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Zavkiddin JULLIEV,
UzAS, Institute of Polymer Chemistry and Physics,Phd student
Ahmad OBLAKULOV,
UzAS, Institute of Polymer Chemistry and Physics,senior reserсher
Doston TOSHMAMATOV,
UzAS, Institute of Polymer Chemistry and Physics,Phd student
Rahimbergan RAKHIMOV,
UzAS, Institute of Polymer Chemistry and Physics, senior reserсher
Nigmat ASHUROV,
UzAS, Institute of Polymer Chemistry and Physics, Prof

Based on PhD , D,D Nematov’s rewiev. S.U.Umarov Physical–Technical Institute of the National Academy of Sciences of Tajikistan.

ANTI-SOLVENT AND GAS-QUENCHING METHODS FOR CONTROL CRYSTALLISATION OF ACTIVE LAYER IN PEROVSKITE SOLAR CELLS

Annotation

Perovskite solar cells (PSCs) have emerged as a promising photovoltaic technology due to their high power conversion efficiencies and low-cost fabrication. The crystallisation of the perovskite active layer plays a crucial role in determining the device's efficiency and stability. This paper comprehensively examines two widely adopted techniques for controlling perovskite crystallisation: anti-solvent treatment and gas-quenching by checking optic properties. A crucial factor in PSC fabrication is the deposition of the perovskite absorber layer, as its quality directly influences device performance. Traditionally, antisolvent quenching has been the primary method for inducing crystallization in perovskite films. However, gas quenching-an alternative approach that utilizes pressurized gases (typically N_2) to supersaturate the perovskite precursor solution has demonstrated substantial advantages.We explores the advantages in gas quenching for high-quality perovskite film formation, offering a comparative analysis with antisolvent quenching.

Key words: Anti-solvent, gas-quenching, perovskite solar cell.

МЕТОДЫ ОХЛАЖДЕНИЯ АНТИРАСТВОРИТЕЛЕМ И ГАЗОМ ДЛЯ УПРАВЛЕНИЯ КРИСТАЛЛИЗАЦИЕЙ АКТИВНОГО СЛОЯ В ПЕРОВСКИТНЫХ СОЛНЕЧНЫХ ЭЛЕМЕНТАХ

Аннотация

Перовскитные солнечные элементы (PSC) стали перспективной фотоэлектрической технологией благодаря высокой эффективности преобразования энергии и низкой стоимости изготовления. Кристаллизация активного слоя перовскита играет решающую роль в определении эффективности и стабильности устройства. В этой статье всесторонне рассматриваются два широко распространенных метода контроля кристаллизации перовскита: обработка антирастворителем и газовое гашение путем проверки оптических свойств. Решающим фактором в изготовлении PSC является нанесение слоя перовскитного поглотителя, поскольку его качество напрямую влияет на производительность устройства. Традиционно, гашение антирастворителем было основным методом для индукции кристаллизации в перовскитных пленках. Однако газовое гашение-альтернативный подход, который использует сжатые газы (обычно N_2) для пересыщения раствора-предшественника перовскита продемонстрировало существенные преимущества. Мы изучаем преимущества газового гашения для формирования высококачественной пленки перовскита, предлагая сравнительный анализ с гашением антирастворителем.

Ключевые слова: антирастворитель, газовое - гашение, перовскитный солнечный элемент.

PEROVSKIT QUYOSH ELEMENTLARIDAGI AKTIVE QATLAMNING KRISTALLANISHINI NAZORAT QILISH UCHUN ANTISOLVENT VA GAZ BILAN SOVUTISH USULLARI

Annotatsiya

Perovskit quyosh elementlari (PSCs) o‘zlarining yuqori quvvat aylanish samaradorligi (PCE) va arzon ishlab chiqarish imkoniyati sababli so‘nggi yillarda eng istiqbolli fotovoltaik texnologiyalardan biri sifatida tanilgan. Qurilma samaradorligi va barqarorligi asosan perovskitning faol qatlamining kristallanish sifatiga bog‘liq. Ushbu maqolada perovskit kristallanish jarayonini boshqarish uchun keng qo‘llaniladigan ikkita asosiy texnika: anti-solvent usuli va gaz bilan sovitish (gas-quenching) metodlari optik xossalar asosida batafsil tahlil qilinadi.

