STIMULATED EMISSION of CdSe/ZnS NANOCRYSTALS IN POLYMER DFB STRUCTURE OBTAINED BY HOLOGRAPHIC ORDERING OF POLYMER NANOCOMPOSITE

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ABSTRACT

Stimulated emission is demonstrated in volume distributed feedback (DFB) structures, formed by colloidal CdSe/ZnS and ZrO_2 nanoparticles in polymer matrix. Periodic redistribution of nanoparticles in organic matrix is produced by holographic photopolymerization of specially developed light-sensitive nanocomposite. The formulation consists of two acrylate photocurable monomers and two types of inorganic nanoparticles - highly photoluminescent CdSe/ZnS and high refractive index ZrO_2. The core-shell CdSe/ZnS nanocrystals are used as a gain medium, while ZrO_2 nanoparticles create the refractive index grating and enhance the distributed feedback. The period of the volume structure provides the feedback for lasing at the wavelength λ_{las} of about 575 nm in the second diffraction order. In proposed DFB structures the active nanocrystals serve as emitting materials and can create the feedback simultaneously. Pumping of DFB-structures by titanium-sapphire laser beam (λ_{pump}=400 nm and pulse duration of 120 fs) normal to the sample plane the appearance of a sharp stimulated emission peak is observed along the grating-vector direction. Output intensity as a function of the laser pumping energy shows a threshold behavior, while a full width at half-maximum (FWHM) of stimulated emission spectral band decreases from 33 to 12 nm.

Key words: holographic polymerization, nanocomposite, nanocrystal stimulated emission

INTRODUCTION

Semiconductor solid-state lasers keep a leading place in modern optical technologies ranging from information processing and storage to optical telecommunications and medicine. Nevertheless, their miniaturization and performance improvement are the subject of scientific research during last

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decades. New impact in the laser improvement gives the utilization of semiconductor nanocrystals, so called nanocrystal quantum dots (NQDs) as optical gain media. Strong quantum confinement in NQDs with $r < 10$ nm provides stable laser generation at room temperature. Additionally, a dependence of energy spacing on the NQD-radius gives the possibility to tune the emission spectrum. Besides an unquestionable advantage of NQDs is the fact that they can be prepared using routine chemical synthesis that ensures precise control of NQDs size with size dispersion as small as 5% and surface passivation by both organic and inorganic shells. By choosing suitable caps, NQDs can be introduced in different organic and inorganic matrices to obtain nanocomposites with high semiconductor fill-factor. Lasing has been realized in CdSe NQDs – titania nanocomposites [1-3]. To obtain lasing the capillary microcavity [2], the transferred second order DFB grating, printed on the surface of NQDs-titania waveguide [1,3] have been used.

In the present paper we demonstrate ASE in volume DFB structures, formed by inorganic nanoparticles (NPs), spatially ordered in a polymer matrix. Core-shell CdSe/ZnS NQDs are used as an optical gain medium. The DFB is formed by the spatial ordering of the NPs in organic polymer via holographic photopolymerization.

RESULTS AND DISCUSSION

The holographic photopolymerisable nanocomposite was prepared by the addition of a dispersion of ZrO_2 NPs and CdSe/ZnS NDQs in chlorophorm to the monomer mixture (SR444 and IOA) containing the photoinitiator and following evaporation of the solvent. The reactive cells were prepared placing a drop of the nanocomposite between two glass substrates. The thickness 50 μm was controlled by Mylar spacers. Volume DFB structures were fabricated using conventional two-beam set-up for the holographic recording of transmission gratings based on an Ar-ion laser operating at λ_r = 364 nm. As it was found earlier [4], the formation of the polymer network from the fast polymerizing monomer SR444 in the regions of the constructive interference causes the displacement of a slow polymerizing monomer IOA to the regions of the destructive interference that favours the diffusion mass-transport of the chemically inert NPs in the regions of the destructive interference. A complete polymerization of the layer freezes the modulation of the NPs concentration in the polymer film.

