13th International Conference Series on
Laser-light and Interactions with Particles
Optical Particle Characterization follow-up !
August 21-26th, 2022, Warsaw, Poland

HIGH-RESOLUTION VOLUMETRIC LITHOGRAPHIC RECORDING OF 3D STRUCTURES BY ACTIVATING UP-CONVERSION LUMINESCENCE IN Yb^{3+} AND Tm^{3+} NANOPARTICLES DOPED INTO A NEGATIVE SU8 PHOTORESIST

Julija PERVENECKA[1*], Jurgis GRUBE [1], Ernests TROPINS[1], Kaspars VITOLS[1], Viesturs-Tenis VIKSNA[1], Janis TETEROVSKIS[1], Aivars VEMBRIS[1], Jelena BUTIKOVA[1], Guna KRIEKE[1] and Maris SPRINGIS[1]

[1] Laboratory of Organic Materials, Institute of Solid State Physics, University of Latvia, Riga, LV-1063, Latvia

Corresponding author: julija.pervenecka@cfi.lu.lv

Abstract

In this work we demonstrate success of an innovative approach to lithographic recording of high-resolution 3D structures from the volume of hybrid inorganic/photoresist systems by activating up-conversion luminescence in Yb^{3+} and Tm^{3+} nanoparticles doped into a negative photoresist SU8. That is highly perspective for the fabrication of various types of microstructures from such hybrid systems as organic-chromophores/UCNPs/SU8, without damaging light sensitive organic compound, demanded in photonic applications.

Keywords: lithography, SU-8 photoresist, hybrid systems, guest-host system, UCNP, luminescence, up-conversion, microstructures.

1 Introduction

In nowadays, great attention has been attracted to the up-conversion nano-particles (UCNPs). One of the greatest advantages and at the same time unique properties of UCNPs are anti-Stokes's shift luminescence, meanwhile all conventional luminescent materials have down-conversion luminescence. Another important advantage of them is well controlled solution chemical synthesis process where through several modifications can be designed and changed core/shell structured UCNP's active light emitting core or comparably passive - shell dopant ions or they concentration, as well as size and form of all UCNP's.

At the present time perspective, but not as widely investigated application for up-conversion luminescence emitting nanoparticles is photolithography. In traditional photolithography exposure are made through the surface, mostly, by i-line UV radiation, which is limited by the thickness of photo sensitive layer. In thick samples most of the radiation is absorbed in the upper layers, which results in unexposed deeper layers, turning to strong distortion (partial) or fully washing off all recorded structures upon development process. More over, traditional i-line photolithography is not the effectivnes for negative tone photoresists as SU8, since appropriates to the range of its absorption spectrum decay (~20-30%). This problem can be solved in case when light emitting sources are placed into photoresist thus ensures uniform absorption of required blue or UV-light in all volume of exposed structure. It can be achieved by doping the photoresist with light sources, such as inorganic nanoparticles [1], which emitts light (luminescence) in appropriate spectral region after excitation with external energy source (laser).

Here luminescence is excited with the wavelength at which the photoresist is transparent, meanwhile, by nano-particles emitted light will be absorbed by photoresist and behaves in similar as blue or UV light. In practis, it can be done by mixing photoresist with nanoparticles activated with rare-earth ions, in which up-conversion luminescence occurs. Up-conversion luminescence is one of the Anti-Stokes process, which can be excited in inorganic nanoparticles prepared in a special way. It occures when UV and visible luminescence is excited with the absorption of multiple infrared (IR) photons [2].

The photoresist and organic compounds are transparent for infrared light; therefore, it is possible to guide the excitation light into the volume of the photoresist. It means, that in perspective similarly, up-conversion luminescence could be used to expose a photoresist mixed with organic chromophores. Overcoming the biggest problem, total degradation of organic chromophores upon traditional i-line UV radiation due to high absorption of it. That allows to create systems containing organic chromophores for possible application in medicine, telecommunications and other technologies demanded light emitting micro-structure creation.