Kalit so‘zlar: erituvchiga-qarshi, gazli-so‘ndirish, perovskit quyosh elementi.

Introduction. Perovskite solar cells (PSCs) have emerged as a transformative photovoltaic technology, achieving remarkable advancements in power conversion efficiency (PCE), scalability, and economic viability. Over the past decade, lab-scale PSC efficiencies have soared from approximately 3.8% to over 26.7% [1]. This remarkable progress stems from the exceptional optoelectronic properties of perovskite materials, including high absorption coefficients, long carrier diffusion lengths, and tunable bandgaps, combined with cost-effective fabrication techniques [2-7]. However, achieving both high efficiency and long-term stability in PSCs critically depends on the formation of high-quality perovskite films with precise control over crystallization and morphology. Persistent challenges such as phase segregation and light-induced degradation remain key concerns [8]. Moreover, the advancement of scalable, large-area fabrication methods is crucial for the successful commercialization of PSC technology. A major challenge in perovskite film fabrication lies in achieving precise control over crystallization during deposition. Most PSC research has relied on spin coating and anti-solvent treatment techniques, which have been widely applied to traditional lead-based perovskites as well as lead-tin mixed and tin-based, lead-free compositions [9-17]. However, the manual nature of these methods introduces variability due to factors such as deposition height, angle, and speed, compromising reproducibility. Additionally, scaling these techniques for large-area, environmentally sustainable production remains difficult and often impractical [15, 16, 18, 19]. To address these limitations, researchers are actively exploring alternative strategies to enhance control over perovskite film formation and improve scalability. Among these emerging techniques, gas quenching has demonstrated significant potential for optimizing perovskite crystallization and morphology, offering a more reliable and scalable solution for the fabrication of high-quality films. Gas quenching, initially introduced during spin coating [20], employs an inert gas (such as nitrogen or argon) during the wet film deposition stage to rapidly remove residual solvents, facilitating controlled crystallization of the perovskite layer. As a result, gas quenching produces smooth, pinhole-free films with large grain sizes and enhanced crystallinity while minimizing solvent consumption.Gas quenching, initially implemented during spin coating [20], employs an inert gas (such as nitrogen or argon) during the wet film deposition stage to accelerate solvent removal, thereby facilitating controlled crystallization of the perovskite layer. While highly promising, gas quenching in PSC research remains in its early stages, with many aspects still requiring thorough investigation. Key areas of ongoing research include optimizing quenching conditions, elucidating the relationship between gas dynamics and film formation, and assessing its impact on different perovskite compositions and device architectures. In this study, we precisely engineered the perovskite active layers using gas quenching (GQ) and anti-solvent (AS) techniques, aiming to evaluate their impact on film quality. Comprehensive characterization was conducted using X-ray diffraction (XRD), UV-Vis spectroscopy, SEM imaging, photoluminescence (PL), and time-resolved PL (TRPL) to assess structural, optical, and morphological properties.

Research Methodology. Precursor and Device Preparation. In this structure, ITO(Indium Tin Oxide) glas were cleaned by an ultrasonic with Distilled water, acetone, Toluol and IPA(Isopropyl alcohol) and drayed Nitrogen gas. Simple is glass/indium tin oxide (ITO)/PTAA/MAPbI3. All device preparation steps were performed in a nitrogen-filled glovebox. PTAA solution (Sigma-Aldrich, 5 mg mL−1 in toluene) was spin-coated dynamically at 6000 rpm for 30 s and afterward annealed at 120 °C for 30 min.As substrate, a 15 × 20 mm ITO-coated glass is used.For MAPbI3 perovskite, a 1 M solution of PbI2 and MAI with 5% excessive PbI2 (for passivation) was prepared with a solvent mixed by NMP/DMF with 3/7 volume ratios. The solutions were spincoated at 3000 (2000) rpm for 120 s with an acceleration speed of 300 rpm s−1(for anti-solvent , 5000 rpm for 30 s ,Xlorbenzole dropping time -9s ,14s, 20 s).After various delay times, a continuous nitrogen gas flow with a pressure of 5,5 bars (filtered with 0,6 μm PTFE filter) was aimed (incident angle-90°) at the substrate with a distance of approximately 10 cm to form the intermediate. Afterward, substrates were immediately transferred to a hotplate and annealed at 100°C for 10 min.

Analysis and results. From Fig-1, Scanning electron microscopy (SEM) analysis revealed that the gas quenching method produced perovskite grains of significantly larger size compared to those formed via the anti-solvent approach. This observation underscores fundamental differences in crystallization kinetics, thin-film morphology, and defect formation between the two methods. Below, we synthesize the implications of these findings, discuss their broader impact on perovskite photovoltaic technology,and outline future research directions to optimize these fabrication techniques.

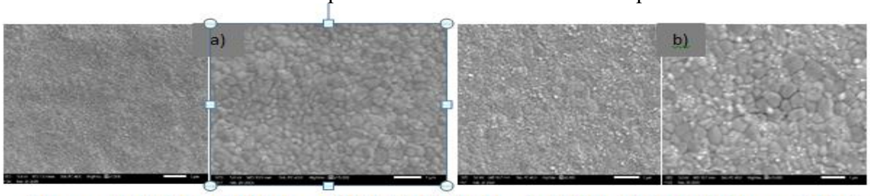

Figure-1: SEM of ITO glass/PTAA/ MAPbI3, a) AS-20s b) GQ-2000rpm (120s) Gas quenching (GQ) and Anti-solvent (AS).

While this study compared the gas quenching (GQ) and anti-solvent (AS) methods, the XRD results showed that the perovskite films formed via gas quenching exhibited significantly higher diffraction intensity at the characteristic 2θ angle of ~14.01°, corresponding to the (110) crystallographic plane of the tetragonal MAPbI3 phase,compared to those produced by the anti-solvent method.This finding underscores the critical role of crystallization kinetics in determining perovskite film quality and provides insights into the mechanistic advantages of gas quenching(Fig-2).

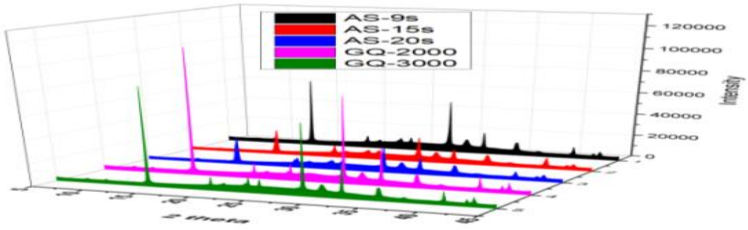

Figure-2: Xray of ITO glass/PTAA/MAPbI3. Gas quenching (GQ) and Anti-solvent (AS).

With a focus on UV-vis spectroscopy analysis (Fig-3).The experimental results revealed that perovskite films fabricated via gas quenching (GQ) exhibit significantly enhanced light absorption across the UV-visible spectral range when compared to films processed using the anti-solvent (AS) method.Notably, at a wavelength of 550 nm, the absorption coefficient for GQ films exceeds 1.5, indicating a more efficient light-harvesting capability.In contrast, the AS-processed films display a comparatively lower absorption coefficient, falling below 1.5 at the same wavelength. This suggests that gas quenching promotes improved film morphology and optical properties, likely due to more uniform crystal formation and reduced defect densities, making GQ a promising technique for optimizing the performance of perovskite-based optoelectronic devices.

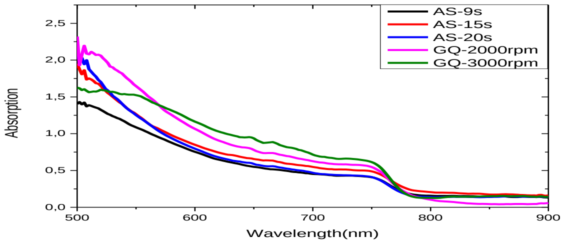

Figure-3: Absorption of ITO glass/PTAA/perovskite. Gas quenching (GQ) and Anti-solvent (AS).

In Fig-4 the PL measurements shown that the perovskite films formed by gas quenching exhibited significantly lower PL intensity at the corresponding emission wavelength compared to those prepared via the anti-solvent method.This observed reduction in steady-state PL intensity for the gas quenched (GQ) perovskite films carries important implications regarding the material's optoelectronic properties and potential device performance. In the context of photovoltaic applications, a lower PL intensity generally suggests a more efficient charge extraction process or reduced non-radiative recombination losses. It implies that photo-generated carriers (electrons and holes) are more effectively separated and collected, rather than recombining radiatively within the perovskite layer.The gas quenching method, which involves the rapid removal of solvent during the perovskite film formation by an inert gas flow, appears to facilitate the formation of films with improved crystallinity, fewer defect states, and enhanced interfacial contact with the underlying PTAA layer. These factors contribute to a reduced probability of radiative recombination events, hence the observed lower PL signal. On the other hand, the higher PL intensity observed in the anti-solvent (AS) processed films indicates that a significant fraction of the photo-generated carriers recombine radiatively without being extracted. This could be due to the presence of a higher density of defects, grain boundaries, and/or sub-optimal contact between the perovskite and the underlying transport layers, all of which can trap charge carriers and promote radiative recombination.

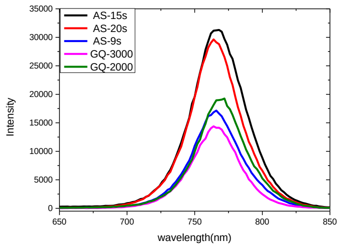

Figure-4: Steady-state photoluminescence (PL) of ITO glass/PTAA/MAPbI3. Gas quenching (GQ) and Anti-solvent (AS).

TRPL data was obtained (Fig-5).This data was fitted and the values of τ1, τ2 were gained. In this model, the faster decay component τ1 is attributed to charge carrier trapping involving defects, and slower decay components τ2 is assigned to the bimolecular radiative recombination in the bulk of the perovskite layer.

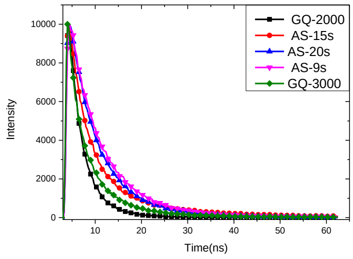

Figure-5: Time-resolved photoluminescence (TRPL) spectra of ITO glass/PTAA/perovskite. Gas quenching (GQ) and Anti-solvent (AS).

The obtained fitted parameters according to the model used are presented in Table 1. The fast decay component for GQ (3000, 2000 rpm) and AS (9s, 15s, 20s) is τ1 (12.91, 5.81 and 4.93, 4.59, 5.645 ns, respectively) as compared to the bare perovskite film (16.6 ns), which indicates the reduced defect density in the perovskite layers. The slower decay component τ2 was also significantly enhanced from 10.95, 19.29,11.69 ns for AS (9s,15s,20s) to 46.14,42.45 ns for GQ(3000 ,2000 rpm), suggesting that optined active layer by gas quenching method reduced recombination losses in the perovskite bulk, which could be attributed to the enhanced film morphology and increased grain sizes.

Table-1

	T_1 [ns]	T_2 [ns]
AS-15s	4.594	19.29
AS-20s	5.645	11.69
AS-9s	4.93	10.95
GQ-3000	12.91	46.14
GQ-2000	5.81	42.45

Recommendations. This study showed that gas quenching promotes improved film morphology and enhanced optical properties, likely due to more uniform crystal formation, larger grain sizes, and reduced defect densities within the perovskite layer. Such improvements contribute to more efficient photon absorption and charge carrier transport, which are critical parameters for the overall performance of optoelectronic devices. The higher absorption coefficient observed in gas-quenched films at 550 nm further underscores their superior light-harvesting capability, which can directly translate into enhanced power conversion efficiencies in photovoltaic applications. Therefore, gas quenching stands out as a scalable and effective approach for fabricating high-quality perovskite films, paving the way for the development of next-generation, high-performance solar cells, photodetectors, and other optoelectronic devices.

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