

PHOTOCHEMICAL ORGANIC RECORDING MEDIA FOR OPTOELECTRONIC DEVICES

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Abstract

The analysis of the results and perspectives for developing light-sensitive organic recording media and their applications in devices of optical memory and optical information output. The properties of photopolymerizable systems and two-photon luminescent as well as photocatalytic materials are discussed. It was shown that optical information carriers based on these media with one-stage or combined many-stage processes for obtaining images in real time may be realized.

Keywords: photochemical, recording, media

Introduction

The advancement of modern optoelectronic devices requires the improvement of light-sensitive media for recording (optical memory) and optical information output. The distinctive property of these devices is the use of lasers for recording, processing, and display of optical information. The necessity of their application stems by requirements of increasing information capacity and the fast response for optoelectronic devices. In its turn application of lasers opens the possibility of using self-developing organic light-sensitive recording media based on photochemical reactions. These media are characterized usually by the low limit light-sensitivity (up to S=50 cm^2/J) but high resolution and image receiving under laser radiation directly that is in real time without any additional chemical processing.

Nonetheless, the question of increasing light-sensitivity for these media remains in force. In this connection light-sensitive materials based on combined many (two or three)-stages (photochemical, optical, thermal, etc.) may be used instead of self-developing media. Clearly that resolution of these materials will be below that for self-developing ones.

On the basis of present knowledge, self-developing media are more acceptable for optical memory and materials with combined processes for the production of images may be used for optical information output from optoelectronic devices.

This paper presents results of the study in the field of the development of photopolymerizable, two-photon photoluminescent and photocatalytic systems which have the principal interest for modern optoelectronic devices.

Self-Developing Light-Sensitive Media for Three-Dimensional Optical Memory

At the present time after the advantageous development and application optical disks the demand exists of increasing information capacity for optical memory by means of using volume light-sensitive media and methods of three-dimensional recording optical information [1]. In principle, there are three methods of this type, namely frequency-selective [2], holographic [3], and bitwise recording with the use of two-photon excitation of photochemical reactions [4].

The first method is based on photochemical processes for destruction of J-aggregates containing dye molecules. These aggregates are characterized by vary narrow absorption bands and provide recording optical information in volume of materials using laser radiation with different frequencies. The information capacity depends on the half width for absorption bands of J-aggregates. At present the reversible optical memory of this type working at the room temperature is realized [5].It is based on J-aggregates of 5 photochromic spiropyrans. The optical disks with these light-sensitive covers are characterized by information capacity which is 10 times as greater than capacity of modern optical disks. The marked increase in information capacity may be realized at the sacrifice of using the phenomenon of photochemical hole-burning [6].Unfortunately, optical memory of this type is working at low temperatures (from helium to nitrogenous temperatures) only. Besides, in connection with the necessity of application spectral-tuning lasers frequency-

selective optical memory is of secondary importance to holographic and two-photon one.

The main problem for the development of holographic optical memory with extreme information capacity is elaboration of self-developing light-sensitive media providing recording deep holograms [1]. At present certain progress has been made in preparation of thick layers based on dichromated gelatin [7,8] which, however, are characterized by low light-sensitivity (S=0.01 cm^2/J) and the restricted storage life for recorded holograms.

The more perspective direction in the field of developing holographic recording media is application of photopolymerizable compositions [9,10]. Recording deep holograms in these media may be provided by application of photobleaching dyes namely phenanthrenequinone [11], phenothiasine dyes [12],etc. as sensitizers of the photopolymerization process. Unfortunately, using these dyes in holographic photopolymerizable media requires post-exposition processing by light with the goal of transformation of amplitude holograms with low diffraction efficiency (DE<10 %) to phase ones (DE>80 %). In this connection we used the photoinduced merocyanine form of photochromic nitrosubstituted spiropyran as a sensitizer for preparation of photopolymerizable media with low strinkage. Materials of this type provide transformation from amplitude to phase holograms at the sacrifice of the spontaneous relaxation of the photoinduced merocyanine form into the initial colorless spiran one [13]. It was found experimentally that acrylamide photopolymerizable layers containing photochromic spiropyran with a thickness of 100 μm provide recording holograms with DE=80 % ($\Delta n=10^{-2}$) after laser radiation with the energy density of 0.1 J/cm^2 [14]. The light-sensitivityof these systems may be increased in the presence of co-initiators including tertiary amines and cetypyridinium n-butyltriphenyl borates [15]. In principle, the light-sensitivity of photopolymerizable media may be very high ($S\cong 10^5$ cm^2/J under irradiation with λ=254 nm [16]) as a result of the high quantum yield of the photopolymerization process ($\varphi \leq 10^6$). Unfortunately, the most of photopolymerizziable systems with acceptable holographic characteristics have the low light-sensitivity because of chain breaking and restricted diffusion of radicals in the polymeric matrix. The conceivable ways around this problem are realization of photochemical reactions in polymer binders at elevated temperatures and application of polymeric matrixes as well as other compounds of the reduced ability with reference to radicals leading chain reaction.

In relation to difficulties in the development of thick photopolymerizable holographic media withrequired characteristics the considerable attention is focused on the development of bitwise optical memory based on two-photon photochemical processes. Efficiency of these processes depends on participation of excited states of organic molecules. Two general types of two-photon processes are distinguished, namely strictly the two-photon process with participation of virtual and singlet energy states as well as graded two-quantum one with the participation of real excited triplet and singlet energy states. Efficiency of the last process is more as the first one.

