancies in the lattice. However, there is a problem near the edges. It is called diffraction edge effect. [28] It means that the microwaves deflect near film and FTO-glass (fluorine-doped tin oxide) edges. Due to deflection, the heat will rise locally near the edges. [28] This will have an effect in the grain size and crystallinity. To minimize this effect an absorbent can be used, for example block of SiC. [28] Block of SiC is placed under the sample. [28] After the absorption excess radiation cannot deflect near edge zone. In addition, the SiC block heats conductively so it will provide extra heat for the post-processing process. [28] Perovskite cannot form if there is no solvent, TiO2, FTO or other microwave absorbers. [13] Solvent, TiO2 and FTO absorb microwaves which causes the materials to heat. The heat is then transferred into perovskite precursor, after which the formation of perovskite happens. [13]

The optimal microwave power of 700W-900W results in the most uniform and nondegraded grains of the average size of 620 nm. [28] Grain size can vary from 200 to 1200 nm after microwave annealing. [28] The wide range of values indicates complex mechanisms like Ostwald ripening and nucleation. [28] Clearly visible boundaries and dense matter mean high crystallinity. Better crystallinity in the thin films can improve absorption intensity when compared to hot plate annealing. [28] Microwave annealed films perform well considering that no glove box is needed during the process. Microwave annealed sample is noticed to be more stable even after months in room humidity. [28] The more stable state can be explained by less active reaction area between the grains. Respectively, the XRD intensity at (110), (220) and (310) is higher with microwave treated film meaning improved crystallinity. [28]

4.3 Laser-induced plasma shock

Low defect density and high charge carrier efficiency are important parameters for a high-performing perovskite film. Internal stress in the PSC can reduce charge mobility [29] and stability [30]. Shock driven gradient annealing (SDGA) means laser-induced plasma shocks used to anneal perovskite films in a semi-sealed glass container. [29] This post processing method improves grain uniformity and releases internal stress in the film. [29] Releasing internal stress lowers non-radiative recombination. The suitable wavelength for the laser is around 1060 nm because lower wavelengths transmit too much energy and the film or substrate can degrade.

Semi-sealed container alleviates fabrication difficulties such as rapid evaporation and non-uniform crystallization. [29] Laser-induced plasma poses pressure in the solution, and it enhances diffusion and fusion of grains. [29] Heat generated by the laser anneals the perovskite precursor film locally and effectively. [29] In Figure 3 different grain sizes can be seen depending on laser power. Laser intensity can easily be modified to fit the need. Organic-inorganic halide perovskites incorporate effective properties like high mobility and high coefficient to light absorption, long carrier lifetime and direct bandgap. [29] The absorption intensity of visible light is higher in SDGA annealed film than in thermally annealed film. [29] Interplanar spacing is also higher, which means the internal stress in the crystal structure is moderate. [29]

