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Version Post-Print/Accepted Manuscript

Citation (published version) Sutherland, B. R., Hoogland, S., Adachi, M. M., Wong, C. T. O., & Sargent, E. H. (2014). Conformal Organohalide Perovskites enable Lasing on spherical Resonators. *ACS Nano*, 8(10), 10947–10952. doi:10.1021/nn504856g

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Conformal Organohalide Perovskites Enable Lasing on Spherical Resonators

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perovskites, atomic layer deposition, whispering gallery mode lasing, $\text{CH}_3\text{NH}_3\text{PbI}_3$

Conformal integration of semiconductor gain media is broadly important in on-chip optical communication technology. Here we deploy atomic layer deposition to create conformally-deposited organohalide perovskites—an attractive semiconducting gain medium—with the goal of achieving coherent light emission on spherical optical cavities. We demonstrate the high quality of perovskite gain media fabricated with this method, achieving optical gain in the nanosecond pulse regime with a threshold for amplified spontaneous emission of 65 ± 8 $\mu\text{J cm}^{-2}$. Through variable stripe length measurements, we report a net modal gain of 125 ± 22 cm^{-1} and a gain bandwidth of 50 ± 14 meV. Leveraging the high quality of the gain medium, we conformally coat silica microspheres with perovskite to form whispering-gallery mode optical cavities and achieve lasing.

Rapid developments in thin-film organometallic perovskites are enabling high-efficiency and low-cost solar electricity devices.¹⁻⁹ The excellent photophysical properties of this material¹⁰ have been further exploited towards light-emissive technology with reports of light-emitting diodes,¹¹ and lasing from i) bulk perovskite faceted crystals,¹² ii) distributed feedback resonators,¹³ and iii) planar whispering gallery cavities.¹⁴

We were motivated to explore whether lasing with spherical resonators could be achieved using perovskite active layers. This would require a continuous spherical coating of the perovskite film. Spherical resonators have yielded some of the highest confinement coefficients (Q-factors) among the full suite of optical cavities, and have promising applications in on-chip integrated optical communications.¹⁵⁻¹⁷

Unfortunately, we found that existing methods of perovskite film deposition from the solution phase or *via* directional co-evaporation failed to produce, with the needed high consistency, the required conformal coverage of the curved resonator surfaces. For example, we attempted dip-coating in a liquid $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor and flash anneal, but found that this approach did not produce consistent-thickness conformal layers of perovskite thin-films on the spheres, and was sensitive to drying conditions.

To couple the perovskite gain material efficiently to spherical resonators, we would require a means of forming films that would provide intimate physical and hence optical coupling, minimize scattering loss, and form a conformal and even-layer on the spheres. Techniques for conformal deposition of active materials are also important in materials science and optoelectronics broadly, such as for the direct integration of optical gain media with CMOS-defined cavities such as rib waveguides.

We developed a perovskite growth process which utilizes atomic layer deposition (ALD), a low-temperature and low-pressure thin film formation method prized for its conformality, wide process window, and precise thickness control. We start from a film of ALD PbS, which forms the conformal seed layer. This film is then completely converted to PbI₂ *via* exposure to I₂ gas in a closed, nitrogen-inert, system. PbI₂ is subsequently converted to CH₃NH₃PbI₃ perovskite (MAPbI₃) through treatment with CH₃NH₃I (complete description in Methods).

Results and Discussion

Lasing relies on an active medium capable of sustaining population inversion and optical gain through stimulated emission of radiation. We studied the optical properties of the perovskite active medium to elucidate the processes that govern lasing operation. All optical studies are performed at room temperature unless otherwise noted. We began by investigating the intensity-dependent spectral emission properties of a perovskite film on a lower-refractive-index substrate. We deposited a 75 ± 18.7 nm MAPbI₃ thin film *via* perovskite ALD onto a glass slide (Figure 1a) and confirmed that the film has an absorption onset at 1.55 eV with an absorption coefficient exceeding 10^4 cm⁻¹ past the bandedge (Figure 1b, blue), indicative of the direct bandgap of the perovskite. Under 460 nm continuous-wave excitation, a broad photoluminescence (PL) signal centered at 1.61 eV with a full-width at half-maximum (FWHM) of 130 meV (Figure 1b, red) is observed. The ultraslow Stokes shift of 60 meV is indicative of a sharp bandedge and minimal vibrational relaxation capable of sustaining optical gain close to the bandedge¹⁸. This increases the upper limit for the open-circuit voltage¹⁹ in perovskite photodiodes, consistent with the impressive values presented in published perovskite solar cells.