It was found that two-quantum photopolumerization is realizcd in the systems containing trimethyltripropane triacrylate, photochromic nitrosubstituted benz0spiropyran, and N-phenylglycine [17]. However, media of this type are characterized by the low light-sensitivity as compared with organic two-photon photoluminescent materials which are used for three-dimension bitwise recording optical information [4, 18-20].

Photoluminescent materials are based on irreversible and reversible photochemical reactions. Media of this type can be separated into two groups, namely positive (with photoinduced formation of luminescent products) and negative (with photoinduced disappearance of initial luminescent substances) photoluminescent materials. In the case of positive ones concentration luminophore is proportional to the exposure. Read-out of recorded information is by photoexcitation of luminophore luminescence. The intensity of luminescence depends on the amount of light absorbed by luminophore. As a result, the positive image with amplitude-frequency transformation for read-out of optical information is achieved [21]. So far as the degree of frequency transformation if independent of concentration of fluorescent photoproducts and the image is the positive one on the dark unexposed background, unlike silver-halide photomaterials photoluminescent media are liable to have the high light-sensitivity and resolution simultaneously [22]. According to calculations [23] the value of the light-sensitivity may achieve to S=!0 ^{6} cm ^{2}/J. The developed materials are characterized by the value of S=10^4 cm^2/J.

It was developed a number of irreversible media of this type using photolysis of aromatic azides, complexes between diarylamines and halogenderivatives as well as reversible photomaterials based on photochromic spirocompounds, thioindigo dyes, and phenoxynaphthacenepyridons, etc. [18-20]. A photoluminescent material for irreversible recording optical information at the sacrifice of transformation of nonluminescent leucodye into luminescent dye as a result of catalytic reaction with the use of photoinduced acid was offered too [24].

Using photoluminescent volume recording it is possible to realize the three-dimensional bitwise optical memory with high information capacity (10^{13} $bits/cm^3$)[25-27].

Light-Sensitive Recording Media for optical information output

At the present time optical information output is provided by application of electrophotographic and inkjet methods using complex devices.

The progress of non-impact printing is linked with the design and performance of materials for dry imaging. Among these materials are thermally developed photographic media based on silver-halide and silver carboxylate compounds («dry silver») with the high light-sensitivity [28].

At the same time there are several nonsilver light-sensitive organic systems with dry light or/and thermal developing which , in principle, may be used for the same goal. Among these media are the photopolymerizable microcapsule material named zzzCycolor paper [29], systems based on complexes with the charge transfer [30, 31], and photocatalytic polymer layers [30].

The improved Cycolor process based on microencapsulated chemical and light-sensitive photopolymerizable compositions opens perspectives to produce the inexpensive, high-resolutions devices for obtaining color images.Photopolumerization of light-sensitive compositions results in tremendous mechanical property changes which can be predictably controlled by appropriate expousure. In this case a color image is a sesult of combined three-stage process including photochemical polymerization of microcapsules, mechanical crushing of unpolymerizable microcapsules, and chemical reaction between dye precursors and acid agents with dye formation.

The results of own investigations of photopolumerizable processes sensitized by ion pairs of cyanine dyes and phenylbutylborates support the possibility of the improvement of this medium exchibiting the high light-sensitivity (up to $S=10^4$ cm ^{2}/J) [32]. It was shown that liposomes may be used for making the light-sensitive sheets instead of synthethic microcapsules. Prescription of color developing covers which are used for preparation of thermo-sensitive papers are applicable to making of the receiver paper sheets.

The certain perspectives may be linked with the improvement of high-sensitive materials based on complexes with the charge transfer. The image is formed as a result of synchronous photochemical reaction, light and/or thermal developing processes. The value of the light-sensitivity for these media containing leucodyes and halogenderivatives may achieve to $S=10^5$ cm ^{2}/J [31]. The own investigations of these materials based on polystyrene, inhibitors, antioxidants as well as styryl or ethylene leucodyes and halogenderivatives showed that their light-sensitivity may achieve $S=10^5$ cm ^{2}/J and 2.10^4 cm ^{2}/J under irradiation with λ=337 nm and 436 nm correspondingly after optical developing [30]. The possibility of thermal developing of the latent image in these materials was demonstrated by us experimentally too. Obtained data were explained by the photocatalutic effect.

Photocatalytic media based on organoelemental complexes were put forward by us for the same goal [30]. The developed materials of this type are characterized by the high light-sensitivity (up to S=250 cm ^{2}/J) because of photoinduced formation of catalyst which oxidizes organic compounds into the polymer matrix. As a result of following dark oxidation peroxides appear and disappear. Peroxides initiate the appearence of dyes forming the latent image. Variation of color forming components provides the image of different color. Unlike media based on complexes with the charge transfer photocatalytic materials of this type are characterized by high dark keeping qualities before light exposition. This property is provided by application of color forming compounds which are poverful antioxidants.

Above mentional organic media with the high light-sensitivity exhibit resolution which is 10 times less than it is for recording media used in optical memory. This effect is caused by mechanical and thermochemical processes decreasing its resolution.

Conclusions

The analysis of the presented results is indicative of perspectives for their application in optical memory and optical information output.

Three-dimensional permanent bitwise optical memory based on irreversible photoluminescent materials as well holographic one with the use of photopolumerizable compositions are very close to realization.

Cycolor media providing color imaging as a result of combined photochemical, mechanical, and thermochemical processes are acceptable for the development of cheap printers using semiconductive lasers.

Improved organic media based on combined photo- and thermochemical reactions may be used for photothermographic dry imaging in devices for optical information output in the future.

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