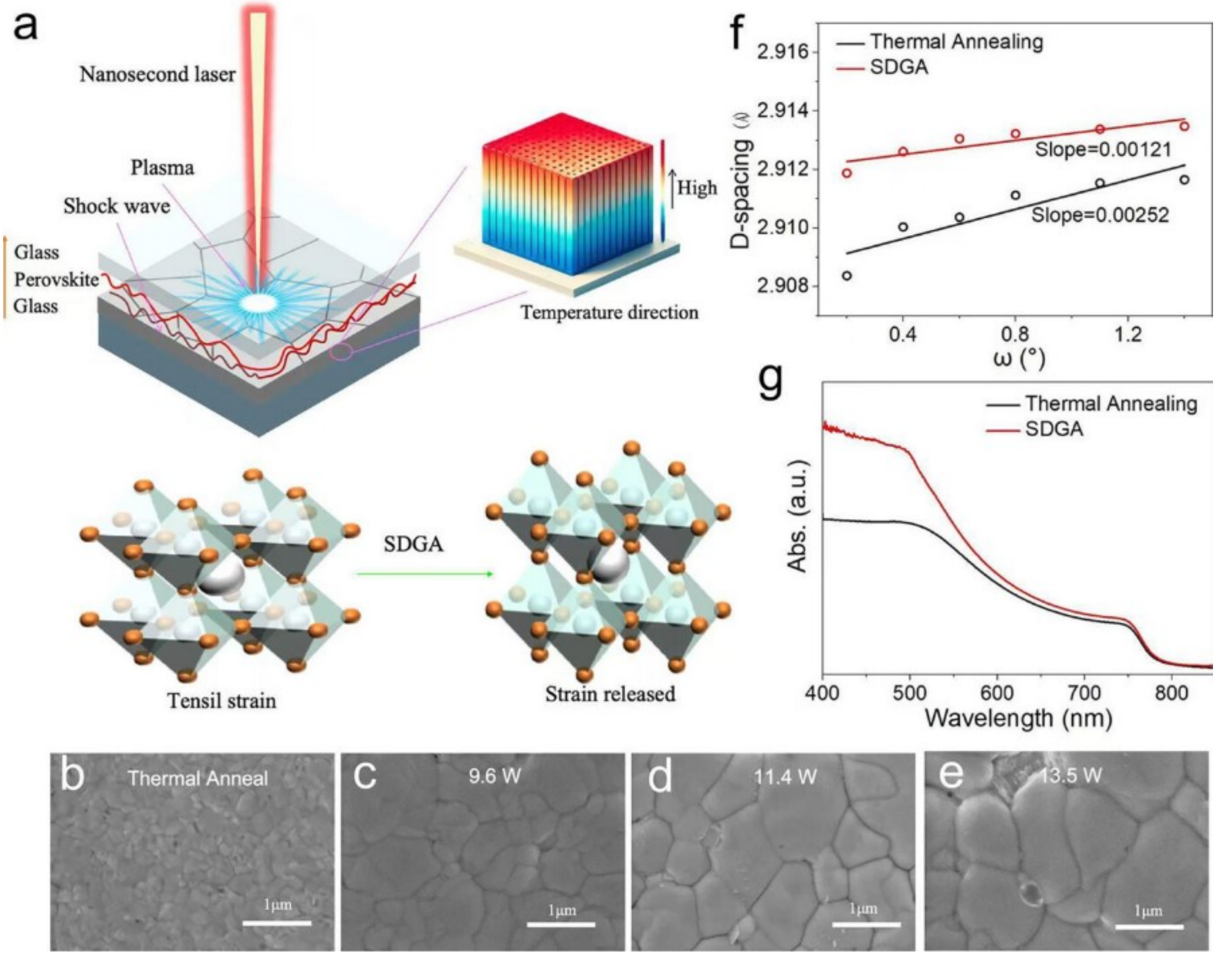

Figure 3 SDGA treatment. a=SDGA; b=TA, c=laser 9,6W; d=laser 11,4W; e=laser 13,5W; f=interplanar spacing; g=UV-VIS spectra (Image reproduced with permission from Sun et al, Copyright 2025 John Wiley and Sons)

Strains in perovskites can occur for two different reasons. The difference in thermal expansion rates between film and substrate, and internal changes of the lattice structure in the film. [29] Different thermal expansion rates result in change in distortion levels throughout the film. These internal strains can have a negative impact in the film's stability, carrier mobility and other important parameters. Temperature annealing of perovskite film generates great internal stresses because of uneven warming of the film and greater temperature coefficient differences between perovskite surface and surface near substrate. [29] Evaporation of solvent is uncontrolled during open air TA. SDGA improves 400 % grain growth, 50 % less defects, 100 % better lifetime of the film. [29] Too powerful laser can induce higher stress which will result in negative results. [29] The XRD peaks are narrower with SDGA-treated perovskite than TA-treated one. [29] This means improved crystallinity.

Plasma induced shock pressure can be calculated with the help of equation 2

$$P(\tau) = \frac{mIa}{2\tau(a+1)}^{\frac{1}{2}}, \tag{2}$$

where α is the ablation layer ability to reflect laser, m is the laser ablation layer mass, I is the laser intensity, and τ is the pulse duration. [29]

Research shows that band gap between valence band maximum and conduction band minimum increases as the laser power increases. [29] This is due to gradient strain engineering with high power laser. [29] Released strain makes the crystal structure more uniform and the interplanar spacing grows between atoms. [29] Change in interplanar spacing can be noticed as grown band gap. In addition, Fermi energy Increases. [29] The change in Fermi energy lowers the energy needed to excite electrons to the conduction band. [29] This indicates N-type behaviour. Conductivity of the material increases after increase in Fermi energy. [29] Improved conductivity can also be explained by increase in carrier diffusion length (SDGA 1.86*10^-4 cm, TA 0.9*10^-4 cm). [29]

