



PROCEEDINGS OF SPIE  
SPIE—The International Society for Optical Engineering

# *Photon Management*

**Frank Wyrowski**

*Chair/Editor*

**27–28 April 2004**  
**Strasbourg, France**

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Volume 5456

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Please use the following format to cite material from this book:

Author(s), "Title of Paper," in *Photon Management*, edited by Frank Wyrowski, Proceedings of SPIE Vol. 5456 (SPIE, Bellingham, WA, 2004) page numbers.

ISSN 0277-786X  
ISBN 0-8194-5383-8

Published by  
**SPIE—The International Society for Optical Engineering**  
P.O. Box 10, Bellingham, Washington 98227-0010 USA  
Telephone 1 360/676-3290 (Pacific Time)· Fax 1 360/647-1445  
<http://www.spie.org>

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Printed in the United States of America.

# Optimization of a PVA/Acrylamide material for the recording of multiple diffraction gratings

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## ABSTRACT

Photopolymers are considered one of the most interesting materials for holographic storage applications. The search for optimum chemical formulations to improve the quality of the final polymer materials has yielded a great deal of experimental work. Different theoretical models have also been developed by different authors to clarify the mechanism of hologram formation inside photopolymer materials. These advances in both experimental and theoretical fields permit obtaining suitable compositions of photopolymer materials for data storage purposes. In this work we present the results of an optimization of a PVA/acrylamide recording material with a high thickness (over 1 mm) to obtain holographic memories. Diffraction gratings of 1125 lines/mm were recorded in this material by using the peristrophic multiplexing technique and using the light from an Argon laser at a wavelength of 514 nm.

**Keywords:** photopolymers, holographic recording materials, holography, acrylamide

## 1. INTRODUCTION

Photopolymers are considered one of the most interesting materials for holographic data storage applications<sup>1</sup>. Their acceptable energetic sensitivity, a variable spectral sensitivity depending on the sensitizer dye used, good resolution, high diffraction efficiency and good signal/noise ratio, imply that these materials have great potential in developing holographic memories, but it's their low price, easy preparation and self-processing properties make them even more attractive for use on a large scale in read only WORM (write once read many) type memories.

One of the basic requirements for holographic memories to be competitive is that the film of recording material must be 500  $\mu\text{m}$  or more thick<sup>2</sup>. A greater number of holograms may be recorded with thicker layers, since in this case the angular selectivity is greater due to the fact that the width of the angular response curve is very small.

The search for optimum chemical formulations to improve the quality of the final polymer materials has yielded a great deal of experimental work, which can be found in the extensive literature, but it is not easy to find such great thicknesses with the recording materials currently available and with good properties for this application: in the case of photographic emulsions and dichromate gelatine, the layers barely reach a thickness of a few tens of micrometers. Only, acrylate oligomer-based photopolymers<sup>3</sup>, photopolymers based on organosilanes and their derivatives prepared using the sol-gel technique<sup>4</sup>, or new CROP commercial photopolymers<sup>5</sup> have suitable thicknesses.

One type of photopolymer, based on acrylamide (AA), it is not aforementioned but it's was used in the past, in the first studies on liquid photopolymers. In solid formulation, in the simplest case, they consist of polyvinyl alcohol (PVA) as binder, AA as the polymerizable monomer, triethanolamine (TEA) as free radical generator and a sensitizer, in our case yellowish eosin (YE), which allows the material to respond at 514 nm (Argon laser). As far as acrylamide photopolymers are concerned, most of the studies found in the bibliography<sup>1,6</sup> refer to thicknesses of less than 300  $\mu\text{m}$ . A summary of the historical evolution of these materials was recently published by Lawrence et al<sup>7</sup>.

In our work, we develop a holographic recording material based on PVA/AA. A detailed study of its method of preparation and the factors governing the process enable high thicknesses of around 1000  $\mu\text{m}$  to be reached, allowing to achieve high storage densities. Additionally, optimization of the composition allows good results to be obtained for the main holographic parameters, measured in order to characterize the material, such as diffraction efficiency (DE), energetic sensitivity (S) or the minimum energy required to reach maximum diffraction efficiency (DE<sub>max</sub>). Diffraction gratings of 1125 lines/mm were recorded in this material by using the peristrophic multiplexing technique and using the light from an Argon laser at a wavelength of 514 nm.

