DRAFT

# Optimization of semiconductor halide perovskite layers to implement waveguide amplifiers

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**ABSTRACT**

Semiconductor organometallic halide ($CH_3NH_3PbX_3$, X=Cl, Br, I) perovskites (HPVK) have been emerged as a potential gain media to construct a new generation of active photonic devices. Indeed, during the last three years a significant effort has been carried out to implement HPVK-based optical amplifiers or lasers with improved quality factors. In particular, minimization of the threshold of stimulated emission has been an important concern to decrease the power consumption, and hence to enhance the performances of the device. For this purpose strategies include a suitable integration of the semiconductor in a photonic structure, or the optimization of the material. Here we propose a novel approach to develop optical amplifiers by an appropriate passivation of HPVK layers incorporated in an optical waveguide. For this purpose, geometrical parameters were firstly properly optimized to demonstrate amplification of stimulated emission with a threshold as a low as 2 nJ. In addition, the passivation of traps of the semiconductor by introducing organic additives (twisted hexaazatrinaphthylene and bisthiadiazolefused tetraazapentacenequinone) resulted in a further reduction of the threshold (down to four fold). These results provide a novel scheme to enhance the applications of perovskite active devices.

**Keywords**: waveguide amplifier, semiconductor perovskite, amplification of the stimulated emission, HATNA, DLC, PMMA

## 1 .INTRODUCTION

In the last five years semiconductor halide organometallic perovskites (HPVK) have been extensively studied as potential material to implement a new generation of optoelectronic devices [1]. Their fabrication, under a simple and cheap chemistry processes, results in polycrystalline semiconductor layers of the compound CH3NH3PbX3 (X=Cl, Br, I); which presents the general chemical formula of the perovskite lattice (ABX3), and exhibits outstanding electrical and optical properties.

For example, their large absorption coefficients and electron mobilities have been successfully exploited to demonstrate a new generation of solar cells with conversion efficiencies up to 22.1 % [2]. Nevertheless, HPVK layers also present excellent light emitting properties, such as a high quantum yield emission at room temperature with a band-gap tunable with the composition [1]. In this way, HPVK resulted also an interesting material to construct coherent or incoherent optical sources in a broad spectral range (400-800 nm) [3-4].

Indeed, since the first demonstration with optical gain with HPVK layers in 2015 [5], a great effort has been carried out during the last 2-3 years to enhance the generation of light and decrease the threshold of stimulated emission [3]. Strategies include a suitable integration of the semiconductor in an appropriate photonic architecture, or the optimization of the perovskite material. Here we propose a combination of both approaches in order to optimize the amplification of the spontaneous emission of $CH_3NH_3PbI_3$ layers. For this purpose, well-passivated HPVK layers in a polymer waveguide able to copropagate the photoluminescence (PL) together with an excitation beam [6]. First, threshold of optical gain was reduced down to 2 nJ by a careful design of the waveguide structure [7]. In addition, results were even improved (up to 4 fold) organic additives (twisted hexaazatrinaphthylene and bisthiadiazolefused tetraazapentacenequinone) were introduced inside the HPVK layers to passivate its grain boundaries [8]. These results provide a novel scheme to exploit the outstanding active properties of HPVK layers in photonic devices.

## 2. EXPERIMENTAL

The waveguide proposed in this work consists of a Poly(methyl methacrylate) (PMMA)/HPVK bilayer structure deposited on a commercial $SiO_2$(2 mm)/Si substrate (see Fig. 1a). For this purpose both $CH_3NH_3PbI_3$ and PMMA layers were spin coated on the substrate following the process described elsewhere [7]. The perovskite material, $CH_3NH_3PbI_3$, is characterized by an absorption band edge (not shown) and PL emission (see Fig. 2) at around 780 nm.

