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ScienceDirect

Pacific Science Review 16 (2014) 178–182

www.elsevier.com/locate/pscr

Features of recording holograms in polymethylmethacrylate doped by boron difluoride anthraceneacetonates

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Received 9 December 2014; accepted 6 February 2015
Available online 17 March 2015

Abstract

Holographic gratings formation in polymethylmethacrylate doped with boron difluoride anthraceneacetonates was studied. It was shown, that the time dependence of refractive index (RI) modulation amplitude for recorded holographic gratings demonstrates M-shaped character, with the first (up to 0.5×10^{-4} RI units) and the second (up to 0.2×10^{-4} RI units) maxima of this dependence being caused by photodimerizability and postexposure diffusion of photoactive additive molecules. It was found that the material's resolution determined by competition of diffusion and photochemical processes for recorded gratings is about 1000 lines/mm. However, due to diffusion this value raises with time after the recording process end reaching 2500 lines/mm. It was shown that the optimal exposure time is inversely proportional to the grating spatial frequency and can be reduced by more than an order of magnitude by material heating from 25 °C to 75 °C.

Keywords: Polymeric phase holographic medium; Diffusion enhancement

Introduction

Nowadays, silver halides emulsions [1], dichromated gelatin layers [2], as well as chalcogenide semiconductor film and glasses [3] are widely used in laser recording and optical information processing systems. However, such materials are either too expensive to produce, or require wet post-exposure treatment leading to material shrinkage, as well as have significant light scattering losses, high contrast and a tendency to nonlinear spatial photoregistration of the optical signal. In this regard, cheap non-shrink materials based on rigid polymeric matrices providing the possibility to adapt their photophysical characteristics for various tasks by doping them with special photosensitive additives are currently of great scientific interest. Such additives must provide the polymer material with a high resolution, low scattering losses as well as a phase registration without using any wet post-processing. Anthracene, in particular, belongs to such photosensitive additives [4]. Reoksane is among the most studied anthracene-based polymer materials, representing a rigid polymethylmethacrylate

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Peer review under responsibility of Far Eastern Federal University, Kangnam University, Dalian University of Technology, Kokushikan University.

http://dx.doi.org/10.1016/j.pscr.2015.02.004

matrix, which is dispersed by the anthracene molecule and sensitizer dye [5]. This material provides the ability to fabricate both transmitting and reflecting volume phase holograms with the high spatial resolution. However, photosensitivity of the reoksane is determined by the anthracene photooxidation requiring a time-consuming procedure of its oxygen diffusion saturation before the material exposure. In this regard, the anthracene-like compounds, in which a photodimerization, a key photosensitivity mechanism, proceeds without oxygen [4], are the promising photoactive additives. In this paper we studies photorecording material based on polymethylmethacrylate (PMMA) doped with the novel anthracene-like compound, a boron difluoride anthraceneacetonates ($AntBF_2$) [6]. We already reported the fabrication of the phase holograms in bulk PMMA + $AntBF_2$ samples with the thickness reaching 1 mm as well as in the 1-μm thick waveguide films made of this material [7,8]. We also experimentally demonstrated that the 15-% diffraction efficiency of the recorded hologram measured immediately after the exposure process can be considerably increased (up to 70%) by heating the described material to 75 °C without using any wet post-processes. In this paper we present our ideas concerning the mechanism of the post-exposure holograms modifications in the PMMA + $AntBF_2$ material, which may be useful in the development of other polymeric recording media.

Grating formation model

It is known that post-exposure change of the phase modulation amplitude of the grating by its heating may occur owing to local changes in a chemical composition, surface relief formation, as well as diffusion of the photoproducts and undisturbed molecules [9,10]. In accordance with the data presented in [6], $AntBF_2$ additive and its photodimer $DiAntBF_2$ are chemically stable at temperatures below 190 °C and do not interact with the polymer matrix of PMMA. Surface relief formation during and after the holographic gratings recording also was not experimentally observed indicating the post-exposure refractive index (RI) changes of the heated material is apparently associated with the diffusion mechanism.

To describe this process, let's us consider all formation stages of the holographic grating. When the material is irradiated by the interfering crossed beams of coherent light, in the interference maxima resulting from the photochemical processes the formation of the $DiAntBF_2$ molecules as well as decrease in the concentration of the original photoactive additive molecules ($AntBF_2$) are occurred according to

$$C(t) = C_0 e^{-\gamma I t},$$

where γ is a proportionality constant, which depends on the photoreaction quantum efficiency; C_0 – initial $AntBF_2$ molar concentration; I – radiation intensity. As a result, in accordance with the sinusoidal intensity distribution of the exposing radiation the two opposite harmonic sublattices of the $AntBF_2$ and $DiAntBF_2$ molecules are formed. By using the Lorentz-Lorenz equation describing the relation between the concentration distribution of these molecules and the spatial RI distribution, as well as by taking into account only the first space harmonic for the recording RI gratings, one can find that its amplitude under the exposure radiation varies with time in accordance with:

$$n_1(t) = \frac{\left(n_0^2+2\right)^2}{6n_0} \Delta R C_0 m \gamma I t e^{-\gamma I t}, \quad (1)$$

where n_0 is an average material RI; m – the registered field contrast, $\Delta R = R_2 - R_1$ (R_1 and R_2 – molar refraction of the $AntBF_2$ and $DiAntBF_2$ molecules, respectively). Maximum of this dependence is observed at $t_0 = 1/\gamma I$, so this value we will assume as the optimal time for the hologram recording. After the optical recording ending at $t \geq t_0$ RI modulation amplitude of the gratings doesn't remain constant and changes with time due to diffusion mass transfer of $AntBF_2$ and $DiAntBF_2$ molecules. It is obvious that diffusion of the molecules occurs during the exposure process as well. However, we will assume that the diffusion does not affect the optical recording of the gratings and appears only at the post-exposure period immediately after the exposure process. This approximation will hold true, since the time t_0 of the photoinduced formation of the RI grating is significantly lesser than the characteristic time τ_0, at which the n_1 value varies considerably due to the diffusion.

To determine the time dependence of the spatial distribution of the molecules concentration we use the second Fick's law of diffusion. This equation is solved for an infinite homogeneous medium, with the initial spatial distribution of the molecules concentrations being described in accordance with the harmonic distribution of the recorded field. Using the Lorenz-Lorentz equation as well as the expression for the molecules concentration and taking into account the information on their molar refraction, one can calculate the value of diffusion-induced change in the RI amplitude modulation. At the case, when $n_1 << n_0$ and