During the last years different theoretical models have also been developed by different authors to clarify the mechanism of hologram formation inside photopolymer materials. These advances in both experimental and theoretical fields permit obtaining suitable compositions of photopolymer materials for data storage purposes. The Rigorous Coupled Wave Theory (RCWT) was used to obtain information about the characteristics of the diffraction gratings recorded. A non-local polymerization driven diffusion model (NPDD) is also used to predict the diffraction efficiencies obtained with the diffraction gratings stored in the polymer material.

## 2. EXPERIMENTAL

### 2.1 Preparation of the material

In recording materials based on PVA/AA, a solution of PVA in water forms the matrix and this is used to prepare the solution of monomer (AA) and photopolymerization initiator system (TEA, YE). The PVA was supplied by Fluka, AA and TEA by Sigma and YE by Panreac. The mixture is usually deposited in a layer on a glass plate and after evaporation of part of the water, a solid plastic film is formed which constitutes the holographic recording material. The conventional method of depositing the layer consists in using a manual or automatic TLC depositor, which by means of a rod or calibrated opening deposits the solution in a uniformly thick layer on a glass plate<sup>8</sup>. In order to increase the final thickness of the layer, the PVA concentration in the initial solution is increased, since in this way a greater amount of water is retained by the PVA in the "dry" layer. However, this also means that there is a significant increase in the viscosity of the solution. Since there is a limit to the viscosity of the solutions that can be used with the depositors, and bearing in mind the process of preparation and subsequent cutting of the coated plates, the maximum thickness that can be obtained by this method is between 200 and 300  $\mu\text{m}$ . Therefore, for the application we are interested in, it is necessary to find another method of preparing the layers which enables greater thicknesses to be obtained.

We prepare the solutions using a conventional magnetic stirrer, under red light and in standard laboratory conditions (temperature, pressure, relative humidity). If the viscosity is too high to use a magnetic stirrer, we stir slowly by hand to prevent the formation of air bubbles, followed by the application of a vacuum to both the prepared solution and the coated mold so that any eventual air bubbles are completely eliminated. The solutions are deposited, using the force of gravity, in polystyrene or polymethylmethacrylate circular molds to avoid strain and distortion in the material during the water evaporation process, and left in the dark to allow the water to evaporate, while recording the laboratory conditions (temperature and relative humidity) during the process. When part of the water has evaporated, the "dry" material is removed from the mold, cut into squares and adhered, without the need for adhesive, to the surface of glass plates measuring 6.5x6.5  $\text{cm}^2$ . The plates are then ready for exposure, which takes place immediately. The thickness of the material is measured using a conventional micrometer.

### 2.2 Holographic setup

To study the behavior of the photopolymer as a holographic recording material, we obtained slanted and unslanted diffraction gratings using a holographic setup. The experimental device is shown in Figure 1. An Argon laser at a wavelength of 514 nm was used to store diffraction gratings by means of continuous laser exposure. The laser beam was split into two secondary beams with an intensity ratio of 1:1. The diameters of these beams were increased to 1.5 cm with an expander, while spatial filtering was ensured. The object and reference beams were recombined at the sample at an angle  $\theta=16.8^\circ$  to the normal with an appropriate set of mirrors, and the spatial frequency obtained was 1125 lines/mm. The working intensity at 514 nm was 5  $\text{mW}/\text{cm}^2$ . The diffracted and transmitted intensity were monitored in real time with a He-Ne laser positioned at Bragg's angle ( $\theta'=20.8^\circ$ ) tuned to 633 nm, where the material does not polymerize. In order to obtain transmission and diffraction efficiency as a function of the angle at reconstruction we placed the plates on a rotating stage. The transmission and diffraction efficiency (TE and DE respectively) were calculated as the ratio of the transmitted and diffracted beam, respectively, to the incident power.