SDGA treatment improves film crystallinity and results in more stable film. [29] After 30 days in normal room humidity the film’s photocurrent can remain in over 80 % of the original. SDGA-treated films have a higher photocurrent than the TA-treated films. [29] The gap in efficiency can be explained by lower grain boundary density in SDGA-treated films. [29] SDGA-films have less defects, and the internal strain is released. Lower grain boundary and defect density leads to less non-radiative recombination and improved stability. [29] Laser treatment could be a huge advantage in the extension process of film lifetime.

4.4 UVA-annealing

One solution in fabricating efficient PSCs is using chlorine additives with UV-LED as an irritator to produce high grade grains in the cell. [31] The results are promising with a PCE of 21,7 % [31]. UV-annealing has been studied due to its higher energy efficiency and faster processing time and ability to produce multilayer PSCs (Figure 4). UVA can be localized to absorbing perovskite layer. UV-light can be used effectively and efficiently on large area surfaces. During this annealing process UVA-LED uses the wavelength of the peak in absorption of MAPI perovskite layer. [31] Absorbed UV-light makes the film heat locally at the absorption point. Local heat causes the nanoparticles in the film to bond together, solution to thicken, and eventually fuse into a denser layer and bigger grains [31]. Localized absorption helps in protecting the sensitive layers under the film.