We subsequently excited the film using a pulsed laser source with an emission wavelength of 355 nm, pulse duration of 2 ns, and repetition rate of 100 Hz. Increasing the pump fluence reveals a threshold behavior at which the emission spectrum abruptly transitions from broad photoluminescence to a red-shifted narrow 17 meV linewidth emission peak centered at 1.58 eV (Figure 1c). The spectral narrowing for excitation above a threshold pump intensity is a signature of stimulated emission, here in the form of amplified spontaneous emission (ASE).

The resulting spectra contain superimposed emission from PL and ASE. To distinguish between these contributions, we estimate the emission intensity due to PL as twice the integrated intensity above 1.61 eV, just past the tail of the ASE signature (Figure 1d, red). The total emission from ASE is then estimated as the total integrated intensity across the entire spectral range from 1.4 – 1.9 eV (Figure 1d, red + blue), minus the total PL intensity. Figure 1e shows the pump-excitation dependence of the deconvolved PL and ASE emission. The integrated power that is emitted from the broad PL portion of the spectra follows a sub-linear behavior (Figure 1e, red), indicative of state-filling near the conduction band edge. In contrast, the narrow spectral component exhibits a clear superlinear behavior with a threshold energy density of $65 \pm 8 \mu\text{J cm}^{-2}$ (Figure 1e, black). This threshold behavior with excitation intensity is another characteristic of stimulated emission, signaling that population inversion has been achieved.

The capability of perovskites to demonstrate stimulated emission in the nanosecond pulse excitation regime, orders of magnitude longer than previous reports,¹²⁻¹⁴ is a strong indication of a high-quality gain medium. The absorption coefficient at the spectral position of the ASE signal is evaluated to be $3100 \pm 830 \text{ cm}^{-1}$. This value is similar to well-developed, single-crystal semiconductors such as GaAs,²⁰ a key performance attribute that suggests promise for thin film perovskites for optical amplification. We also investigated the perovskite gain medium under

continuous-wave, millisecond, and microsecond pulse durations, and found that emission intensity nonlinearity and spectral narrowing characteristic of amplified spontaneous emission were not observed. This is a result of the ASE threshold lying above the damage threshold of the film under these conditions. Strategies that reduce the modal losses and efficiently convey heat from the perovskite thin film could facilitate progress towards achieving population inversion under these pulse durations.

The pronounced threshold as a function of excitation intensity, from photoluminescence alone to the clear emergence of narrowband amplified spontaneous emission, indicates optical gain with a gain relaxation time that is shorter than the carrier buildup time.²¹ We investigated the net modal optical gain in the perovskite medium using the variable stripe length characterization technique.²² Here, we excite our sample at a fixed pump fluence of $150 \mu\text{J cm}^{-2}$, above the threshold for ASE. We focus the circular pump beam to a stripe using a cylindrical lens. An adjustable straight-edge razor blade placed close to the sample controls the length of the excitation stripe and the emission is collected from a cleaved edge of the sample using an optical fiber (Figure 2a).

We examine the dependence of the edge-emission intensity of a stripe-pumped perovskite above the ASE threshold on the length of the excitation beam. The full spectrum for all stripe lengths is shown in Figure 2b. The emission intensity at 1.58 eV, the energy at which the ASE signal is maximum, exhibits an exponential behavior as a function of increasing stripe length prior to gain saturation. For increased stripe lengths, gain saturation occurs in regions in which free carriers have been depleted by ASE.²³ An exponential fit of the collected emission in the small stripe regime (stripe length $< 0.535 \text{ cm}$) with a 1D amplifier model yields an estimated gain value of $125 \pm 22 \text{ cm}^{-1}$ (Figure 2d,e). This gain value corresponds to the modal gain, which

combines the sub-unity confinement of the optical mode to the gain medium, multiplied by the material gain, and reduced by the effect of modal waveguide losses. This value for the net modal gain for 2 ns pump pulse duration is comparable to prior reports on organohalide perovskites under 150 fs pulse durations¹² It is also comparable to the net modal gain in other non-single-crystal semiconducting systems such as colloidal quantum dots,^{24–27} silicon nanocrystals,²⁸ and semiconducting polymers.²⁹ The spectrally-resolved modal gain bandwidth is 50 ± 14 meV, obtained from analysis of ASE signal vs. stripe length at each wavelength. Gain bandwidths of this magnitude are similar to those found in compound semiconductors,²⁰ consistent with the sharp bandedge of perovskites, remarkable considering the perovskite films' polycrystalline nature.

The presence of net optical gain, with a demonstration of ASE, highlights the potential for ALD perovskites to serve as active materials for lasing under nanosecond pulsed excitation. We formed the gain medium using perovskite ALD onto an optical resonator of 52 μm diameter silica microspheres. Lasing can be achieved provided the cavity losses are less than the modal gain: thus only if the microspheres were conformally coated would it be possible to achieve efficient waveguiding and therefore a net positive modal gain in the film that coated the sphere.