In this work system of SU8 photoresist mixed with up-converting nanoparticles were created. Our made method demonstrates an innovative approach for recording high-resoluted three-dimensional structures in a negative photoresists as SU8 by tunable through the synthesis process up-conversion luminescence of the Yb3+ and Tm3+ activated in incorporated core/shell (C/S)-structured nanoparticle as an alternative of an traditional optical lithography. We show that it is possible to create optical writing in systems volume, by exciting nanoparticles with a 975 nm laser diode, by achieving high resolution, uniformly thick 100x500 μm microstructures with a good appropriance to the focused structure dimensions, at less

then 5 min longed exposure in samples with 20-15%wt of UCNPs in SU8.

contact@lip-conference.org

1.1 Synthesis and characterization of Yb^{3+} and Tm^{3+} core/shell structured nanoparticle)

The investigated nanoparticles with a hexagonal (d = 30-50 nm) core/shell structure were synthesized by thermolysis method in two-day long process. To perform the work, the nanoparticle synthesis setup was created: a three-necked flask, which is placed in a magnetic heater. For the synthesis process to be successful, most of the synthesis must take place under an argon atmosphere (three vacuum and argon aeration cycles are performed). The shell and core nanocrystals are made at the same time in different flasks and have the same synthesis procedures. From Yttrium oxide is made shell nanocrystals while core nanocrystals are made from Yttrium (Y), Ytterbium (Yb) and Thulium (Tm) oxides (concentration: Y – 74.7%, Yb – 25%, Tm – 0.3%). At the last stage is added 40 ml of Chloroform and centrifuged for 10 minutes, then prepared solution is poured in storage containers:

1.2 Sample preparation

All samples were made as host-guest systems, by adding guests – UC nano-particles - consisting $CHCl_3$ solution into photoactive host - 400 - 500 nm thin film layer providing solution of dissolved in chloroform SU-8 GM1075 epoxy-based negative type photoresist matrix. Photoactive thin film samples were made from solution by spin-coating method on BK7 glass substrates, precleand with oxigen plasma by Plasma Asher Tepla setup. Keeping constant volume ratio of system compounds to solvent, varying concentration ratios of UCPN in SU8 were made series of the samples with UCPN concentration 10, 15, 20, 25, 30, 40, 50 wt%.

1.3 Up-conversion luminescence based lithographic record

Up-conversion luminescence based lithographic recording were made by the self-made system see Figure. 1.

Figure 1 *Self-made optical system for up-conversion luminescence based lithographic recording*

UC luminescence excitation were made at 975 nm by Thorlabs L975P1WJ CW laser diode mounted on TCLDM9 - TE-Cooled Mount from Thorlabs was used (LD). Laser diode beam was focused on the sample surface 100x500 μm area using anamorphic prism pairs (Thorlabs N-SF11 Mounted Prism Pair, ARC: 650 - 1050 nm, Mag: 4.0) and objective lens (OL) (Thorlabs High-Power MicroSpot Focusing Objective, 5X, 980 - 1130 nm, NA = 0.13). Laser power was set to 700 mW. Exposition times were set to 5, 10, 15 and 25 minutes. As the beam passes through a pair of prisms (APP), it changes from an ellipse to a rectangular-circular profile.

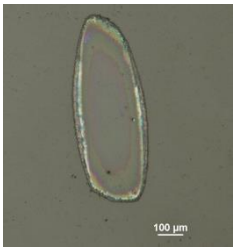

Figure 2 *Optical image of recorded structures in sample with 15wt% of nanoparticles in SU8 (exposed ~10 min , ~ 450 nm thickness). Obtained by high-resolution optical microscope Nikon ECLIPSE L150 at x50 zoom.*

2 Conclusions

Our made method is an alternative of an traditionnal optical litography. It is an innovative approach for recording high-resoluted three-dimensional structures in a negative photoresists SU8 by up-conversion luminescence of the Yb3+ and Tm3+ activated in incorporated core/shell (C/S)-structured nanoparticle.

We proved that it is possible to create optical writing in systems volume, by exciting nanoparticles with a 975 nm laser diode, by achieving high resolution, uniformly thick 100x500 μm microstructures with a close apropriance to the focused structure dimensions, at 5-10 min longed exposure in samples with 20-15%wt of UCNPs in SU8 see Figure. 2.

3 Acknowledgement

This research is funded by the Latvian Council of Science, project "Up-conversion luminescence photolithography in organic compounds using nanoparticles/photoresist composition", project No. lzp-2019/1-0422.

Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01- 2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART².

4 References

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