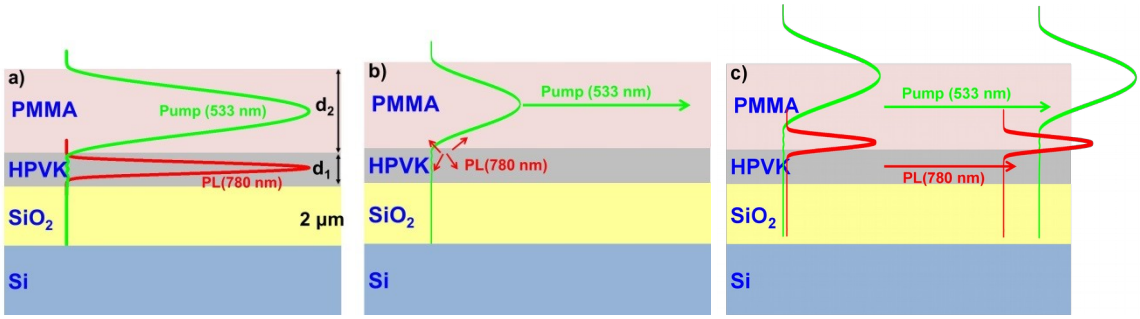


Fig. 1. a) Structure of the sample. b) Excitation beam at 533 nm is propagated along the PMMA layer and excites the semiconductor with the evanescent field. c) Low attenuation of the excitation beam in the PMMA allows the generation of PL along the whole length of the waveguide, which is propagated through the modes confined in the HPVK.

Since the refractive of HPVK (2.34 at 780 nm) is higher than that of $SiO_2$ (1.45 at 780 nm) the structure presented in Fig. 1 conforms an optical waveguide. Indeed, a multilayer algorithm [9] reveals the existence of propagating modes in both the PMMA (refractive index 1.49 at 780 nm) and HPVK films. In this way, the absence of losses in polymer allows the propagation of an excitation beam at 533 nm along the whole length of the structure (Fig. 1 b). Then, the evanescent of the mode at 533 nm, mainly confined in the PMMA, excites the PL of the HPVK at 780 nm (Fig. 1b), which is coupled to the modes confined in the semiconductor (see Fig. 1c). Thus, geometrical parameters of the waveguide demonstrated a critical impact in the propagation of light, and hence in the generation of PL. In these conditions, the optimum thicknesses of HPVK and PMMA ($d_1$ and $d_2$ in Fig. 1a were found to be 0.5 and 2.5 µm respectively.

## 3. RESULTS

### 3.1. Experimental set-up

Waveguides were analysed by end fire coupling a Nd:YAg laser (1 ns, 20 KHz) doubled at 533 nm at the input edge of the structure with the aid of a microscope objective, and collecting the PL from the output edge with another microscope objective. Then, light is analysed by collecting the guided PL in a commercial Ocean Optics HR4000 spectrograph.

### 3.2. Amplification of the stimulated emission

For low excitation fluencies PL spectrum measured at the output edge of the waveguide presented a Gaussian distribution centred at 775 nm (see Fig. 2b), in agreement with the spontaneous emission of $CH_3NH_3PbI_3$ [7]. Nevertheless, above a certain threshold of 2 nJ, spectrum collapses to a narrow peak with a Full Width of Half Maximum (FWHM) of around 3-4 nm, which is signature of stimulated emission. Indeed, integrated PL showed a superlinear increase above this threshold (see Fig. 2b), characteristic of optical amplifiers. Here it is worth mentioning that such a low threshold and narrow linewidth were obtained without the aid of an external resonator, and demonstrated to be one the best parameters obtained with perovskite materials [3].