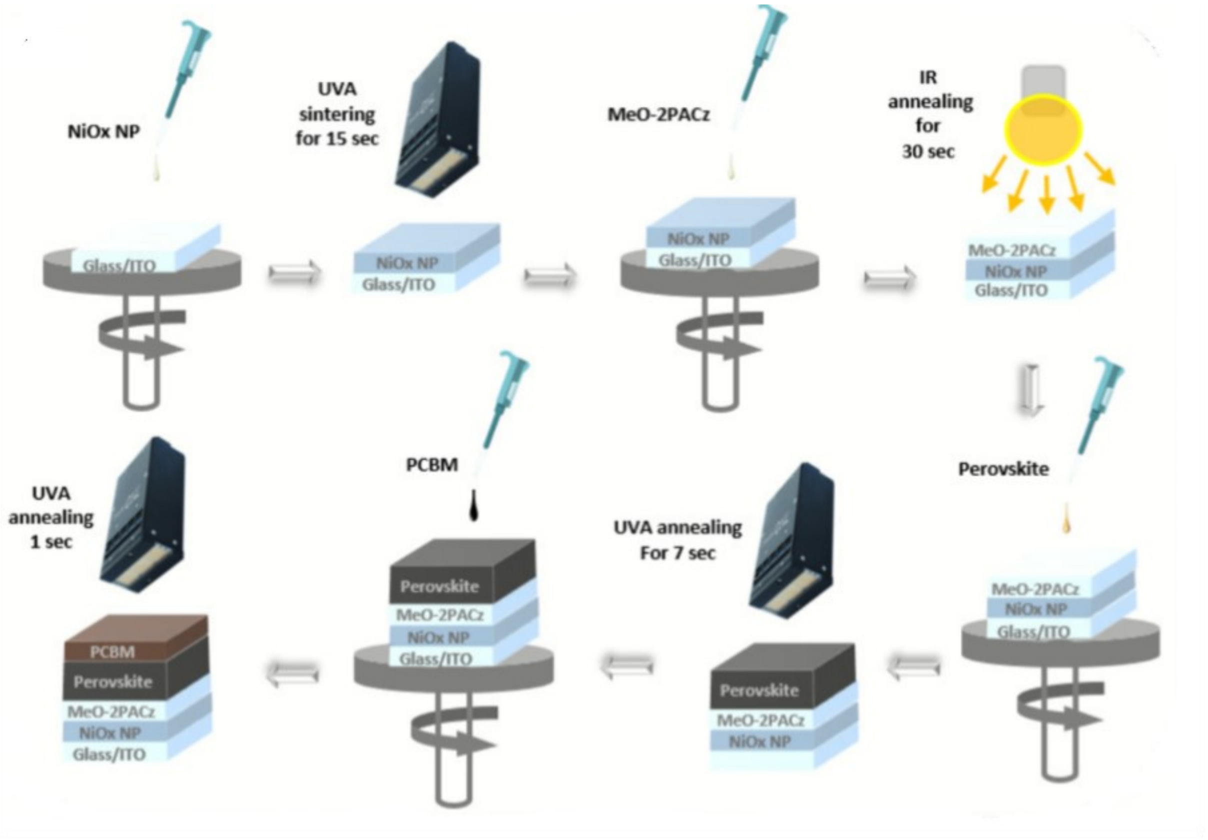

Figure 4 UVA-treatment of a multilayer cell (Image reproduced with permission from Vaezsis et al, Copyright 2025, Jonh Wiley and Sons)

With the addition of MACl in the solution, the grain size can grow exponentially (Figure 5). The 40 % addition has been the most optimal. [31] As seen in Figure 5 XRD-peak is much higher for MACl additive perovskite. This means that with MACl addition the crystallization is more efficient. The UVA-treated optimal MACl-solution perovskite cell has better crystallinity when also fill factor is higher (83,02 %) than the compared TA-treated (80,82 %). [31] Addition of MACl enhances the stability of the cell. Without the addition of MACl the stability of the PSC is noticed to be 30 % lower when compared to

MACl addition. [31] Increase in stability is a consequence of the lower area of grain boundaries and improved crystallinity.

Steady-state photoluminescence (PL) is an efficient indicator about the trap states in perovskite film. [30] PL of the additive film is noticeably higher on glass than without addition. This tells us that there are less defects and non-radiative interference. The Cl-ions migrate in perovskite structure due to energy from UV-radiation and induce the larger and more uniform crystal growth. [31] Cl-ions passivate the crystal interfaces by easing diffusion. [31]