Concentration of the CdSe/ZnS NQDs in the nanocomposite is ca. 2 wt.% (volume content ca. 0.004). The time evolution of diffraction efficiency η of grating shows that such NQDs content does not ensure highly efficient gratings, η=4.4%. To enhance the grating efficiency 24 wt.% of ZrO_2 NPs have been additionally introduced into the formulation. ZrO_2 NPs were chosen because of their weak photoactivity, low absorption in the visible spectral region and

sufficiently high refractive index (RI) (ca. 2.05). The addition of the ZrO_2 NPs causes the increase in η to the value 90%.

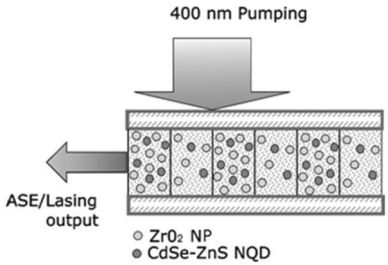

Fig.1 – A scheme of ASE measurement

The recorded phase transmission gratings formed by the modulation of NPs concentration in polymer matrix, have been used as the light-enhancing DFB structures (*Fig. 1*). Transverse pumping geometry provides for a large length of the pumping of the gain medium that leads to the efficient light-amplification due to the second order diffraction regime. Therefore, to obtain lasing at $\lambda_{las} \cong 575$ nm we recorded the gratings having $\Lambda = 379$ nm. For the pumping of the DFB-gratings we used a frequency doubled ($\lambda = 400$ nm) titanium-sapphire laser with pulse duration of 120 fs**,** repetition rate of 76 MHz and pulse energy of 0.5 – 2.5 nJ. A super-linear growth of the emission energy at progressively higher pump energy shows a threshold behavior (*fig. 2a*), that evidences the development of stimulated process. At the energies > 1.9 nJ a reduction in ASE band line-width is observed as well (*fig. 2b*). Pumping of the film outside the grating causes almost linear increase of the PL intensity until the saturation at higher pump energy (*fig. 2*, curve 2)

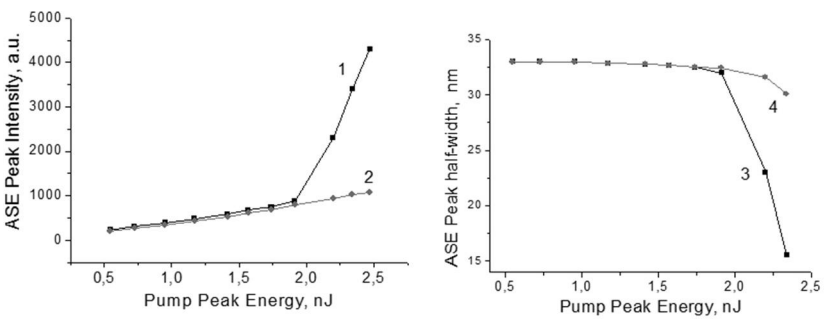

Fig.2 – Peak intensity (a) and FWHW (b) of stimulated (curves 1,3) and spontaneous (curves 2,4) emission as a function of pump energy

In our case we could not suppress ASE and obtain a narrow-band lasing emission. A number of facts can hinder an achieving of lasing conditions: a) low reflectivity of DFB structure at the second diffraction order that does not provide effective feedback; b) low concentration of the active nanocrystals in the composite. Using the similar nanocomposite containing ZrO_2 NPs doped by pyrromethene laser dye as an gain material instead the NQDs we have obtained

an effective lasing emission at λ_{las} = 572 nm in the DFB structures with Λ= 375 nm. This confirms the high reflectivity of used DFB structure. Therefore, the low concentration of the optically active NQDs is a principal cause precluding the achievement of the lasing conditions.

CONCLUSIONS

We have shown the prospective of volume DFB structures based on the spatial modulation of the concentration of optically active nanocrystals with a strong quantum confinement in polymer matrix for obtaining of laser emission. Amplified spontaneous emission was obtained, indicating the possibility to obtain also lasing in such organic-inorganic grating. It was established, that a low concentration of optically active CdSe/ZnS NQDs is the crucial factor preventing the lasing effect. The mentioned disadvantages of the CdSe/ZnS NQDs used are not principally unavoidable because modern development of the chemical routes of the surface modification of inorganic NQDs allows controlling their compatibility with different matrices. Increasing concentration of active NQDs can provide not only lasing but it may also allow creating efficient DFB structure without the use of additional high RI optically non-active NPs in the material formulation.

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