Holographic Recording Media: State-of-the-Art and Modern Trends

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Abstract
The analysis of the results received in the field of the development of light-sensitive (LS) holographic recording media (RM) is presented. The lines of the improvement of these media for color display holography, phototechnology for making of holographic optical elements (HOEs) and perspective information optical technologies are determined.

Introduction
The development and application of the holographic method in different fields require a steady improvement of existing LS RM. The analysis of the development of LS materials for recording, processing and storage of holograms as compared with the advances before 1992 indicates the notable progress in this field, specifically in making RM for color display holography, phototechnology for manufacture of HOEs, and a new optical information technologies. This paper is an attempt to correlate the main advances in the above-mentioned lines during the last years for the purpose of determination of the trends for the following improvement of holographic RM.

Recording Media for Display Holography
The last monograph reviews the main results of the development of AgHal RM for holography. The analysis of the obtained results shows that with the advances in the technique of color display holography the improvement of RM for monochrome hologram becomes the less urgent problem. Nevertheless, the investigations directed to increase of the quality for recording monochrome holograms are being continued. Considerable attention is given to recording pulsed holograms. The noise reduction for AgHal photomaterials is attached particular significance. In this connection a new AgHal photoemulsion with the use of microcrystals with the size about 20 - 25 nm was developed. The sensitivity to He-Ne irradiation (632 nm) for this photoemulsion reaches $S = 10^5$ cm$^2$/J. The LS range is 400 - 540 and 580 - 660 nm. Photomaterials of this type can be made panchromatic media. Holographic characteristics for the known photoemulsions can be improved at the sacrifice of additional processing. At the same time, it is seems that the production of high-performance color holograms is the only condition for promoting of the color holography in practice. This possibility is opened with the advent of monolayer color AgHal fine photoemulsions with high resolution which supply not only good color reproduction, but more high spectral multiplexing and resolution also as compared with monochrome recording media of this type. It turned out that Russian photoemulsions are best suited to making color holograms. The processing is a very critical factor for production of holograms with high DE and good color rendering. The specialized emergency measures shall have to institute against undesirable shrinkage of photolayer distorting color reproduction.

Sensitized dichromated gelatin (DCG) layers are perfect holographic RM. It is truly that holograms into DCG layers are characterized by high DE for effective modulation of the refractive index ($\Delta n = 0.08$) which is in excess of the values for other known holographic RM. The disadvantage of DCG media is the low sensitivity to green and, especially, red laser irradiation. This property hinderes application of these media in color display holography. In this connection the AgHal sensitized layers of DCG were proposed. A new method for production of reflectance holograms with use of DCG was offered. It is based on formation of microcavity structure according to the interference gratings recorded in AgHal microcrystals. Using this method the holograms with high DE throughout the visible spectrum were produced. These media make possible receiving high-performance color display holograms. Application of sensitized DCG layers to color display holography requires further gain in light-sensitivity. Of the particular interest is the high light-sensitive DCG with aminoderivatives of organic compounds, which provide recording hologram with DE = 80% at $E = 50$ mJ/cm$^2$.

Du Pont has been developed a family of dry photopolymer films for production of monochrome and color holograms. Media of this type are characterized by light-sensitivity in the wide spectral range (450 - 650 nm). Holograms with DE = 100% are recorded at relatively low exposition ($E = 10 - 100$ mJ/cm$^2$). The maximum DE value is achieved after fixing UV irradiation (340 - 380 nm) at exposition $E < 100$ mJ/cm$^2$ and heat treatment during 2 hours at 120$^\circ$C. It is significant that the moist processing is not used in this case. With the aim of reflectance hologram recording the photopolymer materials based on radical and cation monomer polymerization with using cyanine dye and biphenyl iode as sensitizers are offered. Holograms with DE = 60% are realized at $E = 20 - 60$ mJ/cm$^2$.
Thus, there have been recent advances in the development of AgHal and nonsilver RM provided the following advancement of the color display holography. The development of AgHal RM will be continued in the direction of increasing light - sensitivity for making color holograms of a big size, the improvement of color reproduction with a goal of the authentic reconstruction for real color images as well as simplification of the manufacture technology and processing of these media. In conclusion of this part it may be noted that reflectance relief holograms are applied not only for design (from watches to outside advertisement), but for the protection of goods and securities against falsification as well. There is no question that photothermoplastic RMs have grate importance for production rainbow holograms.

**Recording Media for Phototechnology of HOEs Making**

A number of above mentioned dry as well as liquid photopolymerizable RM is of interest to not only for making of monochrome volume display holograms, but for manufacture of volume and relief HOEs as well. The development of photopolymers based on acrylamides brought into existence RM for recording of holograms with DE = 40 % at exposition E = 3 mJ/cm². A rise of the light - sensitivity for photopolymers based on pentaerythrol triacrylate can be achieved by using polyfunctional monomers. Undoubtedly, of the great interest for hologram recording is the photopolymer films based on cation polyecondensation by insensitivity of this reaction to oxygen and chemical gain. The sensitivity of these films to irradiation with λ = 488 nm achieves S = 1.7 cm²/J. Lately the improved photopolymerizable media for making full - reflection and transmission HOEs were proposed. The DE value achieves DE = 100 % at power P = 10 mW/cm². Of particular interest is the liquid high - sensitive photopolymerizable media based on polyfunctional acrylic monomers. A number of photopolymers of this type has been developed for recording by long - wave irradiation (700 - 800 nm). The main advantages of these media are the lack of any physical and chemical treatment. The photo polymerizable liquid crystals (LQ) open the perspective of photo - control over properties of HOEs. The developed photopolymer LQ systems provide single - step recording electrically switching holograms with good optical quality, high DE, narrow angle selectivity, and low switching fields.

DCG is used as before for making HOEs. The AgHal sensitized DCG is applied for contact copying of amplitude holographic grating on a metal surface. The practical implementation of DCG films for making of the large format holograms used as sun concentrators. Of special interest is HOEs based on DCG for the 1.5 µm spectral range. Currently, the self - processing polymer recording media based on dichromated polymers, in particular, polyacrylic acid and polyvinylcarbazole have received wide acceptance. These media are close to DCG but they don’t require additional treatment. In this connection the light - sensitivity value is well below as compared with DCG.

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The photomaterial called Reoxan based on photooxidation of anthracene derivatives in polymeric matrix was used for making of volume HOEs. This medium is acceptable for recording of reflectance and transmission holograms. The photoinduced value of the change for refractive index reaches Δn = 2.10⁻². Holograms with DE = 100 % are recorded at exposures of E = 0.5 - 1.5 J/cm². Resolution is more 5000 mm⁻¹. It is very important that Reoxan allows chemical and diffusion amplification of phase holograms.

The quest for maximum improvement of physical, chemical and exploitation characteristics has led to the development of a number of glassy - like light - sensitive recording media. Holograms are recorded in these materials at a sacrifice in photoinduced crystallization of multichrome glasses. The DE value achieves 88 % (ν = 100 mm⁻¹) at E = 3 J/cm². The enhancement of recording frequency up to ν = 2400 mm⁻¹ reduces the DE value to 10 %. However, applications of light - sensitive homogeneous glassy - like materials eliminates the possibility of making RM with post - exposition treatment because of their extreme low penetrability to low - molecular reagents. In this connection, the study of microheterogeneous LS media with capillary (porous) structure is very important. Hologram recording into these materials of 10 - 1000 µm thickness with DE = 100 % requires expositions in the 0.01 - 1.0 J/cm² range. Among media of this type materials containing AgHal emulsion provide making volume HOEs with high DE in the near IR spectral range.

These materials remain as before important RM for making of planar relief HOEs under laser light including IR irradiation (10.6 µm). For wide application of photoreists in holography advances of modern photolithography is of major importance, especially for making of full - size planar HOEs. Photoreist layers with compounds which produce acid under irradiation are characterized by high light - sensitivity. These media are acceptable for recording of large holograms. The relief holograms with DE = 30 % are recorded at exposition E = 2 mJ/cm² of laser irradiation with λ = 488 nm.

Photoresist media based on chalcogenide glassy - like semiconductor - metal systems continue to improve. The fields of application in holography for these media is expanded. The holographic diffraction gratings with sinusoidal, asymmetrical profiles as well as kinoforms were produced by the change of exposition and treatment conditions. HOEs were produced by the copying method with use of master - hologram which was prepared in chalcogenide photoreists.

The thin layer AgHal materials (thickness is about 0.4 µm) are the most acceptable recording media for making precise HOEs of large dimensions. AgHal materials were
used for recording rainbow holograms \(^{43}\) and for making nickel foils for embossing \(^{44}\), much as photothermoplastic RM \(^{45}\). Polarization HOEs are made using AgHal photomaterials too \(^{46}\).

Hence, there is a number of LS RMs, especially, photopolymerizable media which are suitable for phototechnology of HOEs making. These media may be applied for making of volume as well as relief planar HOEs. Preparation of HOEs with large dimensions may be realized using new high light-sensitive organic photoresists with chemical amplification and thin layer fine AgHal photoemulsions. These media as well as photothermoplastic materials are important for embossing relief HOEs. Future trends in this field are connected with following improvement photopolymerizable compositions and photoresists in the directions of the increasing light-sensitive and reducing noises for volume and relief holograms. The HOEs with photocontrol of their properties appear to be urgent. In this connection photopolymerizable LQ media are of chief interest.

**Recording Media for Perspective Optical Informational Technologies**

Holographic optical memory has two main advantages offered by the holographic method, namely, high information capacity in relatively small volume and parallelism in data access. In this connection the development of effective RM for archival and working memory is very important problem.

**Media for archival optical memory**

Among LS RM a number of polymeric systems can be used for holographic permanent optical memory.

Photopolymerizable HRF - 150 medium from Du Pont may even work for volume (3D) optical memory on optical disks \(^{47}\). The surface density of 10 bits/\(\mu m^2\) in the 100 \(\mu m\) layer has been demonstrated by superimposing 32 holograms under laser irradiation with \(\lambda = 320\) or 488 nm. Each hologram has been a surface density of \(0.334\) bits/\(\mu m^2\). In this case the recording rate was 0.7 Mbits/s. The DE per hologram was 0.35 % and average recording time of 840 ms per hologram has been achieved. The analysis shows that the photopolymer layer with 1 mm thickness would yield densities in the range of 100 bits/\(\mu m^2\). This value is very big as compared with a new generation of optical disks which will be characterized a storage density of \(5\) bits/\(\mu m^2\) per layer \(^{135}\). Dual - layer and double - sided systems are expected to have an equivalent storage density in excess of 10 bits/\(\mu m^2\). Increasing the total incident intensity from 2 to 128 mW/\(cm^2\) permits to raise the recording rate up to 45 Mbits/s. Analogous characteristics are closely related to parameters for hologram recording into a non - commercially available photopolymer under irradiation of a diode laser that operates wavelength of 684 nm \(^{48}\). Of particular interest is compositions polymerized under the long - wave light of a semiconductor laser (647 - 854 nm) \(^{52}\).

Photorefractive polymers were offered for hologram recording in 1991 \(^{49}\). As a result of study the medium with holographic properties, much like characteristics for the LiNbO\(_3\) crystal, has been made. The DE value for a p - polarized readout beam increases with electric field and reaches a maximum of DE = 86 % at external electric field \(E = 61\) V/\(\mu m\). The compositions of photorefractive polymers include bifunctional compounds which are responsible for not only photoinduced charge transfer but nonlinear properties as well \(^{71,72}\). Currently, the cross - linked photopolymer - electrolyte - optical materials are used for increasing thermal stability of photorefractive polymeric media \(^{73,74}\).

Media based on photoburning of spectral holes may be used for increasing capacity of optical memory because of the effect of multi - step persistent spectral hole burning by laser irradiation \(^{75}\). The possibility of hologram recording at cryogenic temperatures with capacity about 1000 Gbits/cm\(^2\) and input - output rate of several Gbits/s was supported experimentally using \(Y_2SiO_5:Eu^{3+}\) and \(Y_2SiO_5:Pr^{3+}\) \(^{51,76}\). 6 000 holograms has been recorded on the 100 \(\mu m\) polyvinylbutyral film with chlorin at temperature of 1.8 K in a liquid helium bath cryostat \(^{77}\).

Chalcogenide glassy - like semiconductors are studied during many years with a goal of realization of reversible recording \(^{78}\), but there is not a good data for the possibility of making effective RM of this type.

Photothermoplastic recording materials, however, include chalcogenide semiconductor glass layers as a photo-
The analysis of the development of LS RM for perspective information technologies shows that the best practical advances are elaboration of photopolymerizable layers for 3D archival optical memory and photorefractive crystals for working optical memory on disks. The achievable capacity for holographic 3D disks with use of shift multiplexing is well in excess of 100 bits/μm². The perspectives of the development for working optical memory are associated with photorefractive polymers capable to substitute expensive photorefractive crystals.

Conclusions

The full analysis of the received results in the field of the development of RM allows following conclusions:

- the perspectives of display holography are connected with the development of monolayer AgHal photomaterials as well as dry color photopolymerizable films with high resolution and light-sensitivity for recording color holograms;
- dry photopolymerizable materials become the main media for making of volume HOEs with high DE in the visible spectral range. Application of photopolymerizable LQs opens perspectives for producing HOEs with electro-optical control. HOEs with high DE in IR spectral range may be made using the microheterogeneous media, namely, microporous glasses with the capillary structure. The possibility for making relief HOEs of a large size may be realized by application of organic photochromic materials with chemical amplification or silver halide thin layer photomaterials;
- prospects of application for RM in modern information optical technologies depend on the development of irreversible photopolymer media with shift packing and reversible photorefractive crystals with sensitivity to irradiation of semiconductor lasers. The improvement of noise characteristics is one of the main problem for these media. Of particular interest is photorefractive polymers. Self-developing photochromic and photoanisotropic media may be used for interconnections of optical elements in devices of optical memory.

Future trends for the development of holographic RM are associated with the improvement of characteristics for monolayer AgHal and photopolymerizable materials what is more important for color display holography. The high LS photopolymerizable compositions as well as photoresists are required for making HOEs of the large size. The phase photopolymerizable and photorefractive polymers with high light-sensitivity will be very necessary for the practical realization of archival and working optical memory, correspondingly.

References

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