To study the perovskite growth, we imaged the coated microspheres with scanning electron microscopy (SEM). Figure 3a shows a 45 degree tilt SEM image of the perovskite surface, revealing structured polycrystalline domains. Figures 3b,c show the perovskite coating onto the curved surface of the microsphere. Using focused ion beam milling, we cut the spheres in half down the center to better study the film formation and coverage. Figures 3d-g reveal a uniform, continuous coating of perovskite covering the surface of the sphere with infiltration deep into the

trenches near the sphere-substrate interface, something not readily achievable using traditional deposition methods.

We subsequently optically pumped the perovskite-coated microspheres and measured the emission spectra. We expect whispering-gallery-modes to couple into the sphere and produce optical feedback via various pathways along the circumference of the cavity, resulting in multi-directional lasing (Figure 4a). Figure 4b shows the emission spectra of perovskite-coated microspheres at temperature $T = 80$ K at varying excitation levels. This spectrum exhibits clearly defined modes with a regular spacing of 3 meV, corresponding to an effective refractive index of approximately 1.4, indicating that the mode is predominantly confined to the silica-perovskite region. Figure 4c shows the dependence of emission intensity on pump fluence. The background signal is subtracted from the adjacent cavity mode at 1.642 eV and the dependence of intensity on pump fluence is plotted against the background. A clear threshold is observed for the cavity mode at a pump fluence of $75 \pm 11 \mu\text{J cm}^{-2}$. Further, the slope-efficiency of the cavity mode signal is greater than that of the background. We attribute this combined spectral-threshold dependence to lasing cavity modes and we demonstrate that the perovskite gain medium is stable under these conditions for 24 hours (Figure 4d). The spectral bandwidth of the laser modes are dominantly limited by the resolution of the collection optics, thus we conservatively estimate the lower-bound of the Q-factor for these resonators to be of order 10^3 .

Conclusions

The results presented herein show that ALD perovskites offer conformal deposition onto substrates of various curvatures and aspect ratios. This fabrication strategy forms perovskite films with excellent lasing-relevant optical properties, enabling them to sustain population

inversion when excited using low peak intensity pumping; and with excellent material properties, allowing ready formation of conformal waveguiding films when deposited on spherical resonators. Facile conformal deposition of perovskite light emitters has the potential to enable applications such as low-cost on-chip optical communication systems readily integrated with silicon photonics technology.

Methods

ALD Perovskite sample fabrication. Glass substrates were prepared by first sonicating in acetone, then isopropyl alcohol, and then deionized water, each for 15 minutes. Samples to be used for lasing studies employed silica spheres (52 μm diameter, suspended in water) dispensed onto the surface of the glass. Excess water was dried by heating on a hotplate at 120°C for 1 minute. Samples were exposed to a 10 minute 100 mTorr oxygen plasma treatment immediately prior to atomic layer deposition.

$\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films are fabricated on these substrates by a three-step method. A) PbS deposition: Cleaned glass slides are placed into a Cambridge Savannah S100 atomic layer deposition system with the sample chamber held at 150 °C. Alternating pulses of $\text{Pb}(\text{tmhd})_2$ and H_2S precursors (0.5 s pulse duration for both) build up the PbS film of a desired thickness. The purge time between precursor pulses was 20 s, and a nitrogen carrier gas was used at a volumetric flow rate of 10 sccm. B) PbI_2 conversion: 100 mg of iodine chips are placed into a 250 mL nitrogen-sealed container which contains the PbS films. The container is heated on a 120°C hotplate for 16 hours. After treatment, the samples are completely yellow and have been converted to PbI_2 . C) MAPbI_3 conversion: The PbI_2 films are dipped into a 30 mg/mL solution of

CH₃NH₃I dissolved in isopropyl alcohol (IPA) for 60 s, immediately dipped into IPA for another 60 s, and then dried on a hot plate at 70 °C for 30 minutes.

Focused Ion Beam (FIB) and Scanning Electron Microscopy (SEM). A Hitachi table top ion mill model IM 4000 was used for sample FIB preparation. Argon ions were used at an accelerating voltage of 6 kV and a discharge voltage of 1.5 kV. The sample was milled for 3.5 hours with the glass substrate facing the ion source to allow for gentler milling. Samples were imaged with a Hitachi NB-5000 high-resolution CFEG-SEM. An accelerating voltage of 20 kV was used, a variable pressure of 60 Pa, and imaged using a highly sensitive ultra-variable-pressure detector.