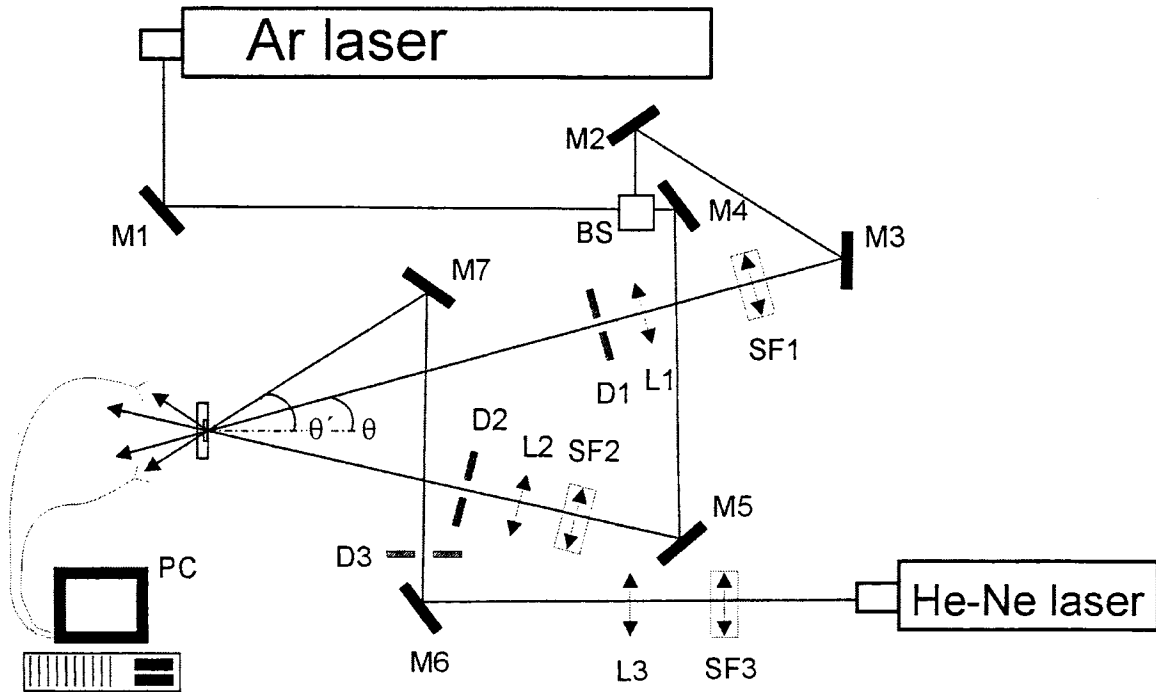


Fig. 1. Experimental setup: BS, beamsplitter, Mi, mirror, SF<sub>i</sub>, spatial filter, Li, lens, Di, diaphragm, PC, data recorder.

### 2.3 Peristrophic multiplexing

In order to analyze the photopolymer characteristics on several holograms recording, we have used the peristrophic multiplexing technique, with rotation axis parallel to media layer. We put the layer on rotation stage to record diffraction gratings changing layer and recording beams angle. In this manner, at the end of register, we are able to reconstruct the holograms by angular scan.

## 3. RESULTS

### 3.1 Influence of the characteristics of polymer binder (PVA)

The different types of commercial PVA are classified according to their molecular weight and degree of hydrolysis, which are the factors that determine the viscosity of the prepared solutions and the polymers' capacity to retain water. The difference in the degree of hydrolysis of the different PVA is small, since they are all hydrolyzed to quite a high degree and have a small number of residual acetate groups. The weight-average molecular weight  $M_w$  of the commercial products does, however, vary to a great extent, between 20000 and 200000. PVA with a low molecular weight have short chains and give solutions of low viscosity and little capacity to retain water per unit of mass. PVA with high molecular weight have very long polymer chains and when dissolved in water give solutions of high viscosity with a great capacity per unit of mass to retain water. The choice of PVA is a fundamental factor in obtaining a material of high thickness. The PVA normally used in the bibliography has a low molecular weight ( $M_w = 25000$ ). This type of PVA is not suitable to obtain very thick layers, capable of being used in holographic memories, since it has little capacity to retain water, which means that a high concentration is necessary and a great deal of solution must be deposited in order to obtain the required thickness. Because of the PVA solution be prepared by means of water reflux and the photopolymer solution is at room temperature, it's not possible use a solution with low molecular weight PVA over 30% w/v without heating it, which involves acrylamide wastage. Moreover, with a high concentration photopolymer solution it's not possible to obtain a homogeneous photopolymer layer. On the other hand, a PVA with highest molecular weight has very long polymer chains, which give rise to a high light scattering and photopolymer layers with high water content and low stability. This is a factor to be borne in mind in the process of recording and reading the data stored in the material.

Consequently, it is necessary to find a type of PVA that allows sufficient water to be retained so as to obtain layers of the required thickness, homogeneous and stable, and with a molecular weight such that the material does not exhibit excessive light scattering, like PVA Fluka 18-88 with  $M_w=130000$ . In Figure 2, it can be seen the typical curve of diffraction efficiency plus transmission efficiency versus exposure for a diffraction grating in a 1000  $\mu\text{m}$  thick photopolymer layer.

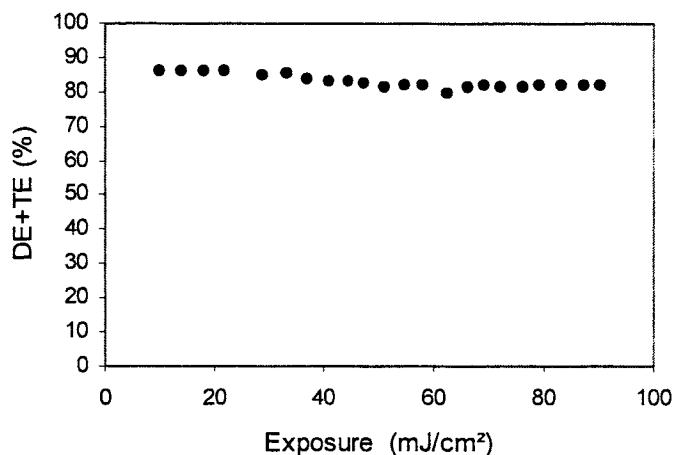


Fig. 2. Diffraction efficiency plus transmission efficiency versus exposure for 1000  $\mu\text{m}$  layer

It can be seen a constant sum of DE+TE higher 80% during the recording. This result does involve a low absorption and scattering losses, therefore this PVA type is a good choice for this layer thickness.

### 3.2 Optimization of monomer concentration

The thickness of the layers of material prepared for exposure determines the monomer concentration necessary to obtain a high efficiency and whether overmodulation occurs or not, moreover, if the concentration of active substances in the dry film increases excessively, this gives rise to poor photopolymerization results, since this process depends directly on the concentrations in the film of material and not on the concentrations in the initial solution<sup>9</sup>. Since the diffraction efficiency obtained is affected by the thickness of the material and the index modulation, for a given thickness, it is necessary to adjust the monomer concentration to delimit the refractive index modulation. In Figure 3 it can be seen a overmodulation example for a diffracton grating recorded on 1060  $\mu\text{m}$  photopolymer layer.

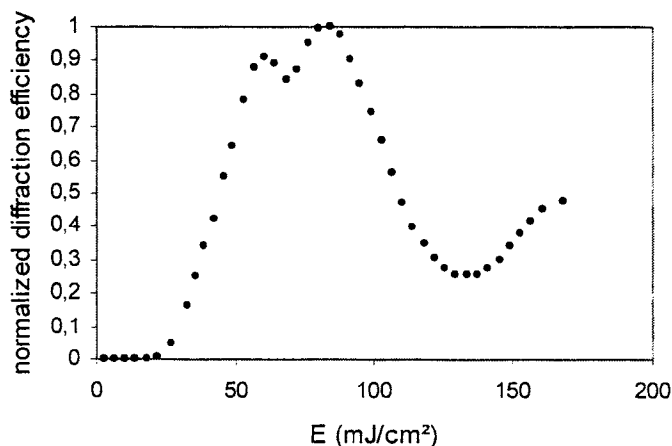


Fig. 3. Overmodulation in a 1060  $\mu\text{m}$  acrylamide photopolymer layer.

For this example the photopolymer layer has enough polymerizable monomer to index refraction overmodulation effect can be observed<sup>8</sup>.

In Figure 4 it can be seen the angular scan for a photopolymer layer with optimized composition. In this case overmodulation effects are not present because the monomer concentration is optimum. It is necessary about 81 mJ/cm<sup>2</sup> to obtain the maximum diffraction efficiency.

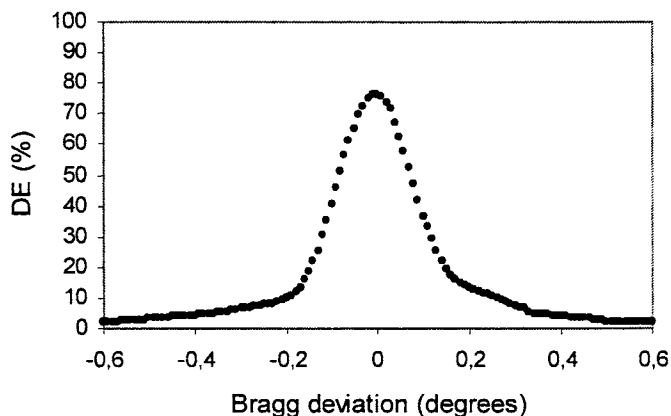


Fig. 4. Angular response for a photopolymer layer with optimum composition.

It can be seen in Figure 4 the high angular sensitivity for this layer, therefore, the maximum diffraction efficiency is in only 0.4° angular interval. In this manner it is possible record several holograms by multiplexing and reconstruct one of them without overlap, as we can see in the next point.

A higher concentration of AA permits obtaining a higher refractive index modulation for a lower energy, although it implies higher noise. A lower concentration results in a lower DEmax with, moreover, a great deal of energy being needed to obtain this maximum, which means a low sensitivity. All these effects should be taken into account in the optimization of a formulation for the photopolymer material depending on the particular application which the material is prepared to. This is due to the fact that in some cases it is necessary to achieve over-modulation to verify the behaviour of the theoretical model, or having high noise values to observe their effects in the form of the angular response curve. The presented formulation in Table 1 is optimized to attain the maximum diffraction efficiency with the lowest values of absorption and scattering of light, in photopolymer coats of 700-1000 μm.

In Table 1 are the concentrations of the components of optimized photopolymer solution which is deposited in order to obtain solid layers of recording media.

Components	Concentration
Polyvinyl alcohol M <sub>w</sub> =130000	13.30% w/v
Triethanolamine	0.15 M
Acrylamide	0.34 M
Yellowish eosin	9.00x10 <sup>-5</sup> M

Table 1. concentrations of the components of optimized photopolymer solution

### 3.3 Optimization of dye concentration

In the very thick layers of recording material needed for information storage applications, the dye concentration must be significantly less ( $9.00 \times 10^{-5}$  M for this thickness) than in the case of thinner layers, about  $80 \mu\text{m}$  ( $\approx 10^{-4}$  M in initial solution). The reason for this is that a high dye concentration in very thick layers implies that there is a large number of dye molecules, which in turn means that a great amount of light is absorbed and only a small amount penetrates the recording material, producing a weak polymerization, and therefore a low value for the maximum diffraction efficiency.

### 3.4 Peristrophic multiplexing

In order to evaluate the behaviour of thick photopolymer layers in terms of their possible application relative to holographic memories, in Figure 5 we recorded 8 diffraction gratings in the same zone of a  $955 \mu\text{m}$  thick recording material using the peristrophic multiplexing technique, by  $0.5^\circ$  recording media parallel axis rotation between recording one diffraction grating and the next.