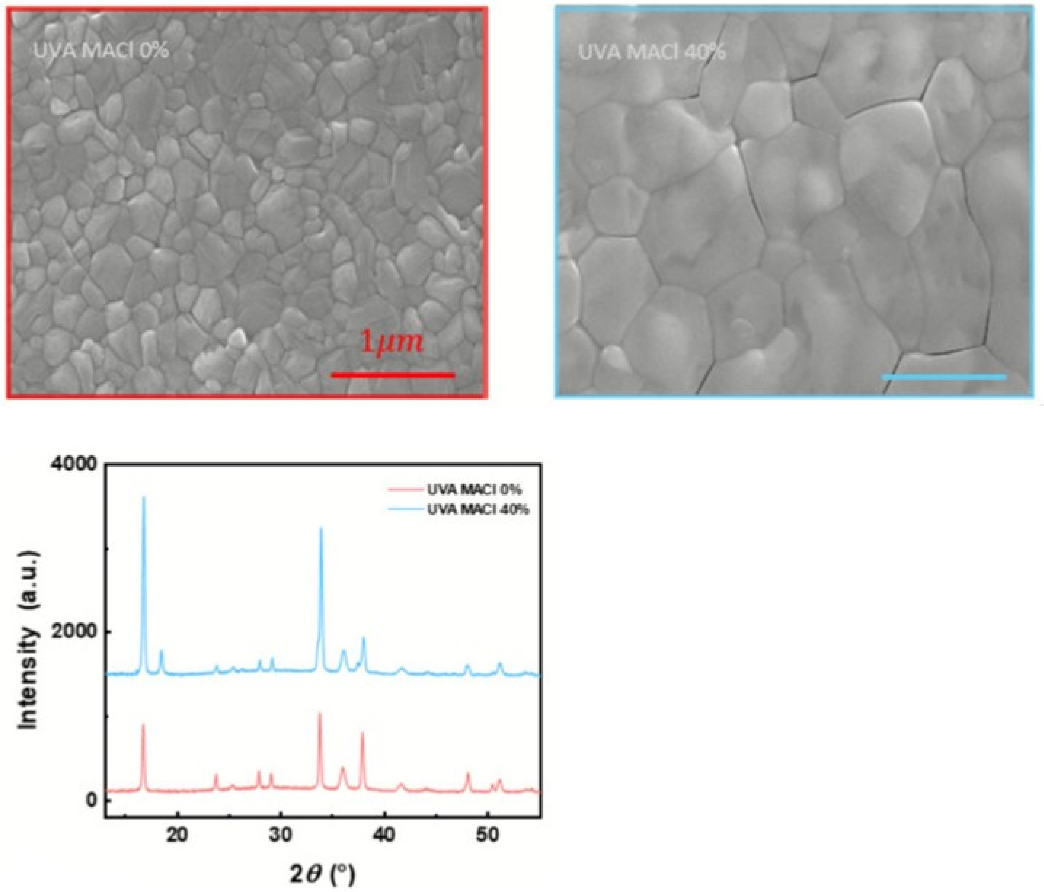

Figure 5 UVA-treated grains without and with MACl addition and XRD-peaks (Image reproduced with permission from Vaezis et al, Copyright 2025, John Wiley and Sons)

4.5 Electrode annealing

Electrode annealing means that electric current in indium tin oxide (ITO)-surface is transformed into even heat by Joule heating which is then used to nucleate perovskite grains at the perovskite/ITO-interface. [30] ITO-surface is supposed to heat to 50 °C because of the Joule effect with a right voltage level. [30] The heat generated in the ITO-surface produces a more uniform surface due to slower nucleation rate. The heat is conducted from the bottom of the film, so the process is more stable, and grains grow in one direction. The treated film is more stable because there are less interfaces between grains and by this mean less area for the oxygen and water to react and degrade the film. [30]

On ITO-surface PL is supposed to be lower for high quality perovskite, because the electrons are supposed to flow through ITO-surface. Electrode annealed (EA) perovskite has much lower PL-value than TA-comparison perovskite. The grain size for EA perovskite is higher than TA comparison. EA perovskite has grains in the size range of 150nm-650nm in Figure 6.

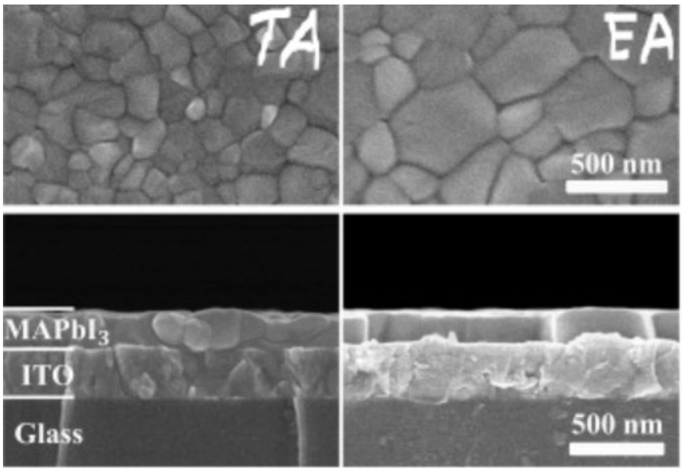

Figure 6 Electrode annealed sample (EA) compared to temperature annealed (TA) sample (Image reproduced with permission from Chiu et al, Copyright 2025, Elsevier)

The best results and biggest grain size with electrode annealing has been achieved by rising the temperature step by step with changing voltage between electrodes. [30] With high heat right away in TA or EA, the grains appear smaller and less uniform. [30] During progressive EA the results are only sufficient when perovskite is fabricated right on the ITO-surface. [30] Additional surfaces lower the efficiency of EA because the local temperature decreases too much between the layers. This is a challenge because additional layers are needed and it affects the post-treatment of $MAPbI_3$ -film. In addition to the temperature, the electric current affects the nucleation of perovskite. [30] Direct electricity on ITO-surface is an option, but it could be changed to induction or other indirect method to ease mass production. With induction the circuit could be on all the time and energy is only consumed when ITO-surface enters the annealing chamber. EA-treated perovskite is more stable than the TA-treated perovskite. The EA-treated films have columnar grain growth due to electric field. [30] Columnar grains have a positive impact in stability and crystallinity. Better crystallinity can be revealed with higher XRD-intensity. [30]