Optical excitation and collection. Unless otherwise noted, samples were optically excited using a 355 nm frequency-tripled Nd:YAG laser with a pulse width of 2 ns and a repetition rate of 100 Hz. All spectral data was collected using an Ocean Optics USB2000+ UV-VIS spectrometer without an input aperture, with the spectral resolution defined by the width of the input fiber core. 62.5 μ m core diameter fiber was used to collect all spectra, except for the data presented in Figures 4b,c which was collected with a single mode fiber, with the SMF case producing a spectral resolution of $\sim$ 0.4 nm, enabling us to distinguish individual laser modes. To detect WGM lasing modes, we focused the pump beam to a circular spot so that it illuminated a cluster of 4 spheres as well as some of the planar background. All measurements of laser power were taken using an Ophir Laserstar 1Z01600 single channel digital power meter.

Absorption coefficient. The optical density, A_{OD} , of the perovskite film was measured using a Perkin Elmer Lambda 950 spectrophotometer with an integrating sphere. A DekTak 3 profilometer was used to measure the film thickness, d . This was used to calculate the absorption coefficient, $\alpha = \log_{10}(e) \cdot A_{OD}/d$.

Variable stripe length measurement. The variable stripe length technique was employed to determine optical gain in the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film. Intensity at each wavelength as a function of stripe position was fit to a linear amplifier model: $I_{\text{ASE}}(L) = A(e^{gL} - 1)/g$, where I_{ASE} is the intensity of the ASE, L is the stripe length, g is the modal gain to be determined, and A is a pre-exponential factor related to the ratio of emitted spontaneous emission to modal gain.²³

Figure 1. Amplified spontaneous emission from nanosecond pulsed excitation in $\text{CH}_3\text{NH}_3\text{PbI}_3$ grown *via* ALD. (a) 75 nm of MAPbI_3 is deposited onto a glass slide *via* perovskite-ALD. (b) Spectral absorption coefficient and photoluminescence under continuous-wave excitation. (c) Development of spectrally-narrow amplified spontaneous emission with increasing pump power.

(d) Emission spectra at 67 uJ cm^{-2} of ASE coupled with PL. (e) Integrated emission intensity of PL and ASE as a function of pump fluence. A clear threshold for ASE is observed at $65 \pm 8 \text{ uJ cm}^{-2}$.

Figure 2. Net modal optical gain in $\text{CH}_3\text{NH}_3\text{PbI}_3$ ALD perovskites under nanosecond pulsed excitation. (a) Variable stripe length measurement setup for gain determination. (b) Emission spectra for increasing stripe length. (c) ASE intensity at an emission photon energy of 1.58 eV as a function of stripe length (black), and a linear amplifier fit (red) prior to the onset of gain saturation (see methods for full details). (d) Spectral dependence of modal gain (red) and sample ASE spectrum at maximum stripe length (black). The peak gain bandwidth is $125 \pm 22 \text{ cm}^{-1}$ and the gain bandwidth is $50 \pm 14 \text{ meV}$.

Figure 3. Scanning electron microscope images of microspheres coated via perovskite ALD. (a) 45 degree image of the perovskite surface. (b) Zoom-out of entire microsphere coated with perovskite. (c) Zoom-in showing coverage all along the curved surface of the sphere. (d) Cross-sectional image of a sphere cut down the center with focused ion beam milling revealing a

uniform coating around the circumference of the sphere. (e) Zoom-in on a cross-section of the sphere showing distinct perovskite and SiO₂ regions. (f) Zoom-in of sphere-substrate interface showing a continuous film with good infiltration into the grooves. (g) Angled zoom-in of sphere cross section, showing a good uniform coating of perovskite around the surface of the sphere. Scale bars: a – g: 0.2, 10, 2, 10, 3, 5, 4 (μm).

Figure 4. Modal confinement and lasing in perovskite coated silica microspheres. (a) Schematic showing a perovskite-coated microsphere absorbing pump light and coupling luminescence into the cavity, resulting in laser emission. (b) Spectral dependence of perovskite coated microsphere emission on pump power at temperature $T = 80 \text{ K}$ for three different pump fluences (100-blue, 175-green, and 300-red $\mu\text{J cm}^{-2}$). Distinct laser modes are observed with a free spectral range of 700 GHz. (c) Lasing emission intensity dependence on pump fluence. The intensity of the dominant lasing peak at 1.642 eV, 'a', with the adjacent background signal at 'b' subtracted is compared to the background signal. The slope efficiency of the lasing mode (blue) is greater than

that of the background (red), and a lasing threshold is observed at a pump fluence of $75 \pm 11 \mu\text{J cm}^{-2}$. (d) 24 hour ASE stability under lasing conditions.

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Acknowledgement

This publication is based in part on work supported by an award (KUS-11-009-21) from the King Abdullah University of Science and Technology (KAUST), by the Ontario Research Fund Research Excellence Program and by the Natural Sciences and Engineering Research Council (NSERC) of Canada. The authors thank S. Boccia for FIB and SEM imaging of ALD perovskite coated microspheres, and S.-R. Jean for help with figure art.

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Table of contents figure: