Silver-doped photopolymer media for holographic recording

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Incorporation of silver ions into a dye-sensitized poly(vinyl alcohol)/acrylamide photopolymer is observed to give better performance compared to other metal-ion-doped photopolymer holographic recording media. Plane-wave transmission gratings were recorded in the photopolymer films using a He–Ne laser, and various holographic parameters were optimized so as to explore maximum potential of the material for various holographic applications. Silver-doped films showed good energy sensitivity, and gratings recorded in optimized film exhibited a diffraction efficiency of more than 75%. The potential of the material for holographic data storage applications is also studied using peristrophic multiplexing. © 2009 Optical Society of America

1. Introduction

Dye-sensitized poly(vinyl alcohol)/acrylamide (PVA/AA) photopolymer films with excellent optical clarity, high diffraction efficiency (DE), high sensitivity, and high resolution have an important place among the photopolymer-based holographic recording media [1–6]. The stability of gratings recorded in these films strongly depends on small variations in laboratory conditions (relative humidity and temperature) and the DE decreased on storage [1,5,6]. Often the recorded gratings were stabilized by postexposure techniques such as UV curing, incoherent or coherent illumination, and thermal treatment. Incorporation of different additives into these films was also tried by several research groups to improve their storage lives, of which incorporation of metal ions was reported to be the best since metal ions formed ionic cross links with the poly(vinyl alcohol) (PVA) matrix, thereby inhibiting the diffusion of unreacted monomers and stabilizing the recorded grating [7–12]. Metal-ion-doped polymers have made a significant impact in holography due to their great advantages such as real-time image development, self-processing, high photosensitivity, and low cost. Metal ions such as chromium (Cr⁶⁺), ferric (Fe³⁺), and cupric (Cu²⁺) have been doped into different polymer matrices such as PVA and poly(acrylic acid) to realize various holographic recordings. Dichromated PVA films doped with dimethyl formamide developed by Manivannan et al. had peak real-time DE of approximately 65% at a high exposure of nearly 1000 mJ/cm² [8]. Fe³⁺-doped PVA holographic recording systems developed by Manivannan et al. exhibited a peak DE of 80% for a total beam power of 40 mW at an exposure energy of 21 J/cm² [9]. Though high DE was achieved in these films, the energy sensitivity was very low. Sugakewa et al. devised a photosensitive liquid system with a mixture of...
acrylamide (AA) and methylene bisacrylamide coupled with ferric ion and tert-butyl hydroperoxide sensitive from 200 to 500 nm that exhibited a high DE of \( \approx 80\% \) \([10]\). However, in this system, holograms have been recorded in liquid phase, the photosensitive liquid being encapsulated between two glass plates separated by a spacer and later fixed by an overall ultraviolet exposure. This method can lead to certain problems of stability during recording and processing. Copper-doped AA films developed by John \textit{et al.} exhibited a DE of 32\% for an exposure energy of 600 mJ/cm\(^2\) \([11]\). Though no postprocessing was required for these films, the DE and the energy sensitivity was low. In the case of chromium-doped films developed by John \textit{et al.}, even though the efficiency reached 42\% after self-enhancement, it reduced to the initial value of 21\% (500 mJ/cm\(^2\)) after three months of recording \([12]\). Hence it can be seen that most of the metal ion-doped holographic recording media required some type of fixing to achieve maximum efficiency while those that required no postprocessing had poor sensitivity and DE. When a photopolymer is used in holographic data storage, the stability of the recorded data is a major challenge, and the media should be free from fixing processes. In this context, the development of a potential metal-ion-doped photopolymer recording medium has great relevance. With this aim, in the present work, silver ions were incorporated into a Methylene Blue (MB)-doped AA containing photopolymer film. This is assumed to be the first report of silver doping in any dye-sensitized polymer for holographic recording. Silver was selected in this study, because silver halide emulsions with high sensitivity and high resolving power is still the most widely used holographic recording medium. The holographic performance of the silver-doped MB-sensitized PVA/AA photopolymer film was studied in detail. The feasibility of recording bright transmission holograms in the material is also successfully demonstrated. The potential of the developed material for holographic data storage applications is studied using peristrophic multiplexing with the axis of rotation perpendicular to the recording medium, which is the most commonly used form of peristrophic multiplexing. Peristrophic multiplexing makes it possible to multiplex many holograms in thin films. In this technique, after a hologram is recorded, the recording material is rotated around a certain rotational axis so as to record another hologram \([13–15]\). This type of multiplexing has the added advantage that it can be combined with other multiplexing methods to increase the storage density of holographic storage systems \([16]\). In the present work, an exposure-scheduling method was used to exploit the entire dynamic range \([17]\) of the material and to record equal strength holographic gratings in it. The dynamic range that is a measure of the storage capacity of the material was determined by calculating the \( M \) number (M#) \([18]\).

2. Methodology

The photopolymer material used in the present study is comprised of PVA as the binder matrix, AA as the monomer, MB and triethanolamine (TEA) as the photoinitiation system, and silver nitrate as the cross linker. The binder matrix is a crucial component affecting the physical properties of the recording medium such as its rigidity, environmental stability, and dimensional changes upon holographic exposure. It also aids in film formation. Monomers are incorporated into the polymerizable recording media to establish the grating formation due to refractive index (RI) modulation. Properties such as recording sensitivity, dynamic range, image fidelity, shrinkage, and environmental stability of the exposed hologram are also influenced by the monomer selection \([18]\). The direct initiation of polymerization by light has a poor yield, and hence the initiation is usually achieved by radical or cationic polymerization, and it requires the use of a photoinitiator (dye and the charge transfer agent) that is sensitive to the recording wavelength. The free radical of the electron donor produced during laser exposure initiates the polymerization reaction. Metal ion crosslinkers are incorporated to improve the storage life of the recording media since metal ions form ionic cross links with the PVA matrix, thereby inhibiting the diffusion of unreacted monomers and stabilizing the recorded grating. A 10\% PVA solution was prepared by dissolving 10 g of PVA (molecular weight 1, 25,000) in 100 ml distilled water. AA crystals were dissolved in the PVA solution, and the resulting solution was sensitized with MB (0.14 × 10\(^{-4}\) mol/l) and TEA (0.05 mol/l). The mixture was then stirred well to get a homogenous solution. To this solution, silver nitrate solution prepared using distilled water was added and stirred again. Keeping the dye concentration constant at 0.14 × 10\(^{-4}\) mol/l, silver concentration was varied from 0.13 to 4.37 × 10\(^{-4}\) mol/l. The films were fabricated using a gravity-settling method \([19]\). The drying period was 48 h under normal laboratory conditions. The dried films had good optical clarity and thickness of 130 μm (measured using Dektak 6 m stylus profiler). The films were named as AgX (where \( X = 1 \) to 6 represent the different Ag\(^+\) concentrations).

Optical absorption studies and real-time transmittance studies were carried out to study the spectral and energetic sensitivity of the material. A JASCO V-570 spectrophotometer was used to record the optical absorption spectra, and real-time transmittance studies were carried out using a He–Ne laser (632.8 nm, Melles Griot). The RI of the films was determined using an Atago DR-M2 refractometer. Plane-wave transmission gratings were recorded in the films by a two-beam recording setup using a He–Ne laser (632.8 nm, Melles Griot), and for DE measurements, a low-power He–Ne laser beam (632.8 nm, Melles Griot) was used. The DE was calculated as the ratio of the diffracted beam intensity to the incident intensity. For peristrophic
multiplexing studies, the photopolymer was mounted on a rotational stage. After each recording, the film was rotated in a direction perpendicular to the plane of incidence by the rotational stage. This rotation causes reconstruction from the stored grating to come out in a different direction, allowing another grating to be recorded at the same location. Gratings were multiplexed in the photopolymer film using variable exposure energy-scheduling schemes. The multiplexed gratings were reconstructed using a He–Ne laser (632.8 nm).

3. Material Sensitivity

Optical absorption studies were carried out to study the spectral sensitivity of the material. The optical absorption spectra of the films were recorded using a JASCO-V-570 spectrophotometer before and after exposing them to a He–Ne laser beam (632.8 nm, 1 mW/cm² for 4 min). The optical absorption spectra of the unexposed films clearly show spectral sensitivity in the red region of the spectrum (Fig. 1). The material sensitivity was determined by monitoring the real-time transmittance as described elsewhere [20]. A possible mechanism of free radical polymerization [21–23] for the reported material is given in Eqs. (1)–(12). When the photopolymer film is exposed to a monochromatic light of suitable wavelength, MB absorbs photons and gets promoted to the singlet excited state \( ^1\text{MB}^* \):

\[
\text{MB} + h\nu \rightarrow ^1\text{MB}^*. \tag{1}
\]

The singlet excited state can then undergo intersystem crossing into the more stable triplet state \( ^3\text{MB}^* \):

\[
^1\text{MB}^* \rightarrow ^3\text{MB}^*. \tag{2}
\]

This triplet state dye can then react with the electron donor TEA. TEA donates an electron to the excited triplet state of MB, leaving the dye with one unpaired electron and an overall negative charge:

\[
^3\text{MB}^* + \text{TEA} \rightarrow \text{MB}^- + \text{TEA}^+. \tag{3}
\]

The TEA radical cation then loses a proton and becomes a free radical:

\[
\text{TEA}^+ \rightarrow \text{TEA}^- + \text{H}^+. \tag{4}
\]

The dye radical (MB\(^-\)) abstracts a hydrogen molecule from the TEA free radical to form the leucoform (MBH):

\[
\text{MB}^- + \text{H}^+ \rightarrow \text{MBH}^+, \tag{5}
\]

\[
\text{MBH}^+ + \text{TEA} \rightarrow \text{MBH}^- + \text{TEA}^+. \tag{6}
\]

The TEA free radical can initiate the polymerization reaction of AA as described by

\[
\text{TEA}^- + \text{AA} \rightarrow \text{AA}_1^+. \tag{7}
\]

The growth of the polymeric radical chain (propagation) is shown by

\[
\text{AA}_1^- + \text{AA} \rightarrow \text{AA}_2^-, \tag{8}
\]

\[
\text{AA}_2^- + \text{AA} \rightarrow \text{AA}_3^-, \tag{9}
\]

\[
\text{AA}_i^- + \text{AA} \rightarrow \text{AA}_{i+1}^- \tag{10}
\]

The termination processes [23], which give the polymeric chain \( \text{p}_i \), are shown in

\[
\text{AA}_h^- + \text{TEA}^- \rightarrow \text{p}_i. \tag{11}
\]

\[
\text{AA}_h^+ + \text{AA}^- \rightarrow \text{p}_i. \tag{12}
\]

As the material sensitivity increases, the transmittance increases at low exposures. This is because, even at low exposure, the dye molecules (MB) get excited and get converted to the leucoform. Films with different Ag\(^+\) concentrations were exposed to a He–Ne laser beam of irradiance 1 mW/cm² for 4 min, and the transmitted power at regular intervals was monitored using an optical powermeter (Ophir 2000). The relative transmittance \( T/T_0 \) was also determined, where \( T \) is the real-time transmittance of the Ag\(^+\)-doped films and \( T_0 \) is that of undoped films. The relative transmittance decreased with silver concentrations as shown in Fig. 2. This may be because, at higher Ag\(^+\) concentrations, the unused silver ions may get oxidized resulting in the formation of a thin layer of silver oxide, thereby leading to a reduction in the optical transparency of the film.

4. Variation of Diffraction Efficiency with \( \text{Ag}^+ \) Concentration

Plane-wave transmission gratings were recorded in the films using a standard holographic setup (Fig. 3).
For this, a 15 mW, CW, linearly polarized He–Ne laser having emission at 632.8 nm was used. The laser beam was split into two using a beam splitter with a reflectance to transmittance ratio of 50/50, and these beams were directed onto the film using front-silvered mirrors. These beams were then expanded using spatial filters and collimated. The collimated laser beams were allowed to interfere in the polymer film from the same side. Path lengths of the beams were made equal. The exposure time was controlled by placing an electronic shutter in front of the laser. The total recording beam power at the recording film was maintained as 4 mW while recording gratings (spatial frequency 1070 lines/mm, beam intensity ratio 1). In order to optimize the exposure energy, gratings were recorded by varying the exposure energy from 50 to 100 mJ/cm². The diffraction efficiencies of the recorded gratings were determined by reconstructing the gratings using a low-power He–Ne laser beam (1 μW, unpolarized, 632.8 nm). The laser beam was allowed to fall on the grating-recorded film kept at the Bragg’s angle. The intensity of the incident beam and the diffracted beam was measured using an Ophir 2000 powermeter. The DE was calculated as the ratio of the diffracted beam intensity to the incident intensity. The variation of DE with exposure energy for different Ag⁺-doped films is plotted in Fig. 4. A peak efficiency of 75% was shown by the grating recorded in the Ag2 film (Ag⁺ concentration 0.5 × 10⁻⁴ mol/l) for an exposure energy of 80 mJ/cm². Figure 5 shows the plot of DE with Ag⁺ concentration. The DE values were slightly low at higher Ag⁺ concentrations. This may be because, at higher Ag⁺ concentrations, the presence of more silver ions restricts the diffusion of monomers, which reduces the RI modulation and thus the DE. Grating formation in photopolymer film is mainly due to the RI modulation produced by the diffusion of unreacted monomers resulting from photopolymerization [11]. The RI of the films was determined before and after exposure to a He–Ne laser beam (632.8 nm, 80 mJ/cm²), and the change in RI was calculated. The change in RI with Ag⁺ concentration is plotted in Fig. 6. Highest RI modulation of 7.5 × 10⁻³ was obtained for the Ag2 film, which also exhibited a peak DE of 75%. In order to determine the resolution of the material, gratings were recorded on the optimized Ag2 film at different interbeam angles maintaining the exposure energy at 80 mJ/cm². The spatial frequency of each grating was determined using a Bragg equation. The peak DE was 75% with 1070 lines/mm. More than 50% DE could be obtained for gratings with 1800 lines/mm. Figure 7 shows the variation of efficiency with spatial frequency. To determine the optimum beam ratio, gratings were recorded in the Ag2 sample for different intensity ratios of the
recording beams maintaining the exposure energy at 80 mJ/cm² and at a spatial frequency of 1070 lines/mm. The variation of DE with beam intensity ratio is plotted in Fig. 8. Maximum DE was obtained for a beam intensity ratio of 1:1, where the fringe visibility is nearly unity.

5. Storage Life and Prerecorded Shelf Life of the Film

The storage life gives an idea of how long the material can store the recorded grating or hologram. To find the storage life of the gratings recorded in the optimized Ag2 film, DE measurements were carried out on successive days after recording. The recorded films were kept inside a dark box, and no postexposure was applied. During the period of storage, the temperature of the storage place was in the range of 28–30°C, and the relative humidity was 45–55%. For reconstruction of the gratings, a low-power He–Ne laser beam (1 μW, 632.8 nm) was used. The DE remained ≈70% for approximately 3 months after recording the grating. Even after 1 yr of recording, an efficiency of 50% could be attained, which is good enough for almost all holographic applications. DE on storage is plotted in Fig. 9. As the weak ionic cross links formed between PVA and silver ions are labile, this results in further diffusion of the unreacted monomers from the destructive to the constructive interference region, thereby decreasing the DE. To determine the shelf life of the film, gratings were recorded in the optimized film each day after drying the film. The films were stored in a dark box (temperature 28–30°C, relative humidity 45–55%). It was found that gratings could be recorded in the film with a DE of ≈70% for approximately 3 months. Gratings with more than 60% DE could be recorded even after 4 months of storage. The efficiency of aging the film for 4 months is shown in Fig. 10. The slight decrease in efficiency may be due to the polymerization of the monomer on aging the film. During the period of storage for both recorded gratings and unexposed films, there was only a slight decrease in the efficiency, which clearly indicates that the prepared material is less affected by the studied humidity range.

6. Recording Transmission Holograms

Volume transmission holograms were recorded on the optimized Ag2 film using the double beam method. A bright transmission hologram recorded using a He–Ne laser (632.8 nm) is shown in Fig. 11. The material has the great advantage of recording and reconstructing holograms in real time.

Fig. 6. Change in RI with Ag⁺ concentration.

Fig. 7. DE versus spatial frequency.

Fig. 8. DE versus beam ratio.

Fig. 9. DE on storage.

Fig. 10. DE on aging.
7. Peristrophic Multiplexing

Plane-wave transmission gratings were multiplexed with an interbeam angle of 40°, which produced holographic gratings with a spatial frequency of 1070 lines/mm. In order to record multiple gratings at the same volume, the photopolymer film was rotated by an angle of 2° between successive recordings. This angle was chosen so that the first-order diffracted peak of each grating would not contribute to or detract from the DE of neighboring gratings. A combined exposure of 4 mW/cm² was used to record individual gratings, and the beam intensity ratio was 1:1. The exposure energy was varied for each grating by varying the exposure times, because for holographic data storage applications, the multiplexed gratings should have uniform DE so the output electronic detector array can detect all the signals effectively. Therefore, when a large number of holograms are to be recorded, their maximum DE should be as constant as possible in order to make efficient use of the available dynamic range. Hence attempts were made to equalize the DE of the multiplexed gratings by adopting the exposure-scheduling method. This method was designed to share all or part of the available dynamic range of the recording material among the gratings to be multiplexed. Exponential growth energy scheduling was used to record 15 gratings in a 130 μm thick photopolymer film. Several exposure-scheduling schemes were used to record gratings in the film, of which a better result was obtained for the scheme shown in Fig. 12. The variation of DE with grating number is shown in Fig. 13. Multiplexed gratings had diffraction efficiencies between 0.5% and 2.9%, and the mean DE was 1.3%. The dynamic range (M#), which refers to the total response of the medium when it is divided among many holographic gratings multiplexed in a common volume of the material, is calculated using

\[ M# = \sum_{i=1}^{M} \eta_i^{1/2}, \]  

where η is the maximum DE of each of the gratings recorded, and the sum is over the M holographic gratings multiplexed in one location [17]. The photopolymer layer with 130 μm thickness was found to have an M# of 1.7. This compares favorably to the AA-based photopolymer system developed by Sherif
et al. [24]. They obtained an M# of 3.6 while recording a set of 18–30 multiplexed gratings in a 160 μm thick material by the peristrophic technique and iterative energy-scheduling method. One of the requirements to obtain competitive holographic memory is that the material must have a thickness of 500 μm or more [18,24,25]. Thicker samples of 1.5 mm thickness are reported to have an M# as high as 50. The M# of the reported material is still unknown at these higher thicknesses. This material is also expected to yield higher M# values at higher material thickness. Work on the development of thick photopolymer films with good optical quality is in progress.

8. Conclusions

Silver-doped photopolymer (PVA/AA) films developed were found to have good energy sensitivity and exhibited a peak DE of more than 75% for an exposure energy of 80 mJ/cm². Various chemical and physical parameters influencing the holographic performance were optimized so as to explore maximum potential of the material. Gratings recorded in these films could be stored for more than a year with good DE. The importance of the material is that it is very cost effective and requires no wet postprocessing technique. The feasibility of recording bright transmission holograms in the material and its potential for holographic data storage applications are successfully demonstrated.

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References