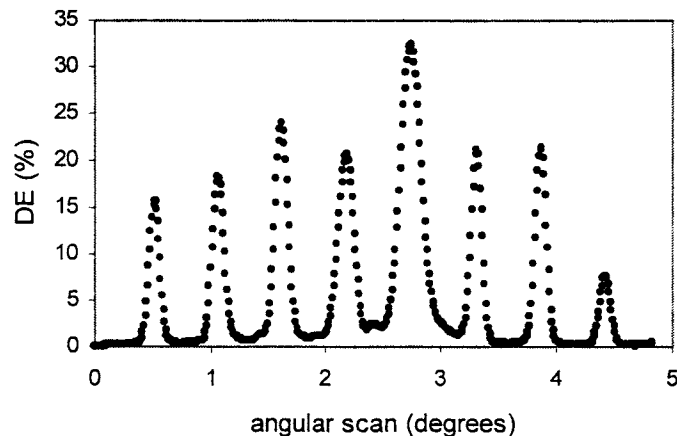


Fig. 5. Eight diffraction gratings recorded by peristrophic multiplexing

In this way a variation of  $5^\circ$  in rotation is sufficient to include the 8 gratings. We obtained high values for each individual maximum DE and sufficient separation between the gratings to enable their independent reconstruction. In these conditions,  $M\#=3.5$  which represents a good dynamic range. In Figure 6 it can be seen in real time recording the diffraction and transmission efficiency for each hologram.



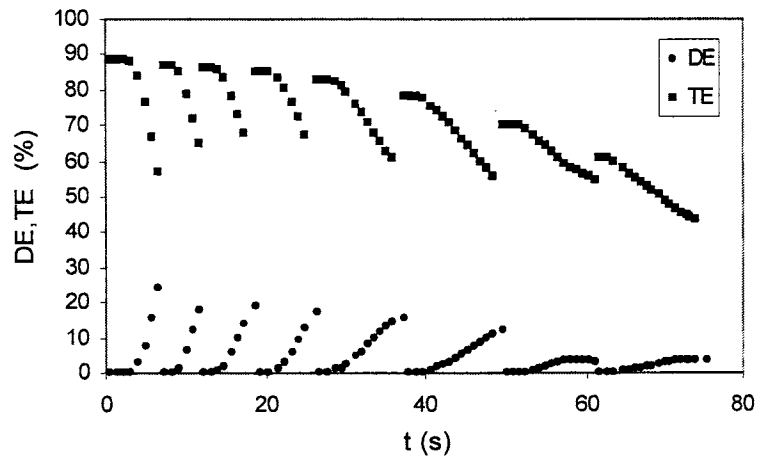


Fig. 6. Diffraction and transmission efficiency in recording for each hologram

It can be seen a fall in  $DE_{max}$  for 1 to 8 holograms because of the monomer concentration progressive decrease in photopolymer. On the other hand, the noise gratings recorded with main grating, because of light scattering by excessive exposure, are decreasing the transmission efficiency level<sup>10</sup>. This aspect can be seen more easily in DE+TE curve, Figure 7.

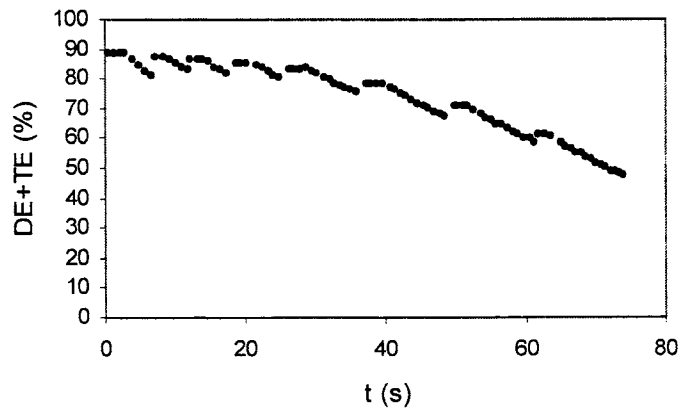


Fig. 7. DE+TE decreasing by excessive exposure in recording

#### ACKNOWLEDGMENT

This work was supported by the Ministerio de Ciencia y Tecnología, CICYT, Spain, under project MAT2000-1361-C04-04, and by Generalitat Valenciana, Spain, project GV01-130.

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