5 Discussion

There are many ways to anneal perovskites. In this thesis only a few of the ways are studied. The small scope of the work weakens the generalizability of the results. Articles used in the work were only regarding samples fabricated of MAPI. Temperature annealing is the easiest to understand and the technique is quite simple. The modified TA (bar-coating) achieves the largest grain sizes reported, reaching up to 300 μm. While this is nearly 1000 times larger than the typical nanometer grains found in other references, it raises concerns regarding film uniformity and the practical scalability. The fabrication is slow and usually batch processed. Temperature annealing uses large amounts of energy and is inefficient compared to other techniques. The energy produced is challenging to focus on the sample so most of it escapes to the environment. High temperatures can damage the film or other layers of the cell and can lead to loss in the overall quality and stability of the solar panel. Internal stress is also a critical factor regarding stability. Temperature annealing at large scale makes the precursor solution evaporate too quickly from the panel area and the rapidly drying film produces voids and cracks in the film. These defects lower charge carriers lifetime and other optoelectrical properties. Many ways have been developed to control evaporation rate and make the process faster. A brief comparison of the techniques studied in this thesis is in Table 1.

Table 1 Different post-processing techniques

POST-PROCESSING TECHNIQUE	GRAIN SIZE	POSITIVE	NEGATIVE	SOURCE
TEMPERATURE	100-300 μm	-easy and accessible -scalable -very big grain size	-high energy consumption -cracks and voids -slow annealing -internal stress	[25], [26], [27]
MICROWAVE	200-1200 nm	-more focused energy usage -fast annealing -easy to change energy -scalable	-needs a microwave absorbent -microwaves bending in corners	[13], [28]
LASER-INDUCED PLASMA SHOCK	800-1600 nm	-big grainsize -good stability -semi sealed environment rejects too fast evaporation -very focused energy -fast annealing	-expensive -too much power can degrade the film -not so easy to scale up	[29]
UVA+CL-ADDITIVE	600-1000 nm	-medium grain size -focused energy to absorber layer -low cost -can be used to fabricate multilayers -scalable	-UVA-radiation can be harmful to perovskites -Cl is not environmentally friendly	[31]
ELECTRODE	150-650 nm	-can be used with induction -scalable -columnar grain growth	-multiple layers lower the heating efficiency -small grain size	[30]

Microwave annealing is an efficient technique because the power is easily adjusted to produce optimal grain structure. Optimal microwave power should be experimentally tested for the fabricated area and film thickness. Powers of 700 W – 900 W can be a good point to begin. Too high annealing power and time will result in film degradation. Other challenge to consider is the bending of the microwaves in the corners which results in higher local temperature at the corners.

Laser annealing gives advantages like local energy usage in specific point. In semi-closed environments plasma is formed due to laser power which improves the diffusion and grain fusion. Laser power is easily adjusted but too high power results in film degradation or risen internal stress. Laser sources are quite expensive which limits its usage. In this thesis SDGA gave the best results regarding grain size and stability of the new techniques.

UVA-annealing can be used to easily and effectively fabricate multilayer cells. Annealing time is short and the radiation can be absorbed by the perovskite film. UVA-sources are more affordable, and it uses much less energy than temperature annealing. UVA-technique could be used in film healing. UV-light can be summoned on a larger area than the laser mentioned earlier. Laser is more focused on a small area.

Electrode annealing is interesting from the view that electricity could be induced with induction. Direct current is too tricky to be used in large scale production. Inducted electricity could optimize the production when the energy is only consumed when needed. This automation is a huge advantage compared to continuous heating of the heating resistors in temperature annealing. Downside of the technique is the limited grain size and applicable layers.

6 Conclusion

The purpose of this thesis was to introduce and evaluate a few of the post-processing methods. While temperature annealing remains a straightforward approach post-processing technique it has some challenges like high energy consumption, quick precursor evaporation and long processing times. In contrast, laser annealing in semi-closed environment demonstrated promising results with the moderate grain size of 1600 nm (compared to TA 300 μm) and high photocurrent. Downside to laser annealing is that the equipment is expensive. Ultimately, microwave and UVA-annealing are more efficient ways to manage post-processing of MAPI-perovskite films. These annealing methods resulted in moderate grain size with a fraction of energy usage compared to energy and time consumption of temperature annealing. Smaller grain size didn’t affect the stability negatively because the grains were uniform and the internal stresses were lower. Also defect density was smaller. The most promising techniques for large scale industry could be microwave, UVA or electrode annealing due to quick annealing time, cost effectivity, energy efficiency and scalability. These methods can be line processed which makes it easier to manage operations.

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