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Fabrication of halide-perovskite resonant microcylinders by nanoimprint lithography

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Abstract. Halide perovskites are promising materials for optoelectronic devices, solar cells and various photonic applications due to their unique optical and electronic properties and low-cost fabrication. Halide perovskites micro and nanoscale structures have demonstrated high resonance properties last decade. Moreover, these materials allow high throughput creation of advanced nanophotonic designs employing nanoimprint lithography. Here, we develop this fabrication approach to create halide perovskites resonant microcylinders. Our study of the obtained microobjects demonstrates that the nanoimprint lithography yields desirable size and shape, as well as preserved photoluminescent properties of the microcylinders.

1. Introduction

Halide perovskites introduce a class of material for variable photonics design application due to their unique properties. In particular, room temperature excitonic states, high quantum yield luminescence efficiency, high efficiency of laser emission, high optical gain at room temperature, broadband bandgap spectral tunability, as well as simplicity of their low-cost fabrication [1, 2]. Also, organic-inorganic perovskites have been explored as a material with high refractive index (n > 2.5) for perovskite-based resonant structures: active nanoantennas [3], metasurfaces [4, 5], spectrally tuned nanoparticles [6], nanowire lasers [7], WGM microdisks lasers [8] and WGM nanoplates lasers [9]. There are several methods of perovskite nanostructuring preparation. Focused ion beam (FIB) lithography [10, 11] and electron beam etching (EBE) allow one to create different designs of nanostructures by removing the part of material from surface and provide the resolution around 1 nm [12, 13], whereas direct laser ablation [8] makes the fabrication process much faster. In turn, the halide perovskites can degrade after heating, high humidity and high-intensity light. Accordingly, after FIB and EBE methods thin films can be destroyed or lose important properties. In contrast, nanoimprint lithography developed recently for the perovskites [4, 5, 14] saves the emission properties of the material without large destroying. Furthermore, the perovskites are good materials for nanoimprinting due to their soft structure, allowing for filling in the mold pits under applied pressure. Employment
nanoimprint lithography method allows one to obtain nanostructures at large scale easily and rapidly, which demonstrated photoluminescence enhancement at room [4] and cryogenic [5] temperatures, photodetectors efficiency enhancement [15], and improvement crystallinity and surface quality [4]. Here we fabricate and investigate microcylinders made of MAPbI₃ perovskite by the nanoimprint lithography method. As a result, we obtained perovskite microresonators with high potential for lasing applications.

2. Results and discussion

To fabricate microcylindrical resonators we use nanoimprint lithography [14] on the 500-nm thick thin film (MAPbI₃) covering silica glass substrate. The thin film was prepared by a solvent engineering method [15]. Nanoimprint lithography is a multistep process where the thin film and preliminarily prepared silicon (Si) mold with specific design put under high pressure in a press machine. The operation proceeds in the vacuum atmosphere at the room temperature. We varied the pressure from 0.2 to 0.8 ton and kept it for 1-2 minutes. The nanoimprint process is then finished, and perovskite nanocylinders were formed as negative replications of the Si molds (Fig. 2). In our case, the depth of holes in the molds was 1 µm, the radius of cylinders varied from 650 to 950 nm, outer ring radius varied from 2 to 8 µm (Fig. 1).

Size and shapes of produced structures we studied by scanning electron microscopy (SEM) (Fig. 2). As a result, we obtained MAPbI₃ perovskite microcylinders. As we can understand from SEM images (45 degree on Fig. 2), the height of microcylinders is different because of the variable thickness of the thin film due to the spin coating process.

![Figure 1. SEM images of silicon mold for a) 1.9 µm and b) 1.8 µm disk diameter](image)

After the nanoimprint fabrication process, we studied photoluminescence (PL) and scattering spectra of the microcylinders. To study PL properties of an individual microcylinder, we used frequency doubled Yb-doped femtosecond laser (TeMa, Avesta Project) yielding laser pulses at wavelength 525 nm, repetition rate 100 kHz after a Pockels cell, and pulse duration shorter than 150 fs. The laser beam was focused onto the sample surface at normal incidence by a 50× objective (Mitutoyo M Plan APO NIR, NA = 0.42), focused into Horiba LabRam HR spectrometer, and projected onto a thermoelectrically cooled charge-coupled device (CCD, Andor DU 420A-OE 325). PL emission spectra from nanostructure were studied by using a 600 g/mm grating. All measurements were obtained at the room temperature in air.

The scattering spectra from microcylinders was analyzed by the confocal dark-field (DF) spectroscopy method. The microcylinders were excited at an oblique angle (65 degrees with respect to the normal of the surface) by linearly polarized light from a halogen lamp (HL-2000-FHSA) through a weakly focusing objective (Mitutoyo M Plan Apo NIR, 10×, NA = 0.28). Scattered light is collected from the top by a 50× objective (Mitutoyo M Plan APO NIR,
NA = 0.42), sent to Horiba LabRam HR spectrometer and projected onto a thermoelectrically cooled charge-coupled device (CCD, Andor DU 420A-OE 325) with a 600 g/mm diffraction grating. Scattering spectra for the different radii of microcylinders demonstrate some features, which can be related to optical resonances with spectral positions at wavelengths more than 780 nm, i.e. in the transparency range of the perovskite (Fig. 2). In the range with high optical losses (<760 nm) and high absorption of this material (MAPbI₃), we didn’t observe any resonances. Also, the important point for the optical properties is roughness of the obtained microcylinders. Previous results demonstrated that quality factor quadratically decrease with the increase of roughness amplitude [8]. In our next works we are going to improve the employed nanoimprint

![Figure 2](image)

**Figure 2.** Characterization of microcylindrical resonators. SEM images (at 90 and 45 degree angle), PL and scattering spectra of perovskite microcylinders with a) 1.64 µm, b) 1.81 µm, c) 1.95 µm diameter. All scale bars are 4 µm.

![Figure 3](image)

**Figure 3.** Comparing of PL spectra of pristine perovskite film and PL spectra of cylinder.
method for the enhancement of the optical modes quality factors in our designs and to achieve lasing.

3. Conclusion
We have applied the nanoimprint lithography method for fabrication hybrid perovskite (MAPbI$_3$) microcylinders. We have demonstrated the emitting and resonant optical properties of achieved nanostructures. By using this method, we can control the size and shape of structures to obtain the required resonant properties. The development of this technique paves the way to advanced nanoscale and microscale structures fabrication and for perovskite-based photonic and optoelectronic devices.

4. Acknowledgments
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