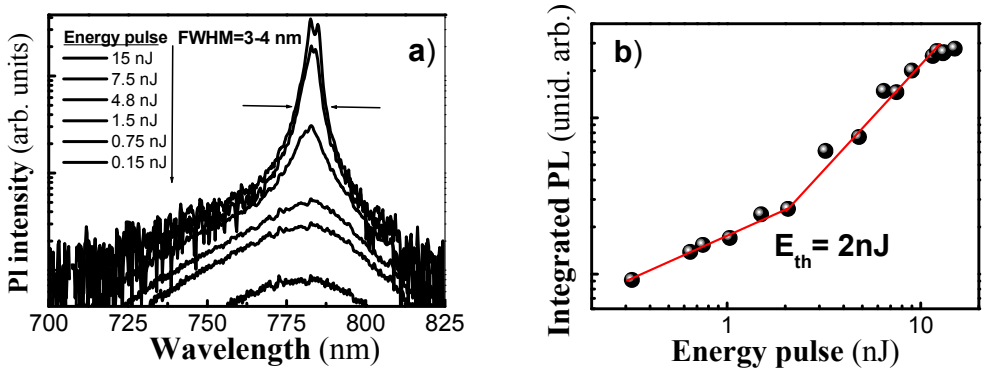


Fig. 2. a) PL spectra at the output edge of the waveguide for different excitation fluencies. b) Integrated PL as a function of the energy pulse. Narrowing of spectrum and superlinear increase of the integrated intensity indicates the generation of stimulated emission.

### 3.3. Incorporation of organic additives

In order to improve even more the performances of the device shown in Fig. 1a, grain boundaries of HPVK layers were properly passivated by incorporating the organic compounds DLC97 and HATNA [8]. Consequently, PHVK-organic compound films not only demonstrated an enhanced emission of PL, but also a reduction of the threshold of the stimulated emission up to 4-fold (see Fig. 3). In this experiment layers of HPVK were deposited on glass and measured by transmission. Future works will incorporate them on waveguides.

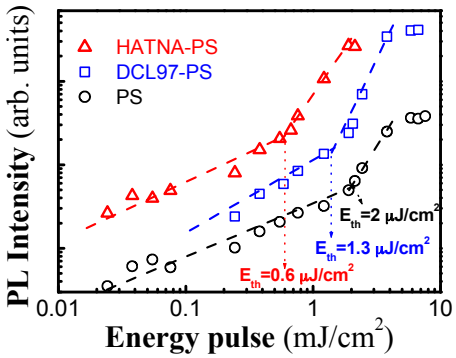


Fig. 3. PL intensity of HPVK layers (black), and HPVK layers incorporating DLC97 (blue) and HATNA (red) organic additives as a function of the energy pulse. Threshold of stimulated emission clearly decreases with the passivation of the organic compounds.

## 4. CONCLUSIONS

In this work the excellent light emission properties of organometallic halide perovskite are properly exploited to generate optical gain efficiently. For this purpose the material is integrated in waveguide structure able to copropagate the PL with the excitation beam. As a consequence, amplification of the stimulated emission was demonstrated with with linewidth as narrow as 3-4 nm and a threshold down to 2 nJ. Moreover, when the grain boundaries of perovskites were passivated with HATNA or DLC97 organic compounds threshold of stimulated emission was further reduced by 4 fold.

## ACKNOWLEDGEMENTS

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## REFERENCES

[1] C.C. Stoumpos, *et al.*: Phase transitions, high mobilities, and near-infrared photoluminiscence properties, *Inorg. Chem.*, vol. 52, pp. 9019-9038, 2013.
[2] https://www.nrel.gov/pv/
[3] I. Suárez: Active photonic devices based on colloidal nanocrystlas and organometallic halide perovskites, *Eur. Phys. J.*, vol. 75, pp. 30001, 2016.
[4] B.R. Sutherland and E.H. Sargent: Perovkiste photonic sources, *Nat. Photon.*, vol. 10, pp. 295-302, 2016.
[5] G. Xing , *et al.*: Low-temperature solution-processed wavelength-tunable perovskites for lasing., *Nat. Mater.*, vol. 13, pp. 476-480, 2014.
[6] H. Gordillo, *et. al.*: Quantum-dot double layer polymer waveguides by evanescent light coupling, *J Lightwave Technol*, vol. 31, pp. 2515-2525, Aug. 2013.
[7] I. Suárez, *et al.*: Polymer/Perovskite amplifying waveguides for active silicon photonics," *Adv. Mater.*, vol. 27, pp. 6157-6162, Aug. 2015
[8] T.T. Ngo, *et al.*: Enhancement of the Performance of Perovskite Solar Cells, LEDs, and Optical Amplifiers by Anti-Solvent Additive Deposition," *Adv. Mater.*, vol. 29, pp. 1604056, Dec. 2016
[9] G. Lifante: Integrated Photonics:Fundamentals, Ed., John Wiley& Sons, 2003.