A new metal ion doped panchromatic photopolymer for holographic applications

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PRAMITHA V.

Applied Optics Division
Department of Physics
Cochin University of Science and Technology
Cochin - 682 022, Kerala, India

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A new metal ion doped panchromatic photopolymer for holographic applications

Ph. D Thesis in Optics

Author

Pramitha V.
Applied Optics Division
Department of Physics
Cochin University of Science and Technology
Cochin - 682 022, Kerala, India
email: vpramitha@yahoo.co.in

Supervising Guide

Dr. C. Sudha Kartha
Professor, Department of Physics
Cochin University of Science and Technology
Cochin - 682 022, India
email: csk@cusat.ac.in

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Cover Page Illustration

Front page: *Transmission hologram of a swan recorded in the developed film using 488 nm Ar*$^+$ *laser*

Applied Optics Division, Department of Physics, Cochin University of Science and Technology, Cochin - 682 022, Kerala, India

To my dear Parents........

Dr. C. Sudha Kartha
Professor
Department of Physics
Cochin University of Science and Technology
Cochin – 682 022

Certificate

Certified that the thesis entitled ***"A new metal ion doped panchromatic photopolymer for holographic applications"*** submitted by ***Ms. Pramitha V*** is an authentic record of research work carried out by her under my supervision at the Department of Physics in partial fulfilment of the requirements for the award of degree of Doctor of Philosophy of Cochin University of Science and Technology and the work embodied in this thesis has not been included in any other thesis submitted previously for the award of any other degree.

Cochin – 22
Date:

Prof. C. Sudha Kartha
Supervising guide

Phone: +91 4842577404. **Fax:** +91 484 2577595. **Email:** csk@cusat.ac.in

Declaration

I hereby declare that the thesis entitled ***"A new metal ion doped panchromatic photopolymer for holographic applications"*** submitted for the award of degree of Doctor of Philosophy of Cochin University of Science and Technology is based on the original work done by me under the guidance of ***Dr. C. Sudha Kartha***, Professor, Department of Physics, Cochin University of Science and Technology, Cochin - 682 022 and this work has not been included in any other thesis submitted previously for the award of any other degree.

Cochin – 22 **Pramitha V.**
Date:

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"It is difficult to say what is impossible,
for the dream of yesterday is the hope of today
and the reality of tomorrow"

- Robert H. Goddard

Optics is not Light work, but it is making Light work……

Preface

Holographic technology is emerging from research laboratory to find wider and more effective applications in communication and engineering problems. Volume holography is considered as a potential candidate for future 'ultra' storage technologies because of its terabyte storage capacity and fast data write and read rates. The development of suitable recording materials has been one of the primary challenges in the advancement of holographic storage. Holographic storage can fulfil its promise as a universal storage technology only when highly efficient, higher capacity, highly stable and economic recording media will become available.

Eventhough several materials have been investigated as holographic recording media, none of them was able to fulfil all the requirements for an ideal recording material. Recording materials for holography includes silver halide photographic emulsions, dichromated gelatin, photoresists, photochromics, photothermoplastics, photopolymers, photorefractive crystals and photorefractive polymers. Of these, photopolymers have been widely studied due to their excellent properties like high sensitivity, high diffraction efficiency (DE), large dynamic range, real-time imaging capabilities and relatively low cost. Intensive research is now triggered in the development of holographic photopolymers which possess excellent holographic characteristics compared to conventional recording materials. The advent of commercial holographic data storage (HDS) systems and photopolymer media developed by companies such as InPhase Technologies, Optware, and Aprilis indicates that the technology is no longer merely confined to the optical bench.

The present work focuses on the development of an efficient metal ion doped acrylamide based photopolymer recording media for holography. The feasibility of the developed photopolymer material for holographic data storage applications was also studied. The proposed thesis is entitled "**A new metal ion doped panchromatic photopolymer for holographic applications**" and consists of seven chapters.

Chapter 1 provides a brief description on the current relevance of holography and important holographic applications. Major requirements of holographic recording media and available recording media for holography are discussed. An overview on the utilization of photopolymers for holographic applications is also presented. The motivation for the present study and the major objectives are also discussed in this chapter.

A brief description on the materials used for fabrication of the photopolymer films is presented in **chapter 2**. Details of preparation of the photopolymer solution and fabrication of films are discussed. Gravity settling and spin coating techniques were used for film fabrication. Various experimental techniques adopted for characterizing the films are also described in this chapter.

Chapter 3 describes the preparation and characterization of silver doped photopolymer system consisting of poly (vinyl alcohol) (PVA) as the binder matrix, acrylamide (AA) as monomer, methylene blue (MB) and triethanolamine (TEA) as photoinitiation system and silver nitrate as crosslinker. The films were fabricated by gravity settling method and experiments were performed to optimize various parameters influencing the holographic performance of the films. The films were found to have good spectral sensitivity in the visible region of the spectrum with peak absorption in the red region of the spectrum. Holographic characterization of the films using He-Ne laser with emission at 632.8 nm is discussed in this chapter. Plane-wave transmission gratings were recorded in the film using He-Ne laser. Incorporation of silver ions into methylene blue sensitized poly(vinyl alcohol)/acrylamide photopolymer was observed to give better holographic performance compared to other metal ion doped photopolymer holographic recording media. Silver doped films were found to have good energy sensitivity and exhibited peak diffraction efficiency of above 75% for gratings with spatial frequencies of 410-1100 lines/mm and exposure energy of 80 mJ/cm^2. Gratings recorded in these films could be stored for more than three years with good diffraction efficiency. The importance of the material is that it is very cost effective and requires no post development. The feasibility of recording bright transmission holograms in the material could be successfully demonstrated.

The holographic characterization of the films using Nd: YAG (532 nm) and Ar$^+$ (488 nm) lasers is presented in **Chapter 4**. From the study, it was noted that gratings with high diffraction efficiency could also be recorded using Ar$^+$ and Nd: YAG lasers thereby elucidating the possibility of using the silver doped MBPVA/AA film as a competent panchromatic recording material. The developed panchromatic photopolymer system is outstanding on account of its wide spectral sensitivity, high diffraction efficiency, good energy sensitivity, high resolution, cost effectiveness, ease of fabrication and lack of chemical development. The film is expected to have important applications in the fields of true-colour display holography, wavelength multiplexing holographic storage and holographic optical elements.

Chapter 5 presents the holographic multiplexing studies carried out in the films**.** Angle and peristrophic multiplexing techniques were employed for storing multiple transmission gratings in the films. Gratings were multiplexed by constant and iterative exposure scheduling methods. The storage capacity of the film was determined by calculating the dynamic range (M-Number, M/#). Diffraction efficiency (DE) and M/# obtained were compared to determine which method enabled the greatest number of gratings to be recorded with uniform diffraction efficiencies. By peristrophic multiplexing method, thirty nearly uniform plane wave gratings with M/# equal to 4.7, could be recorded in the 130 μm thick photopolymer layer. The M/# value obtained while recording thirty gratings in the developed silver doped MBPVA/AA photopolymer layer is assumed to be larger than the reported values for multiplexing equal number of gratings in acrylamide based photopolymer materials with similar composition and layer thickness.

Chapter 6 describes the fabrication of uniform films by spin coating technique and the studies carried out to record data pages in the film. Holographic transmission gratings with 80% diffraction efficiency were recorded in the optimized film using 632.8 nm He-Ne laser. The image of a checker board pattern was recorded in the film using frequency doubled Nd: YAG laser (532 nm). The reconstructed image captured using CCD camera had good image fidelity. From the study, the suitability of developed film for holographic data storage could be successfully demonstrated.

The summary of the research work and the relevant results obtained from the study are outlined in **chapter 7.** The scope for future work is also presented.

Publications

Journal Publications

- Peristrophic multiplexing studies in silver doped photopolymer film, **V. Pramitha**, Rani Joseph, K. Sreekumar and C. Sudha Kartha, J. Mod. Opt. **57**, 908 (2010).
- Silver-doped photopolymer media for holographic recording, **V. Pramitha**, K. P. Nimmi, N. V. Subramanyan, Rani Joseph, K. Sreekumar and C. Sudha Kartha, Appl. Opt. **48**, 2255 (2009).
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- On the panchromaticity of silver doped poly (vinyl alcohol)/acrylamide photopolymer, **Pramitha V**, Rani Joseph, K. Sreekumar and C. Sudha Kartha (communicated)

Conference Publications

International conferences

- Performance of grating's diffraction efficiency of photopolymer film on the addition of cross linker, K. P. Nimmi, **V. Pramitha**, K. Sreekumar, C. Sudha Kartha and Rani Joseph, *International Conference on Advances in Polymeric Materials-APT 2010*, Cochin, India, February 26 - 27, 2010.
- Study on the effect of molecular weight of poly (vinyl alcohol) on the properties of photopolymer film, K. P. Nimmi, V. **Pramitha**, C. Sudha Kartha, K. Sreekumar and Rani Joseph, *International Conference on Materials for the Millenium - MATCON 2010*, Cochin, India, January 11 - 13, 2010.

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1

Photopolymers for Holographic Applications

This chapter gives a brief account on the current relevance of holography and important holographic applications. Major requirements of holographic recording media and available recording media are discussed. An overview on the utilization of photopolymers for holographic applications is presented here. The motivation for the present study and the major objectives are also discussed in this chapter.

1.1. Introduction

Holography, the technique to record and reconstruct three-dimensional images was invented in 1947 by Dennis Gabor, who was awarded Nobel Prize in Physics in 1971 for the discovery. The unique feature of holography is the recording of complete wave field, that is, both the amplitude and the phase of the light waves scattered by the object [1]. With advances in laser and material technologies, the holographic industry is rapidly growing. Holography plays an essential role in today's science, technology and industry. Relevant applications making use of this principle have been developed, including three-dimensional (3D) displays and holographic cameras, interferometers for non-destructive material analysis, archival data storage systems, diffractive optical systems and embossed display holograms for security features. Holography is considered as one of the future data storage paradigms that may answer the constantly growing need for higher-capacity and faster access memories.

One of the crucial issues for the success of this elegant technology is the lack of a suitable recording medium. Eventhough several materials have been investigated for holographic recording, none of them was able to fulfil all the requirements for an ideal recording medium. Holographic recording materials include silver halide photographic emulsions, dichromated gelatin, photoresists, photochromics, photothermoplastics, photopolymers, photorefractive crystals and photorefractive polymers. Of these, photopolymers have been widely studied due to their excellent properties like high sensitivity, high diffraction efficiency (DE), large dynamic range, real-time imaging capabilities and relatively low cost. Intensive research is now triggered in the development of holographic photopolymers which possess outstanding holographic characteristics compared to conventional recording materials. The advent of commercial holographic data storage (HDS) systems [2] and photopolymer media developed by companies such as InPhase Technologies, Optware and Aprilis indicates that holographic technology is no longer merely confined to the optical bench.

1.2. Holography- major applications

Holography is emerging as the new generation technique for digital data storage and engineering applications. It has applications in various areas including medicine, artificial intelligence, holographic optical elements (HOE), optical interconnects, optical correlators and security holograms. Besides these, holography has become a prominent art and advertising tool as well.

The use of holographic three dimensional images on credit cards to prevent falsification has made holograms a well known concept. Holograms show up more often on tickets and on original covers of software computer programs. Holographic images are also used in non-destructive material testing. Computer generated holograms (CGH) permits the generation of wavefronts with any prescribed amplitude and phase distribution [1]. They are therefore extremely useful for testing optical surfaces as well as in applications such as laser-beam scanning and optical spatial-filtering. Off-axis holography has found significant application in particle size analysis [1]. The applications of holographic particle size analysis include studies of fog droplets, dynamic aerosols and marine plankton.

Holographic diffraction gratings formed by recording an interference pattern in a suitable light sensitive medium are replacing conventional ruled gratings in spectroscopy. Holographic gratings have several advantages over ruled gratings. They are cheaper, simpler to produce and exhibit much less scattered light [1]. It is also possible to produce larger gratings of finer pitch, gratings on substrates of varying shapes and gratings with curved grooves and varying pitch. Bar-code readers in shops, warehouses, libraries and so on are based on the application of holographic components like optical gratings. This large industry has contributed to make holography an industrial success. Holographic scanners could solve many of the problems associated with mirror scanners. Most promising applications of holographic scanners are in point-of-sale terminals and for high-speed non-impact printing [1]. Head-up displays (HUDs) used in the aircraft industry is an important application of holographic technology. HUD allows essential flight or weapon aiming information to be optically superimposed into the pilot's field of view, thereby making flying easier [3].

Holographic interferometry is an extension of interferometric measurement methods in which at least one of the waves which interfere is reconstructed by a hologram [1]. The unique advantage of holographic interferometry is that holography permits storing a wavefront for reconstruction at a later time. Wavefronts which are originally separated in space or time, or even wavefronts of different wavelengths, can be compared by holographic interferometry. As a result, changes in shape of quite rough surfaces can be studied by interferometric precision. One of the most important applications of holographic interferometry is in non-destructive testing. Microscopic displacements on the surface of an object can be measured by holographic interferometry. Crack detection and the location of areas of poor bonding in composite structures are other fields where holographic interferometry has been found very useful.

Holography has potential application in medical education. Some of the earliest works in medical holography was in the area of dental records [4]. There are holographic techniques that will enable to obtain three dimensional image of any histological specimen. Holographic interferometry has the potential to play an important part in orthopaedics. Development of diffractive optics for the correction of refractive errors such as short sight was a great achievement in the field of ophthalmic holography. One of the successes in this area has been the fabrication of bifocal contact lenses for older persons or those who have had lens implants for cataract.

Holographic optical elements (HOEs) and holographic data storage (HDS) are important applications of holographic technology and are discussed in the following sections.

1.2.1. Holographic Optical Elements

Holographic optical elements are diffractive structures that are constructed holographically by the interference of an object beam and a reference beam. One beam resembles the "playback" beam that illuminates the HOE in the final system. The second beam correspond to the "image beam" that is supposed to exit the HOE upon its playback [5]. Optical elements such as lenses, beam splitters, diffraction gratings and filters can be produced by holographic imaging. Compared with conventional reflective and refractive optics, the HOEs are thinner and lighter, and have many attractive features. One of the main advantages of HOEs is the fact that, unlike conventional optical elements, their function is independent of substrate geometry [1]. They are relatively light, even for larger apertures, since they can be produced on quite thin substrates. HOEs have the advantage of being low cost and are easily reproducible by embossing polymer materials. Since the fabrication of HOE involves the recording of wavefront information, special attention needs to be paid in the selection of proper recording medium. Hence much research has been focussed over the development of suitable recording medium for HOEs. The frontline recording materials for the fabrication of HOEs have been the conventional silver halide emulsions [6]. Materials such as dichromated gelatin (DCG), photoresists and photopolymers also have been employed in the fabrication of HOEs [1].

HOEs have applications in optical and opto-electronic systems. Areas like optical sensors, optical interconnect, optical information processing, fibre optics, optical scanners, optical disc pick-up heads and solar concentrators have benefited from the use of HOEs. Since the HOEs are thin and planar, the optical systems can be made more compact and several elements performing complicated functions can be integrated into one HOE. One of the important applications of HOEs which has been commercially exploited is laser beam scanning. HOE based scanning has found applications in bar-code readers, computer printers and laser displays [7, 8]. HUDs include HOEs, mainly holographic combiner featuring diffractive control over both optical power and spectral sensitivity [9, 10].

1.2.2. Holographic Data Storage

The rapid growth of internet and digital communications has increased the demand for new high capacity and fast data-transfer rate devices. Holographic data storage has been considered as a promising technology since 1960s because of its outstanding characteristics such as parallel storage and retrieval, high density storage and fast data transfer rates. In holographic data storage, information is stored in volume as opposed to current storage solutions that record data on a plane. This extra dimension offers the advantage of increased storage capacity. The theoretical storage density limit of holographic data storage is amazing. P. J. van Heerden is widely credited for being the first to elucidate the principles behind holographic data storage

[11]. In his paper in 1963 on the theory of optical information storage in solids, he postulated that the recording of interference patterns in a three dimensional medium could be used as a means of storing and retrieving information. It was also pointed out that multiple holograms can be superimposed or multiplexed in volume media. The Bragg selectivity property of volume holograms, suggested and calculated by van Heerden, Leith and collaborators [12] and Kogelnik [13], is the basis of the enormous storage capacity of holographic memories.

Researchers have demonstrated a data storage density as high as 500 Gbits/sq. in. [2] and sustained optical data transfer rate as high as 10 Gbits/s [14] separately in different optical systems. Several important technical milestones have recently been achieved in this area, such as InPhase Technologies launching the prototype of their holographic disc-drive in 2008. The commercial possibilities may explain why several companies, including Bayer, DuPont, General Electric and Sony have entered this research area [15].

1.2.2.1. Holographic multiplexing

Multiplexing many holograms in the same volume of the recording material is necessary for high-capacity data storage [16]. P. J. van Heerden discussed the multiplexing of numerous holograms in a common volume by changing either the angle of the reference beam or the wavelength of both beams and Leith and his colleagues demonstrated the storage of multiple images by rotation of the recording plate. To store numerous pages of data holographically, various multiplexing techniques such as angle, peristrophic (rotational), shift and wavelength multiplexing are commonly used.

In the case of angle multiplexing (in-plane), the reference beam is a plane wave and the addressing mechanism is the angle of incidence of the reference wave [12]. The reference beam angular positions are such that the reference and the optical axis of the signal beam are all on the same plane. The angle multiplexing (out of plane) is similar to the previous one, but the reference beams are on a plane normal to the plane defined by the optical axis of the signal beam and its projection on the surface of the holographic medium [17-19]. In peristrophic multiplexing, the reference beam is a plane wave, and the addressing scheme is the relative rotational position of the storage medium [20]. The axis of rotation is arbitrary, but typically it is chosen normal to the holographic medium. In the case of wavelength multiplexing technique, the reference beam is a plane wave, and the addressing mechanism is the wavelength of incidence of the reference wave [12, 21, 22]. In phase-coded multiplexing, the reference beam is a plane wave modulated in one dimension (in the plane defined by the optical axes of the reference and signal beams) by a phase spatial light modulator (SLM) [23]. The addressing mechanism is the pattern displayed on the SLM. The phase pattern must belong to a set of orthogonal codes.

In the case of shift multiplexing (in plane), the reference beam is a spherical wave, and the addressing mechanism is the location of the holographic medium relative to the reference beam [24, 25]. The relative displacements are small enough that multiplexed holograms in subsequent locations overlap significantly. The reference beam locations are such that the optical axes of the reference beams and the signal beam all belong to the same plane. In the case of shift multiplexing (out of plane), the reference beams are on a plane normal to the plane defined by the optical axis of the signal beam and its projection on the surface of the holographic medium [26].

In spatial multiplexing, **s**tacks of holograms multiplexed using one of the above discussed methods are successively positioned in non-overlapping locations of the holographic medium [27, 28]. Each stack is well defined and separated from its neighbours by the lateral size of the holograms for all methods (e. g., the case of angle and spatial multiplexing) except that in the case of shift multiplexing, the stacks themselves are overlapping. Two holograms are shift multiplexed if they overlap and spatially multiplexed if they do not overlap. Pairs of multiplexing methods can be combined to achieve higher capacity. For example, angle multiplexing in and out of plane [29], angle and peristrophic multiplexing [30], angle and wavelength multiplexing [31] can be used as combinations.

1.2.2.2. Holographic storage and retrieval

To use volume holography as a storage technology, the digital data to be stored must be imprinted onto the object beam for recording and then retrieved from the reconstructed object during readout. Data storage is the conversion of abstract information, representing the data into physical changes in an appropriate medium. Data retrieval is the inference of the stored information from the storage induced changes [32]. Conventional storage technologies (magnetic and optical disks) are bit oriented and therefore are serial. In addition to high storage density, holographic data storage promises fast access times, because the laser beams can be moved rapidly without inertia, unlike the actuators in disk drives [33]. Fig. 1.1 shows a basic holographic data storage system [34]. The data to be stored are imprinted onto the object beam with the spatial light modulator (SLM). The SLM is a planar array of thousands of pixels. Each pixel is an independent optical switch that can be set either to block or pass light. A pair of high-quality lenses images the data through the storage material onto a pixelated detector array such as CCD camera. A reference beam intersects the object beam in the storage material, allowing the storage and later retrieval of holograms. During retrieval, the stored data is read out by a light beam carrying the address of the page selected for retrieval. Addressing during retrieval is similar to the storage phase. That is, the probe beam replicates the reference beam used for storing the desired page. The portion of probe light diffracted by the multiplexed volume holograms forms the reconstruction, which is detected by an appropriate detector array or camera.

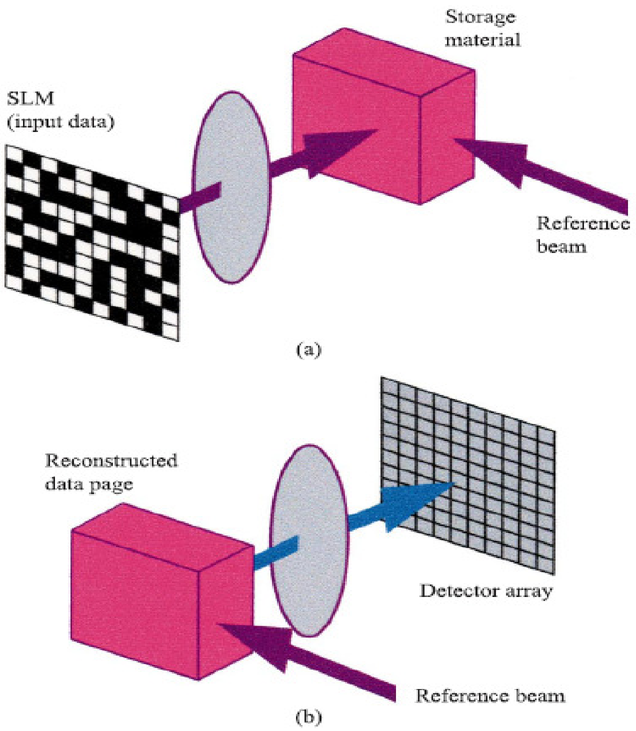

Fig. 1.1. Holographic data storage system

There is a rapidly increasing demand for high capacity and fast-access data storage in virtually all avenues of human endeavour from medicine and education to business and communications, from multimedia and entertainment to military and space. With the development of suitable architectures and recording materials, and the cost effective availability of suitable technologies, holographic storage is well positioned to meet this demand in the near future.

1.3. Storage materials for holography

The characteristics of the recording material are of paramount importance for volume holographic applications. The choice of proper recording media greatly influences the performance of holographic technology. There are several criteria, which an ideal holographic recording material should satisfy:

- **High resolution and a flat spatial frequency response**: - This will ensure that the desired interference pattern is completely stored, i. e., no fine fringe detail is lost.
- **Large dynamic range**: - This results in sufficient modulation during recording, which will lead to a good signal-to-noise ratio.
- **High optical quality**: - This will lead to high optical efficiencies (bright images).
- **Good environmental stability**: - Changes in environmental conditions should not affect the material and the stored hologram should be stable for long periods of time.
- **High energy sensitivity**: - The material should be sensitive enough to react to a low energy exposure.
- **Low cost**: - material should be readily and cheaply available.

Numerous recording materials like silver halide photographic emulsions, dichromated gelatin, photoresists, photochromics, photopolymers etc. have been investigated for holographic applications. A brief description on holographic recording materials is presented below.

1.3.1. Silver halide photographic emulsion (SHPE)

Silver halide photographic emulsion is one of the oldest and most widely used recording materials for holography [1]. It consists of a gelatin layer in which microscopic grains of silver halide (usually silver bromide) are dispersed. This layer is usually coated onto glass or film substrate, with an emulsion thickness in the range of 5 to 15 μm. The material works by recording a latent image which is then developed by chemical post-processing. An advantage of the formation of a latent image is that the optical properties of the recording material do not change during exposure, unlike materials in which the image is formed in real-time [1]. This makes it possible to record several holograms in the same photographic emulsion without any interaction between them. Because of the high sensitivity (10^{-5} to 10^{-3} mJ/cm^2) and good resolution (greater than 6000 lines/mm), silver halide photographic emulsions are one of the most popular holographic recording materials in use [35]. Agfa-Gevaert and Eastman Kodak plates are the commonly used commercial silver halide photographic materials for holography. However, the main disadvantage of these materials is the need for cumbersome chemical processing and development.

1.3.2. Dichromated Gelatin (DCG)

DCG was first applied to holography in the late 1960s. DCG consists of a gelatin layer that contains ammonium dichromate which becomes progressively harder on exposure to light. This hardening is due to the photochemically produced Cr^{3+} ion forming localized cross-links between the carboxylate groups of neighbouring gelatin chains [1]. Compared to silver halide photographic emulsions, DCG has low energy sensitivity, but, it has higher efficiency and quite high resolution. Large refractive index modulation capability, high diffraction efficiency, high resolution, low noise and high optical quality make DCG an almost ideal recording material for volume phase holograms [36]. However, it is very sensitive to environmental changes and needs chemical post-processing. It is not commercially available and has to be prepared in the laboratory before use as it has a useful life of only a few hours [3, 37].

1.3.3. Photoresists

Photoresists are light sensitive organic films which yield a relief image after exposure and development. Several photoresists have been used to record holograms [38]. Low sensitivity (10^2 J/m^2 to blue light (442 nm)) is their main disadvantage. Photoresists have the advantage that replication using thermoplastic is easy. Negative and positive photoresists are the two types of photoresists [1]. In negative photoresists, the exposed areas become insoluble and the unexposed areas are dissolved away during development. Long exposures are required for negative photoresists to ensure that the exposed photoresist adheres to the substrate during development. Hence positive photoresists in which the exposed areas become soluble and washed away during development are preferable. Need for chemical development is a major drawback of these materials.

1.3.4. Photochromics

Photochromic materials undergo reversible changes in colour when exposed to light [1]. Photochromism is due to the reversible charge transfer between two species of electron traps. Organic photochromics are prone to fatigue and have a limited life. Inorganic photochromics are crystals doped with selected impurities. These are grain free and have high resolution. A number of holograms can be stored in them due to their relatively high thickness. They require no processing and can be erased and re-used almost indefinitely. But their use has been limited by their low diffraction efficiency and low sensitivity.

1.3.5. Photothermoplastics

Surface relief holograms can be recorded in a thin layer of a thermoplastic when it is combined with a photoconductor and charged to a high voltage [1]. On exposure, a spatially varying electrostatic field is created. The thermoplastic is then heated so that it becomes soft enough to be deformed by the field and finally cooled to fix the pattern of deformations. They have practically high sensitivity over the whole visible spectrum and yield a thin phase hologram with fairly high diffraction efficiency. They also have the advantage that they do not require wet processing. If a glass substrate is used, then, the recorded hologram can be erased and the material can be reused a number of times. Most commonly used type of photothermoplastic is a multilayer structure consisting of a substrate (glass or mylar) coated with a thin transparent, conducting layer (usually indium oxide), a photoconductor and a thermoplastic [39]. A problem encountered with most photothermoplastics is 'frost'- a random surface modulation whose power spectrum is very similar to the modulation transfer function (MTF) of the material [1].

1.3.6. Photorefractive crystals

In some electro-optic crystals, exposure to light frees trapped electrons, which then migrate through the crystal lattice and are again trapped in adjacent unexposed regions. This migration usually occurs through diffusion or an internal photovoltaic effect. This spatially varying electric field produced by the resulting space-charge pattern modulates the refractive index through electro-optic effect, resulting in the formation of a phase hologram [1]. This hologram can be erased by uniformly illuminating the crystal. Eventhough this reversibility is highly needed for erasable holographic memories, destructive readout is a major problem associated with these materials. Photorefractive effects have been observed in electro-optic crystals like $LiNbO_3$, $LiTaO_3$, $BaTiO_3$, $KNbO_3$ and so on [32]. Good availability, excellent homogeneity and high robustness, long dark storage times, large storage capacities and reversibility make $LiNbO_3$ and $LiTaO_3$ the favourites among inorganic photorefractive materials for holographic data storage applications. If problems like low sensitivity, high cost and destructive readout can be solved, inorganic photorefractive crystals can be considered as a good choice for holographic read-write memory systems.

1.3.7. Photorefractive polymers

In photorefractive polymers, the recording mechanism is similar to that of inorganic photorefractive crystals except that the mobile charges are holes, and strong electric fields have to be applied to enable charge migration and to enhance the electro-optic effect. Photorefractive (PR) effect in an organic polymer was discovered in 1990 by a group at Eastman Kodak [32]. This composite was developed by doping an electro-optic polymer with charge transport molecules. Fully functionalized side-chain polymer with multifunctional groups was developed independently at the University of Arizona and University of Chicago [32]. Properties of photorefractive polymers differ from those of inorganic photorefractive crystals in many ways. Basic properties like photogeneration, transport and index modulation are different. Polymers are amorphous materials as opposed to crystalline for most of the inorganic photorefractive crystals. The mechanism of index change is also different. Rapid advances in the field of PR polymers and composites have led to the development of high performance materials with refractive index (RI) modulations approaching 0.01 and diffraction efficiencies close to 100%.

1.3.8. Photoaddressable polymers

Photoaddressable polymers (PAP) are polymers that react to light with a change in their molecular configuration. An advantage of these polymers is the fact that the light induced reaction is a local effect. Therefore no diffusion processes take place, and the change of the optical parameters is related only to the molecular orientation. The PAPs are basically azobenzene containing liquid crystalline co-polymers. Azobenzene chromophores exist in two isomeric states: the long rod like *trans* form and the bend *cis* configuration. The isomerization can be induced by light in both directions, from *trans* to *cis* and from *cis* to *trans*, whereas the *cis* isomer can also undergo a thermal back relaxation to the thermodynamically more stable *trans* isomer. Illumination leads to a series of *trans-cis-trans* isomerization cycles, resulting in a photostationary equilibrium that depends only on the wavelength of the actinic light and the temperature of the sample [40]. Polyacrylates, polymethacrylates, polysiloxanes, polycarbonates, polyurethanes, polyimides and aliphatic polyesters have been investigated as the main chain.

Recently, many research groups have started to investigate systems of photoaddressable polymers. The Central Research Department of Bayer have synthesized many photoaddressable polymers and were optimized for optical data storage applications. Light induced birefringence (Δn) as high as 0.5 could be obtained. Long term stability of the light induced birefringence is one big advantage of these PAPs. The polymers are amorphous and can be easily processed. Since the physical properties are polarization dependent molecular orientation mechanisms, no further chemical development is needed. PAPs are dry recording materials. The light induced reorientation is reversible, and the material can be used as a rewritable medium.

1.3.9. Photopolymers

Photopolymers are systems of organic molecules that rely on photoinitiated polymerization to record volume phase holograms. Characteristics such as good light sensitivity, real-time image development, large dynamic range, good image stability and relatively low cost make photopolymers one of the most promising materials for holographic applications. Photopolymer systems for recording holograms usually comprise of one or more monomers, a photoinitation system and an inactive component called binder [32]. Other components are sometimes added to control a variety of properties such as pre-exposure shelf life and viscosity of the recording medium.

1.3.9 (a). Monomer

Monomer selection is very important since most of the holographic properties like recording sensitivity, dynamic range, shrinkage, environmental stability, dimensional stability and image fidelity are influenced by the monomer. Vinyl monomers such as acrylate and methacrylate esters which polymerize through a free radical mechanism and monomers capable of polymerizing by a cationic ring-opening mechanism (CROP) are commonly used in photopolymer systems [41]. Acrylamide, dimethylacrylamide, 2-hydroxiethylmethacrylate, vinyl acetate, acrylic acid and so on are commonly used.

1.3.9 (b). Photoinitiation system

Direct initiation of polymerization by light is very slow. Hence initiation is usually achieved by radical or cationic polymerization which requires a photoinitiator (dye and the electron donor) that is sensitive to the recording wavelength. Holographic photopolymers use at least two different molecules to form a photoinitiation system that is sensitive to the visible wavelengths commonly used in holography. A photosensitizer molecule absorbs the incident light, and in its excited state interacts with a radical generator or acid generator molecule, either through energy transfer or a redox reaction, to produce the initiating species. Free radical of the electron donor produced during laser exposure initiates the polymerization reaction. Proper selection of photosensitizer helps in recording holograms throughout the visible spectral range. Photosensitizer dyes like methylene blue, yellowish eosin, brilliant green, rose bengal etc. and electron donors like triethanolamine (TEA), diethanolamine (DEA), ethanolamine (EA), triethylamine (TETN), diethylamine (DETN), N-phenyl glycine, diphenyl iodonium chloride, dimethyl formamide and so on are commonly used.

1.3.9 (c). Binder matrix

The binder matrix is a crucial component affecting the physical properties of the recording medium such as its rigidity, environmental stability, dimensional changes upon holographic exposure etc. It also aids in film formation. Poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), poly(acrylic acid) (PAA) and poly(vinyl chloride) (PVC) are the commonly used binders.

1.3.9 (d). Crosslinker

Crosslinker is incorporated into the photopolymer film to improve the storage life of the recorded hologram, since it forms crosslinks with the binder matrix, thereby inhibiting the diffusion of unreacted monomers and stabilizing the recorded grating. Organic crosslinkers like N-N'-methylenebisacrylamide, gluteraldehyde etc. and metallic crosslinkers like ammonium dichromate, ferric chloride, cupric chloride and so on are often used.

The most important property of photopolymer systems is that they can spontaneously develop their holographic image during recording without the need of post-exposure processing steps. This real-time recording characteristic eliminates the need for complicated development procedures and makes it a promising candidate for data storage applications. Photopolymerization is not a reversible process and hence photopolymer holograms cannot be erased and reused. They are suitable materials for write-once-read-many (WORM) applications only.

1.4. Holographic grating formation in photopolymer systems

Photopolymer systems usually comprise of a photoinitation system, one or more monomers, and binder matrix. The grating recording mechanism in photopolymers involves several stages: photoinitiation, propagation and termination [42, 43]. Photopolymerization begins by the absorption of light by the photoinitiator, which results in the formation of primary free amine radicals. A redox reaction takes place between the excited dye molecule and amine, generating the semireduced dye radical, which is not involved in the initiation of polymerization reaction [44, 45]. A second electron transfer between the amine and the radical and a protonation process give rise to the leucoform (colourless form) of the dye. In the second step of the initiation, the amine cation radical loses a proton to become the α-amino radical. In the propagation stage, the α-amino radical subsequently adds to the carbon-carbon double bonds of the monomer unit to form a growing radical of one repeat unit in length, and thus initiates the polymerization reaction in the constructive interference region. The monomer depletion in the exposed region causes a concentration gradient, which then induces monomer diffusion from the destructive to the constructive interference regions. This causes refractive index (RI) modulation and results in grating formation (fig. 1.2). Two separate paths exist for termination. The first is the normal biomolecular combination, in which two growing macro radicals come together and terminate. The second path for termination is disproportionation, in which a labile atom (usually hydrogen) is transferred from one polymer radical to another [46, 47].

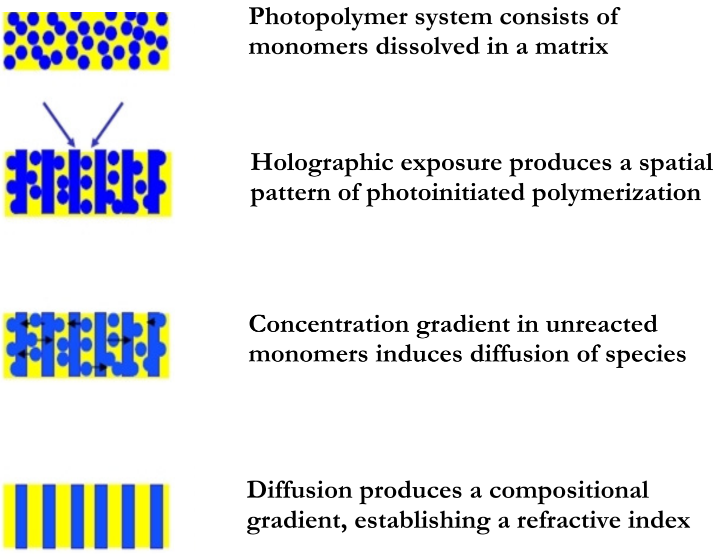

Fig. 1.2. Mechanism of grating formation in photopolymers

1.5. Photopolymers for holographic recording - a brief review

A review of the history of photopolymer materials is given here. A brief description on the early photopolymer systems and commercial photopolymers developed for holographic recording is also presented.

Photopolymers were first introduced as holographic recording materials by Close *et al* in 1969 [48]. This liquid state material consisted of monomer solution (mixture of acrylamide, barium acrylate and lead acrylate) and photocatalyst solution comprising methylene blue, p-tolulenesulfinic acid sodium salt and 4-nitrophenylacetic acid sodium salt. Good resolution and diffraction efficiency around 45% (interbeam angle of 30^0, exposure energy of 1 to 30 mJ/cm^2) were observed in 10-20 μm thick photopolymer layer using ruby laser. The exposed material was fixed by exposure to ultraviolet radiation.

This was followed by the preparation and characterization of numerous photopolymer systems. Commercial photopolymer materials like DuPont photopolymer by E. I. du Pont de Nemours and Co. Inc. and DMP-128 by Polaroid Corporation were also developed. The suitability of these photopolymers for holographic recording was studied by various research groups.

Colburn *et al* [49] studied the mechanism of volume hologram formation in DuPont photopolymer materials sensitive to both ultraviolet and blue-green radiation. This photopolymer system exhibited DE of nearly 10%. The energy density required for the initial exposure at 364 nm was 1 mJ/cm^2 and at 514 nm, the initial exposure requirement was about 10 mJ/cm^2. The characteristics of DuPont photopolymer material which consisted of an acrylate type photopolymerizable monomer, an initiator system and a cellulose polymer binder was studied by Booth [50]. The properties of DuPont photopolymer material for holographic applications were also studied [51]. The material exhibited high diffraction efficiency and excellent resolution. The suitability of the material for applications like real-time interferometry and hologram copying was studied.

The suitability of Polaroid's DMP-128 photopolymer for recording phase holograms was reported [52]. The film was found to be capable of recording efficient and stable holograms with good signal-to-noise ratios suitable for holographic applications. The exposure induced refractive index change in DMP-128 was quite small and produced weak holograms with diffraction efficiencies ~1%. Mechanism of hologram formation in DMP-128 photopolymer was reported by Ingwall *et al* [53]. The difference in material density between the solid and porous regions accounts for the refractive index modulation and for holographic activity of DMP-128 photopolymers.

Lougnot *et al* [54] developed a photopolymer system composed of pentaerythritol triacrylate (PETA) monomer, methyldiethanolamine (MDEA) and sensitizer dyes (Eosin Y, Erythrosin B, Rose Bengal and Phloxine B) and studied its suitability for real-time holographic interferometry. The effect of time modulated illumination and thermal post effect was also studied [55]. Photopolymer system comprising a monomer mixture of dipentaerythritol pentaacrylate with the acrylate of 3-(2-hydroxyethyl)-2-oxazolidone was developed [56]. Diffraction efficiency was nearly 10% for exposure of 30 mJ/cm^2 and 80% for 150 mJ/cm^2 and holograms could be recorded from green to the infrared upto 850 nm. Fimia *et al* [57] developed a photopolymer system based on dye-sensitized photopolymerization consisting of 2-hydroxyethyl methacrylate (HEMA), ethylene glycol dimethacrylate (EGDMA) and 4, 5-diiodosuccinylfluorescein (2ISF). DE of ~30% was achieved with 500 mJ/cm^2 and for intensities lower than 1 mW/cm^2.

Photopolymer system for recording reflection holograms was reported by Kawabata *et al* in 1994 [58]. The photopolymer system consisted of radically and cationically polymerizable monomers. The exposure energy required for recording was 20-60 mJ/cm^2 and diffraction efficiencies of ~60% at each colour component was achieved. Phenanthrenequinone (PQ) doped poly(methyl methacrylate) (PMMA) photopolymer was fabricated and characterized for holographic recording [59].

Curtis *et al* investigated the suitability of DuPont's 38 μm thick HRF-150 photopolymer in three dimensional holographic memories [60]. Rhee *et al* studied the dynamic aspects of DuPont photopolymer film HRF-150-38 for holographic data storage using Ar$^+$ laser at 514.5 nm [61].

Fimia *et al* have reported photopolymer with trifunctional monomer for holographic applications [62]. The mixture consisted of pentaerythritol triacrylate (PETA) and 2-hydroxyethylene methacrylate (HEMA) monomer. A diffraction efficiency of 80% was achieved with an energetic sensitivity of 3 J/cm^2 at 514 nm.

Lin *et al* [63] reported multiple storage and reconstruction of 250 holograms at a single spot of a 1cm^3 phenanthrenequinone doped poly(methyl methacrylate) photopolymer block. By peristrophic multiplexing, 355 plane-wave holograms were stored in the sample with equal exposure energy of ~8 mJ/cm^2.

Ushamani *et al* reported the feasibility of using poly(vinyl chloride) (PVC) matrix as an optical recording medium by converting it into copper acetate complexed methylene blue (MB) sensitized poly(vinyl chloride) (CMBPVC) films [64-67]. The change of state occurring to the dye molecules (MB) on laser irradiation was permanent in PVC and it existed in the leucoform itself. No monomer or electron donor was incorporated into the material. The gratings recorded in the films showed an efficiency of 4.46% at 1500 mJ/cm^2 for the intensity ratios of the first order diffracted beam to that of the transmitted beam. DE was only 0.26% for intensity ratios of the diffracted beam to that of the incident beam. The recorded grating vanished within a few hours [65]. Experimental investigations on the dependence of pH on real-time transmission characteristics of CMBPVC recording media was also reported [66]. The optimum pH value for faster bleaching was found to be 4.5. Dark room storage was not needed for CMBPVC films compared to other methylene blue sensitized conventional polymer systems. The rate of bleaching was found to be higher for an optimum pH of 4.5. Diffraction efficiency of 4.46% was attained and direct imaging was successfully carried out on the films.

Polymer blend of methylene blue sensitized poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) in methanol was prepared and characterized for holographic recording by Ushamani *et al* [68]. A comparison of methylene blue sensitized poly(vinyl alcohol) and poly(acrylic acid) in methanol with methylene blue sensitized PVA in methanol and complexed methylene blue sensitized poly(vinyl chloride) (CMBPVC) was also presented. A very slow recovery of the dye on irradiation was observed when a 7:3 blend of poly(vinyl alcohol)/poly(acrylic acid) at a pH of 3.8 and sensitizer concentration of 4.67×10^{-5}g/ml were used. DE of 11% could be attained for an exposure of 2000 mJ/cm^2, and the recorded fringes could be stored for approximately 10 days. The studies on the rate of bleaching and exposure energy revealed that this material needs more exposure than the MBPVA/methanol and CMBPVC films. A maximum diffraction efficiency of about 35% was achieved on the MBPVA/methanol system due to self-enhancement. It was found that methylene blue sensitized PVA/PAA blend or CMBPVC could be used as a permanent recording material without employing any fixing process, whereas, MBPVA/methanol requires suitable fixing technique. Optimization of the composition of methylene-blue-sensitized polymer blend of poly(vinyl alcohol) and poly(acrylic acid) system gave best results at a sensitizer concentration of 1.46×10^{-4} mol/l and pH of 3.8 [69]. The recovery of dye in this matrix could be controlled by changing the pH, and the recovery was found to be slow compared with MBPVA films. The stored information was stable for two weeks and does not need any fixing processes.

Kim *et al* [70] synthesized six-armed dendrimer using the initiating mixture of hexaarylbiimidazole (HABI), mercapto-benzoxazole (MOBZ), and 2,6-bis(4-

diethylaminobenzylidene) cyclopentanone, which is sensitive to 514 nm wavelength. Photopolymer sample doped with this dendrimer showed around 80-83% diffraction efficiency.

A photopolymerizable recording media based on poly(vinyl alcohol) and vinyl acetate (VAc) sensitized with methylene blue was introduced by Beena *et al* [71]. It was observed that the MBPVA/VAc system can be reused a number of times without significant decrease in diffraction efficiency. The PVA-VAc ratio was optimized at 2:1. Diffraction efficiency of 6.3% was obtained without any fixing at a dye concentration of 9.3×10^{-4} mol/l at an exposure of 750 mJ/cm^2.

Beena *et al* [72] have modified the preparation technique of the methylene blue sensitized poly vinyl chloride (MBPVC) system and pyridine was incorporated to the PVC matrix as a charge transfer agent. The diffraction efficiency and storage life of the gratings recorded on MBPVC were improved with the incorporation of pyridine. Maximum diffraction efficiency obtained for an exposure of 1500 mJ/cm^2 was 0.465%, and the grating could be stored for 2-3 days.

Ortuno *et al* [73] developed a new photopolymer with a higher environmental compatibility than that of standard photopolymers of the same type and with similar holographic properties. The highly toxic components of the photopolymer were eliminated, thereby obtaining a material with a lower potential toxicity. The photopolymer consisted of sodium salt 5’-riboflavin monophosphate (PRF) sensitizer dye, sodium acrylate (NaAO) monomer, N, N’- (1, 2-dihydroxyethylene) bisacrylamide (DHEBA) crosslinking monomer and a binder of poly(vinyl alcohol). High diffraction efficiencies (77%) with an energetic exposure of 197 mJ/cm^2 were obtained in 900 μm thick layers.

The recording of holographic diffraction gratings with a spatial frequency of approximately 1940 lines/mm in photopolymerizable epoxy resin materials was experimentally demonstrated by Jeong *et al* [74]. Diffraction efficiency near 92% and an energetic sensitivity of 11.7×10^{-3} cm^2/J were achieved by designing proper structure of matrix and also by optimizing photopolymer compositions. The effect of photopolymer compositions on the fundamental optical properties was also studied.

Liu *et al* [75] characterized holographic scattering and demonstrated its application in determining the kinetic parameters in materials with high transmittance and strong holographic scattering like phenanthrenequinone doped poly(methyl methacrylate) (PQ-PMMA). The preparation and characterization of Irgacure 784 doped photopolymers for holographic data storage at 532 nm was also reported [76]. The material was found capable of supporting a holographic data storage system with a data recording rate of 760 Mbs^{-1}. A study of diffusional enhancements in holographic gratings stored in phenanthrenequinone doped poly(methyl methacrylate) photopolymer was presented [77]. The enhancement provided an efficient method to obtain high and steady diffraction efficiency and prevented the amplification of holographic scattering under consecutive exposure. Dark enhancement in multiplexed gratings was introduced to optimize the response of the photopolymer and enhance its applicability. This process provides an alternative way to improve the homogeneity of diffraction efficiency and simplify the complex exposure schedule.

In addition to the above discussed photopolymer systems, several acrylamide based photopolymer systems also have been reported with different sensitizing dyes and other matrix additives. An overview on acrylamide based photopolymers is presented in the following section.

1.5.1. Acrylamide based photopolymer systems

Dye sensitized acrylamide based photopolymers are one of the most widely studied photopolymer materials for holographic recording. They exhibit excellent holographic properties like high dynamic range and photosensitivity, real-time image development, good optical quality and high diffraction efficiency. The dye sensitized polymerization of acrylamide and other vinyl monomers was first reported by Oster [78]. In 1965, Chen *et al* [79] studied the polymerization of aqueous acrylamide induced by visible light in the presence of methylene blue-triethanolamine sensitizing system.

The first photopolymer system introduced by Close *et al* [48] was a liquid state material consisting of a monomer mixture of acrylamide, barium acrylate and lead acrylate. In 1970, Jenney [80] reported the recording of real-time phase holograms in self-developing photopolymer systems consisting of acrylamide and a dye-sensitized photocatalyst. The monomer mixture of barium and lead acrylate plus acrylamide exhibited higher sensitivity than acrylamide alone. Recording sensitivities as high as 0.6 mJ/cm^2 have been achieved and reconstructions from gratings with 3000 lines/mm could be achieved. Refractive index modulation was identified to be the dominant image-storage mechanism in thick films resulting in the formation of volume holograms. The fixing of photopolymer holograms by flash fixing and thermal fixing techniques was reported [81]. The composition used for the study was barium acrylate, acrylamide and gelatine mixture. Flash fixing using a Xenon flash lamp had advantages like faster access to the reconstructed image, no requirement of chemical additives in the photopolymer solution and was more convenient to use. Thermal fixing has not provided rapid access, but completely permanent holograms could be developed by thermal fixing.

Sadlej *et al* [82] improved the original system proposed by Close by including a poly(vinyl alcohol) (PVA) binder which allowed the production of dry photopolymer layers. Sugawara *et al* [83] investigated the dye-sensitized polymerization of acrylamide inorder to develop holographic media with high diffraction efficiency and long photosensitive life. The photosensitive system consisted of methylene blue as photosensitizer and acetylacetone or triethanolamine as an initiator. In system containing triethanolamine, a diffraction efficiency of upto 65% was obtained and photosensitivity could be maintained for more than 80 days.

In 1980s, Calixto [84] developed a photopolymer system consisting of acrylamide monomer, triethanolamine (TEA) electron donor, methylene blue (MB) photosensitizer and PVA binder. Crosslinking agent such as N, N'-methylenebisacrylamide (MBA) was incorporated to speed up the polymerization reaction by Martin *et al* [85]. The surface relief formation in an acrylamide photopolymer was reported by Boiko *et al* [86].

Fimia *et al* [87] developed a holographic photopolymer system consisting of AA, zinc acrylate and MBA as monomers, photoinitiator system consisting of MB and Rose Bengal (RB) in 4:1 ratio and p-toluensulfunic acid. Diffraction efficiency of ~35% was obtained using 633 nm He-Ne laser. The possibility to fabricate volume phase off-axis HOEs on spherical substrates with this acrylamide based photopolymer was also reported [88]. Belendez *et al* [89] reported the observation of self-induced gratings or noise gratings in acrylamide based photopolymer. The possibility of using the noise source as an optimization technique for the material was also pointed out. A hybrid material containing acrylamide and acrylic acid as monomers was proposed by Zhao *et al* [90]. The material consisted of methylene blue as photosensitizer, TEA and p-toluenesulfonic acid as sensitizers and gelatine as binder.

Blaya *et al* [47] described the mechanism of grating formation in methylene blue sensitized poly(vinyl alcohol) acrylamide (MBPVA/AA) photopolymer films and obtained 80% efficiency. Eventhough high efficiency and sensitivity (40 mJ/cm^2) were achieved, the resolution was limited to 1000 lines/mm. The sensitivity was improved by incorporating the crosslinker, N, N'- dihydroxyethylenebisacrylamide (DHEBA) [91]. A sensitivity of 5 mJ/cm^2 and diffraction efficiency of 70% was achieved for holograms recorded with a spatial frequency of 1000 lines/mm in 100 μm thick films.

Neumann *et al* [92] described a simple technique suitable for the direct laser writing of surface relieves (~3 μm height) in dry photopolymerizable film comprised of AA, MB, TEA and PVA dissolved in ethanol and water. Garcia *et al* [93] studied the influence of beam ratio and intensity on the optical quality of transmission holograms of diffuse object stored in eosin doped PVA/AA systems. Mallavia *et al* [94] reported a photopolymer formulation with an ion pair isolated from rose bengal (RB) and methylene blue (MB) as photoinitiator. This photopolymer system showed wide spectral response and exhibited diffraction efficiencies of 30% at 514 nm and 60% at 633 nm. The holographic behaviour of an eosin doped acrylamide photopolymer at high thickness and high monomer concentrations was studied [95]. It was observed that by increasing the concentration of monomer and decreasing the recording intensity, it is possible to reduce scattering even when working with thicknesses greater than 100 μm. Lawrence *et al* [35] studied the mechanism of hologram formation in acrylamide based photopolymer.

Studies on optimization and characterization of Erythrosine B doped photopolymerizable recording material consisting of two monomers acrylamide and N, N'-methylenebisacrylamide was presented by Yao *et al* [96]. The effect of variation of the concentration of each component was investigated. DE of 55%, with an energetic sensitivity of 60 mJ/cm^2 have been obtained with a spatial frequency of 2750 lines/mm.

The effect of bifunctional crosslinking agent in PVA/AA photopolymer was studied by Blaya *et al* [46]. The material consisted of acrylamide (monomer), methylene blue (photosensitizer), triethanolamine (electron donor) and two monomers (N, N'-methylenebisacrylamide (BMA) and N, N'-dihydroxyethylenebisacrylamide (DHEBA)). The effects of intensity, thickness and variation of concentration of each of the crosslinking agent was studied using the angular responses of the diffraction gratings recorded with a spatial frequency of 1000 lines/mm by 633 nm He-Ne laser.

Blaya *et al* [97] reported the development of a poly(vinyl alcohol) based photopolymer in which recording was achieved by the co-polymerization of acrylamide and 2-hydroxiethylmethacrylate (HEMA). Diffraction efficiencies near 70% were obtained with exposures of ~ 65 mJ/cm^2 using 633 nm He-Ne laser in 110 μm thick materials. The addition of HEMA increased the film thickness and improved the storage capacity for holographic optical storage.

Garcia *et al* [98] have reported the recording of holograms in acrylamide based photopolymers by pulsed laser exposure. The photopolymer used was an acrylamide-poly(vinyl alcohol) dry film with a yellowish eosin-triethanolamine mixture as photoinitiator system. Holograms were recorded with a collimated beam from a frequency doubled Nd: YAG (532 nm) Q-switched laser. Diffraction efficiency of 60% and refractive index modulation of 2.8×10^{-3} was obtained. Gallego *et al* [99] studied the temporal evolution of diffraction efficiency of a hologram stored in eosin doped PVA/AA/dimethyl acrylamide (DMAA) photopolymer system by measuring the angular response of the hologram immediately after exposure and subsequent hours. The efficiency was found to decrease on storage and the fast temporal evolution of the diffraction grating stored was due to residual DMAA. With the addition of DMAA, the crystallization due to high AA concentrations could be prevented and thicker layers could be obtained.

Marquez *et al* [100] demonstrated the feasibility of a holographically edge-enhanced imaging system that uses a PVA/acrylamide photopolymer grating. Neipp *et al* [101] have analyzed the effect of addition of a cross-linking monomer on the temporal evolution of transmission efficiency in PVA/acrylamide photopolymer. It has been shown that the addition of a cross-linking monomer to the material resulted in an increase in the polymerization rate and also a slight increase of the polymer refractive index. Good agreement between the theoretical model and the experimental data was obtained, which confirms the validation of the diffusion based model to explain the mechanism of hologram formation in photopolymer materials.

Gallego *et al* [102] proposed several methods to eliminate the residual monomer in eosin/PVA/AA films inorder to stabilize the holographic gratings. The residual dye and residual monomer were identified as the main problems in achieving high diffraction efficiencies stable under white light. Inorder to polymerize the residual monomer, the gratings were illuminated with coherent green light and incoherent white light and the grating was heated at 80^0C for different times. After stabilization, high diffraction efficiencies (90%) were achieved.

Gong *et al* [103] developed a PVA based holographic recording material composed of Erythrosine B as dye, TEA as electron donor, AA and N-hydroxymethyl acrylamide (HMA) as monomers. The recording was achieved by the co-polymerization of AA and HMA and an efficiency of nearly 50% was achieved with energetic exposure of 80 mJ/cm^2 using 514 nm Ar$^+$ laser. The formation of photoinduced surface relief modulation in an Erythrosine B doped acrylamide-based photopolymer system is also reported [104]. Gallego *et al* [105] carried out three-dimensional analysis of holographic memories on PVA/AA films. SeO_2 crystals were incorporated to a polymer system containing PVA, AA and eosin to improve the stability after exposure [106]. The initial sensitivity of SeO_2 incorporated crystals was found to be lower than that of the undoped film. The application of an acrylamide-based holographic photopolymer for bit-format holographic data storage was investigated [107]. Holographic reflection gratings with a spatial frequency of 5640 lines/mm were recorded at 532 nm and diffraction efficiency of 0.2% was achieved. Copper doped methylene blue sensitized poly(vinyl alcohol)/acrylamide films were developed by Beena *et al* [108]. The films were fabricated by gravity settling method. Gratings recorded in the optimized film could be stored for years with stable diffraction efficiency (32%) without any chemical or thermal fixing techniques.

The optical modulation properties of eosin PVA/AA for wide range of thicknesses (ranging from 75 to 800 μm) were studied by a technique based on a Young's based double beam interferometer [109]. Post-exposure of the gratings recorded on the photopolymer system (AA, MBA, TEA, PVA and Erythrosine B) to uniform UV light resulted in more than 30% increase in the surface relief amplitude. The surface relief amplitude modulation was found to decrease with increase of TEA content [110]. PVA/AA films sensitive to 500-630 nm were fabricated with methyl violet as photoinitiator [111]. The recording characteristics of the holographic film were examined and the composition was optimized. Only 8% diffraction efficiency was obtained and the recorded gratings gradually disappeared on storage.

Gallego *et al* [112] proposed an alternative, direct method to calculate monomer diffusion times in photopolymer materials. Very long period gratings were recorded in the photopolymer and the real-time variation in diffraction efficiency due to monomer diffusion was analyzed. The method proposed was applied to two PVA/AA based photopolymers with different molecular weights.

The nonlocal photopolymerization driven diffusion (NPDD) model was generalized to more closely model material behaviour during grating formation by Gleeson *et al* [113]. An expression for the change in the absorbed intensity during exposure was presented and the key material parameters controlling the absorption characteristics were estimated. The spatial frequency response of PVA/AA photopolymer was improved by the addition of a chain transfer agent (CTA), sodium formate (HCOONa). It was also demonstrated that the CTA has the effect of decreasing the average length of the poly(acrylamide) (PA) chains formed, thus reducing the nonlocal response parameter.

Naydenova *et al* [114] demonstrated the suitability of a reflection hologram recorded in a self-developing photopolymer for visual indication of environmental humidity. A colour change was observed when the hologram was exposed to a change in humidity and was fully reversible. The range of colour change, reversibility and the response time of the hologram was studied in a controlled humidity environment.

Holographic data pages were multiplexed in different thickness layers of a poly (vinyl alcohol)/acrylamide photopolymer by Fernandez *et al* [115]. The photopolymer studied composed of acrylamide (AA) as the polymerizable monomer, triethanolamine (TEA) as radical generator, N, N'- methylene-bis-acrylamide (BMA) as crosslinker, yellowish eosin (YE) as sensitizer and a binder of poly(vinyl alcohol) (PVA). Four different data pages with different pixel sizes were multiplexed by peristrophic multiplexing method. Twisted-nematic liquid crystal displays (TN-LCDs) were used as a spatial light modulator to modify the object beam and store the data pages in the material. The bit error rate (BER) was calculated by fitting the histograms of the images so as to quantify the quality of the images.

The effect of chromium doping on methylene blue sensitized Poly(vinyl alcohol)/Acrylamide photopolymer material was studied by Beena *et al* [116, 117]. The storage life was improved on doping with ammonium dichromate. A self-enhancement in efficiency was observed for a particular ratio of methylene blue and ammonium dichromate. Diffraction efficiency of 20% at 500 mJ/cm^2 was achieved just after recording. The diffraction efficiency was found to slowly increase to 40% by 3 months. It remained the same for months and then the efficiency gradually decreased and reached the initial efficiency of 20%.

Garcia *et al* [118] reported the recording of holographic lens in photopolymer material made up of PVA binder, AA and BMA monomers, TEA coinitiator and MB dye. The image quality of the recorded lenses was evaluated by means of modulation transfer function (MTF) and contrast. Lenses of different focal lengths (100, 150 and 250 mm) were recorded with high diffraction efficiency and temporal stability.

Yoshida *et al* [119] have simulated the formation of diffraction gratings in photopolymers using the diffusion model based on elementary reactions consisting of initiation, propagation, and termination. The diffraction characteristics were analyzed in detail by the beam propagation method. Interference fringe recording was performed and the recording characteristics of photopolymer media were evaluated.

Gallego *et al* [120] studied the possibility of poly(vinyl alcohol)/acrylamide based photopolymers to store diffractive elements with low spatial frequencies. Photopolymer compositions with and without crosslinker was chosen for the studies. The composition with BMA crosslinker provided higher energetic sensitivity.

The optical and holographic characteristics of acrylamide-based photopolymer layers were studied by Yovcheva *et al* [121]. The refractive index changes upon illumination of liquid and solid photopolymer layers at 532 nm were measured with a laser microrefractometer. In solid films, the refractive index change was approximately twice than that in liquid layers. The investigated photopolymer was found suitable for holographic recording both in solid and liquid form.

Silver doped methylene blue sensitized poly(vinyl alcohol)/ acrylamide (MBPVA/AA) photopolymer media was developed [122]. Silver doped MBPVA/AA photopolymer films exhibited better holographic performance compared to other metal ion doped photopolymer holographic recording media. The films were found to have good energy sensitivity and exhibited peak diffraction efficiency of above 75% for gratings with spatial frequencies of 410-1100 lines/mm and exposure energy of 80 mJ/cm^2. Gratings recorded in these films could be stored for more than three years with good diffraction efficiency.

Mahmud *et al* [123] studied the characteristics of acrylamide based photopolymer layers ranging in thickness from 250 μm to 1 mm. By measuring the diffraction efficiency growth of the holographically recorded gratings and studying the diffraction patterns obtained, the influence of scattering on the diffraction efficiency of thick volume holographic gratings was analyzed. It was found that, above a particular thickness and absorbance, the diffraction efficiency significantly decreased because of increased holographic scattering. Scattering effects were identified as important reasons for the thickness limitations that should be taken into account when different applications are envisaged.

The capacity of AA-based photopolymer with different compositions to record holographic reflection gratings with high spatial frequency has been investigated by Fuentes *et al* [124]. The photopolymer studied composed of AA as the polymerizable monomer, TEA as the radical generator, BMA as the crosslinker, YE as the sensitizer, and a binder of PVA. The high spatial resolution of the photopolymer material was demonstrated by recording reflection gratings with a spatial frequency of 5174 lines/mm. Three different compositions of recording material were studied, and the best results in terms of diffraction efficiency (9.1%) were obtained for the composition which included BMA.

A panchromatic acrylamide-based photopolymer for multicolour reflection holography was recently developed by Chakrapani Meka *et al* [125]. This photopolymer system consisted of acrylamide (monomer), N, N'-methylene-bisacrylamide (cross-linking monomer), PVA (binder) and triethanolamine (electron donor or coinitiator). The photopolymer was sensitized using methylene Blue (MB), erythrosine B (EB) and acriflavine (ACF) dyes to record at red-green-blue (RGB) wavelengths respectively. The maximum diffraction efficiency for the reflection gratings recorded using 633 nm, 532 nm and 473 nm wavelengths were 11.5% (144 mJ/cm^2), 6% (216 mJ/cm^2) and 1.6% (180 mJ/cm^2) respectively.

Kveton *et al* [126] reported the suitability of acrylamide-based photopolymer recording material for real-time holographic interferometry and have successfully acquired time average interferograms of vibrating piezoelectric elements with various vibration modes. Lu Hai *et al* [127] studied the holographic parameters and photobleaching kinetics of acrylamide based photopolymers with five different amine photoinitiators (triethanolamine (TEA), diethanolamine (DEA), ethanolamine (EA), triethylamine (TETN) and diethylamine (DETN)). The maximum values of DE, photobleaching coefficient and quantum yield followed the sequence, TEA> DEA> EA> TETN >DETN. Maximum DE was ~60% and sensitivity was 1.72 x10^{-3} cm^2/mJ.

An improvement in the spatial resolution of a red-sensitive PVA/acrylamide based photopolymer (from 1000 lines/mm to 3000 lines/mm) by employing a poly(vinyl alcohol) binder of low molecular-weight (9000) was recently reported by Zhu *et al* [128]. The photosensitivity of the photopolymer was increased about 5 times by increasing the ambient temperature during the holographic recording. The optimized photopolymer system exhibited high photosensitivity (8 mJ/cm^2), high spatial resolution (over 3000 lines/mm) and high diffraction efficiency (94%).

Besides the experimental works on the development and characterization of photopolymers, several theoretical models describing the mechanism of hologram formation and material behaviour are also reported. A brief review of the theoretical modelling of free-radical photopolymerization is presented by Gleeson *et al* [129].

1.5.2. Nanoparticle-photopolymer composites for holographic applications

For photopolymer systems to be practical for holographic data storage applications, they ought to produce large refractive index modulation and must have high dimensional stability as well [130]. But satisfying both of these requirements simultaneously is considered difficult in conventional all-organic photopolymers due to the limited refractive-index range of organic materials. Since inorganic materials possess a wide variety of refractive indices, the use of inorganic nanoparticles as an optically mobile component in photopolymer syrup offers the opportunity to obtain much larger refractive index change (Δn) compared to conventional all-organic photopolymers. Several research groups have demonstrated that the addition of solid inorganic nanoparticles to different photopolymer materials improves the holographic properties of the resulting nanocomposite. In photopolymer mterials, holographic recording is accompanied by light-induced mass transport of photopolymer components. A basic formulation for a photopolymerizable nanocomposite requires inclusion of nano-dopants with appreciably different refractive index than that of the host material. Redistribution of the nano-dopants during the holographic recording stage must also be achieved with significant increase in the light-induced refractive index modulation (fig. 1.3). The addition of nanoparticles contributes to rapid grating growth and noticeable reduction of polymerization shrinkage, yielding high recording sensitivity and dimensional stability. But significant scattering is a main drawback of nanocomposites.

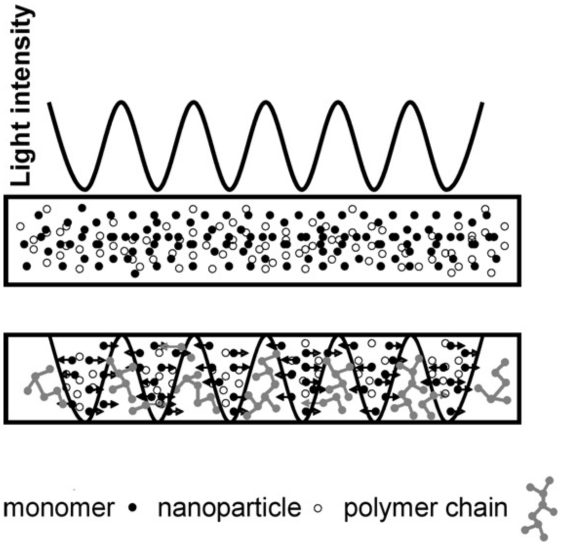

Fig. 1.3. The light-induced redistribution of photopolymer components

Nanoparticles dispersed in photopolymer can be assembled by light, providing the realization of multi-dimensionally structured materials, highly relevant for photonic and electronic applications. An outline of the photopolymer nanocomposites developed for holographic applications is presented here.

Vaia *et al* [131] introduced the idea of introducing inorganic nanoparticles having substantially higher (or lower) refractive index in photopolymer mixtures as a movable non-reactive component. The work on the incorporation of inorganic nanoparticles was further developed by several groups, particularly by Tomita *et al* [132-140]. Suzuki *et al* [132] reported the first demonstration of volume holographic recording in TiO_2 (titania) nanoparticle (average diameter of 15 nm) dispersed methacrylate photopolymers. The photopolymer showed refractive index modulation (Δn) as high as 5.1×10^{-3} and polymerization shrinkage suppression of approximately 69% was achieved at nanoparticle concentration of 15 vol%. Sanchez *et al* [136] also reported a similar TiO_2 nanoparticle dispersed photopolymer system. They employed TiO_2 nanoparticle having average diameter of 4 nm, which were dispersed in two kinds of acrylate monomers. Holographic recording was performed at 351 nm and Δn as large as 15.5×10^{-3} at 633 nm was obtained.

An improvement of holographic recording sensitivities in the green was observed by doping pyrromethene dye (PM 597) into SiO_2 nanoparticle-dispersed methacrylate photopolymer films [133]. Electron-probe microanalysis (EPMA) of a hologram recorded in a silica-nanoparticle dispersed photopolymer film was carried out. It was shown that the density distribution of the formed photopolymer is 180^0 phase shifted with respect to that of nanoparticles. The result showed evidence for the mutual diffusion of monomer molecules and silica nanoparticles in the film under holographic exposure.

Tomita *et al* [135] have reported the mass transfer of nanoparticles during holographic recording in nanoparticle dispersed photopolymers. It was demonstrated that holographic exposure causes nanoparticles to be redistributed from bright to dark regions, leading to a periodic assembly of nanoparticles and thereby to the formation of high-contrast holograms. The use of hyper branched polymers (HBPs) acting as mobile organic nanoparticles doped in methacrylate photopolymers for highly efficient volume holographic recording was also studied [140]. Two types of reduced HBPs having the average size of 10 nm were used. Diffraction efficiency near 100% using 532 nm and substantive polymerization-shrinkage suppression in this photopolymer system was demonstrated. The periodic assembly of HBPs under holographic exposure was observed. It was also confirmed that the grating formation mechanism was essentially the same as that of inorganic nanoparticle dispersed photopolymers.

Kim *et al* [138] demonstrated that the diffraction efficiency of photopolymers could be significantly enhanced by the interfacial interactions induced at the surface of inorganic nanoparticles. The photopolymer system consisted of poly(methyl methacrylate-co-methacrylic acid) as polymer matrix, acrylamide as monomer, triethanolamine as plasticizer and Irgacure 784 as an initiator. Hydrophilic silica (SiO_2) nanoparticles with size of 10-12 nm were introduced into this photopolymer system.

Suzuki *et al* [141] demonstrated volume holographic recording in ZrO_2 (zirconia) nanoparticle dispersed acrylate photopolymers. High contrast holograms with very low scattering loss were fabricated. High refractive index modulation of $5.3x10^{-3}$ was obtained at nanoparticle concentration of 15 vol%. The real-time measurement of the phase shift between the light interference pattern and a volume holographic grating recorded in nanoparticle dispersed photopolymers was carried out [142]. It was confirmed that phase shifts in nanoparticle dispersed photopolymers depend on the magnitude of the refractive index of nanoparticles relative to that of polymerized monomers. The surface of the ZrO_2 and TiO_2 nanoparticles was modified by *p*-dodecylbenzenesulfonic acid to render them highly compatible with organic monomer mixtures avoiding aggregation [139]. A high refractive index modulation amplitude of about 0.0165 was achieved in the composites containing 25 wt% of TiO_2 nanoparticles. Tomita *et al* [143] investigated thermal distortions of volume holograms recorded in (meth) acrylate photopolymers doped with SiO_2 or ZrO_2 nanoparticles. It was found that the incorporation of inorganic nanoparticles into photopolymer leads to the effective suppression of these thermal changes, thereby extending the range of operating temperatures for their use in photonic applications.

Nanocomposites containing functionalized acrylate monomers and Au nanoparticles (NPs) have been developed for an all-optical fabrication of periodic bulk structures by holographic photopolymerization [144]. The materials with 1.5 wt % Au nanoparticles showed high amplitude of the refractive index modulation of 0.0073. The redistribution of both nanoparticles and monomers provided efficient grating formation with spatial period of 0.5 - 4.5 μm.

The redistribution of colloidal zeolite Beta nanoparticles during holographic recording in an erythrosine B doped acrylamide-based photopolymers was reported by

Leite *et al* [145]. The fraction of nanoparticles redistributed as a result of the holographic recording was estimated to be 40%. The effect of the nanoparticles on the average refractive index of the nanocomposite layers was studied by UV-visible spectroscopy. It was also shown that mass transfer of MFI zeolite nanoparticles takes place during the recording of holographic gratings [146].

Lavinia Balan *et al* [147] have developed a process allowing in situ photochemically assisted synthesis of silver nanoparticles (NPs) in a polymerizable acrylic formulation and studied the photopolymerization of this formulation. This system was used to record holographic gratings. The holographic sensitivity and the diffraction efficiency were significantly improved in the presence of nanoparticles.

Photopolymerizable nanocomposites consisting of a water-soluble acrylamide-based photopolymer and colloidal zeolite nanoparticles of zeolite Beta and zeolite A were recently reported by Leite *et al* [148]. The interactions between the photopolymer components and zeolite nanoparticles in the photopolymerizable nanocomposites were characterized for the first time by ^{13}C nuclear magnetic resonance and visible spectroscopy. The nanocomposite containing zeolite Beta nanoparticles showed selective sensing behaviour towards toluene and this effect could be exploited for the fabrication of holographic sensors.

1.6. Objectives of the present study

Methylene blue sensitized poly(vinyl alcohol)-acrylamide photopolymer (MBPVA/AA) film which exhibited 70% diffraction efficiency for exposure of 120 mJ/cm^2 using 632.8 nm He-Ne laser was developed earlier by our research group [116]. But the efficiency of the gratings recorded in the film was found to be decreasing on storage. Since incorporation of metal ions was one of the recommended ways to improve the storage life, efforts were made to incorporate copper and chromium ions into the MBPVA/AA films [108, 116, 117]. Dichromated MBPVA/AA films showed 21% efficiency for 500 mJ/cm^2. The storage life could be improved on doping with ammonium dichromate. The diffraction efficiency was found to slowly increase to 40% by 3 months. It remained the same for months and then the efficiency gradually decreased and reached the initial efficiency of 20%. Copper doped films exhibited 30% efficiency at 600 mJ/cm^2 and stable efficiency could be maintained for years without any fixing technique. Although the storage life could be improved by copper and chromium doping, the efficiency and sensitivity was found to be low. It was also found that most of the metal ion doped holographic recording media required some type of fixing for achieving high diffraction efficiency, while those that required no post processing had poor sensitivity and diffraction efficiency [149-151]. For a photopolymer material to be useful for holographic applications, it should have good energy sensitivity, high diffraction efficiency, good storage life and should be free from fixing processes. In this context, the development of a potential metal ion doped photopolymer recording medium has great relevance. The main objectives of the present work were to fabricate metal ion doped photopolymer film with enhanced holographic properties and to investigate the suitability of the developed film for holographic data storage applications.

1.7. Conclusions

Various holographic applications are discussed with special emphasis to holographic data storage and holographic optical elements. Requirements of holographic media and available media are described. The relevance of photopolymer based recording media and a brief review on holographic photopolymers was also presented in this chapter.

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2

Materials and Methods

A brief description on the materials used for fabrication of the photopolymer films is presented here. Details of preparation of the photopolymer solution and fabrication of films are discussed. Gravity settling and spin coating techniques were used for film fabrication. Various experimental techniques adopted for characterizing the films are also described in this chapter.

2.1. Introduction

Photopolymer based holographic recording media generally consists of a photoinitiator (photosensitizer dye, electron donor), one or two monomers and an inert polymer matrix (host or binder) [1]. Other components are sometimes added to control a variety of properties such as pre-exposure shelf life and viscosity of recording medium. The various constituents of the photopolymer film are described in the following sections.

2.1.1. Binder Matrix

Poly(vinyl alcohol) (PVA) was used as the binder or the host matrix. PVA is one of the most interesting vinyl polymers. It is manufactured by the polymerization of vinyl acetate followed by partial hydrolysis. PVA has many optical uses which results from its lack of colour, clarity and high transmission in the near infrared and ultraviolet. Additional properties which account for its versatility are its hydrophilic character, easy dyeability and ability to be crosslinked. It can be plasticized internally or externally to modify its mechanical properties and can be bonded to other surfaces. The optical uses of PVA are concerned with the polarization and filtration of light, and with photography and relative imaging fields [2]. When dry, the low permeability of PVA to moisture and gases probably accounts for its stabilizing effect on substances such as dyes. Water is the most common solvent for poly(vinyl alcohol). Other solvents for

PVA are diethylene triamine and dimethylsulphoxide. The structure of PVA is shown in fig. 2.1. PVA with molecular weight 1, 25, 000 (SD fine) was used in the present study.

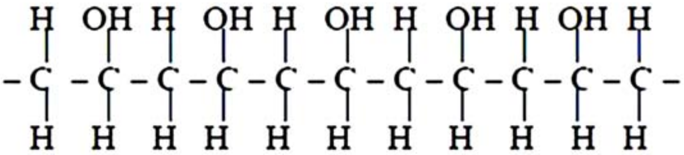

Fig. 2.1. Structure of PVA

2.1.2. Photoinitiator

The direct initiation of polymerization by light is very slow 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. In the present work, methylene blue (MB) was used as the photosensitizing dye and triethanolamine (TEA) was used as the electron donor. MB (molecular weight - 319.86) and TEA (molecular weight -149.18 g/mol) supplied by Merck were used. Chemically MB is 3, 7-bis (dimethyl amino) phenanthrolinium chloride ($C_{16}H_{18}ClN_3S$). MB is a basic dye of thiazine group and is also known as swiss blue and tetramethyl thionine [3]. The structure of MB is shown in fig. 2.2. At room temperature, it appears as a solid, odourless, dark green powder which yields a blue solution when dissolved in water. The absorption maxima of MB, if pure, reside at 668 nm and 609 nm.

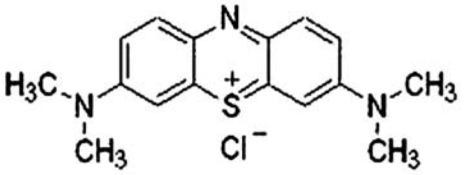

Fig. 2.2. Methylene Blue

Triethanolamine is an organic chemical compound which is both a tertiary amine and a tri-alcohol. Molecular formula of triethanolamine is $C_6H_{15}NO_3$. Fig. 2.3 shows the structure of triethanolamine. It acts as a weak base due to the lone pair of electrons on the nitrogen atom.

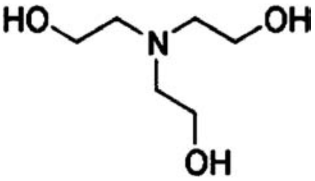

Fig. 2.3. Triethanolamine

2.1.3. Monomer

Monomers are incorporated into the polymerizable recording media to establish grating formation due to refractive index modulation [1]. Properties like recording sensitivity, dynamic range, image fidelity, shrinkage and environmental stability of the exposed hologram are also influenced by the monomer selection.

Acrylamide (AA) (C_3H_5NO) was used as the monomer. The structure of acrylamide is shown in fig. 2.4. It is a white odourless crystalline solid, soluble in water, ethanol, ether and chloroform. Acrylamide (molecular weight: 71.08) supplied by Merck was used in the present study.

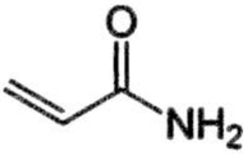

Fig. 2.4. Structure of acrylamide

2.1.4. Crosslinker

Metallic crosslinkers are incorporated to improve the storage life of the recording media since metal ions form ionic crosslinks with the PVA matrix, thereby inhibiting the diffusion of unreacted monomers and stabilizing the recorded grating. Silver nitrate ($AgNO_3$) was selected as the crosslinker. It is relatively stable to light and dissolves in numerous solvents including water. The structure of silver nitrate is shown in fig. 2.5. Silver nitrate supplied by Merck was used.

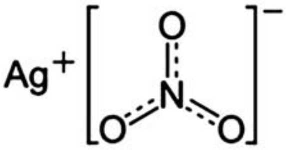

Fig. 2.5. Structure of $AgNO_3$

2.2. Preparation of photopolymer solution

The preparation of photopolymer solution involves the preparation of binder and dye solutions and the incorporation of dye, monomer, electron donor and crosslinker into the binder solution. The detailed procedure is as follows:

Step 1: Preparation of PVA solution

PVA solution was prepared by slowly adding solid PVA to distilled water taken in a dry beaker containing magnetic fish with continuous stirring using a magnetic stirrer at room temperature. The solution was kept under stirring for 24 hrs to get a uniform solution. The stirred PVA solution was then filtered to remove impurities. In the present study, 10% w/v and 15% w/v PVA solution was used.

Step 2: Preparation of MB solution

MB solution (6.25×10^{-3}M) was prepared by dissolving MB powder in distilled water taken in a beaker. The solution was stirred using a magnetic stirrer.

Step 3: Preparation of silver nitrate solution

Silver nitrate solution (1.17×10^{-2} M) was prepared by dissolving silver nitrate crystals in distilled water.

Step 4: Preparation of photopolymer solution

To the filtered PVA solution, the co-initiator triethanolamine and the monomer acrylamide were added. This mixture was stirred using magnetic stirrer for about 2 hrs to get a homogenous solution. To this solution taken in a beaker, methylene blue solution was added so as to get the desired dye concentration. The dye concentration was varied from 0.007 mM to 0.21 mM. The dye sensitized polymer solution was stirred for about two to three hours. To the dye sensitized polymer solution, silver nitrate solution was added and stirred again for 2 to 3 hrs. Concentration of silver nitrate was varied from 0.013 mM to 0.44 mM.

2.3. Fabrication of photopolymer film

The fabrication of the dye doped polymer films involves the deposition of the respective dye sensitized polymer solution on a suitable substrate and allowing the solvent to evaporate slowly. There are different techniques for coating the polymer film on the substrates. Some of them are dip coating, doctor blade method, gel casting, gravity settling, spin coating etc. In the present study, gravity settling and spin coating methods were used for film fabrication.

In gravity settling method, fixed volume of the photopolymer solution was deposited on thoroughly cleaned glass substrates placed on glass trays kept on a levelled surface. The substrates used for coating were soaked in freshly prepared chromic acid for 12 hrs, washed and cleaned in running water followed by distilled water and then dried using a hot plate. Glass substrates of dimensions 7.5 cm x 2.5 cm x 1.2 mm and 6 cm x 6 cm x 2 mm were used. The films were kept in dark for two to three days for evaporating water completely under normal laboratory conditions (temperature (T) = 28-30^0 C and relative humidity (RH) = 50-65 %.). Eventhough the edge effect due to surface tension could not be avoided, fairly uniform films were obtained after drying. The resulting thickness of the film was measured using stylus profiler (Dektak 6m).

Inorder to achieve uniform thickness over the entire film surface, films were fabricated by spin coating technique. Spin coating is an excellent method for preparing uniform films since it is possible to obtain a highly uniform film over a large area with a highly controllable and reproducible film thickness**.** The spin coating process involves the deposition of the solution onto a substrate and then spinning the substrate at a required speed. Spin coating unit SPIN 150 supplied by S. P. S Europe was used in the present study. A fixed volume of photopolymer solution was deposited on the centre of glass substrate (6 cm x 6 cm x 2 mm) kept over the vacuum chuck (bearing area (size) - 50 mm, vacuum diameter - 10 mm). Films were prepared by spinning the substrate at different speeds. Spin parameters like speed (rpm), quantity of solution and time were varied so as to fabricate films with good optical quality.

2.4. Thickness measurements

Stylus profiler (Dektak 6M) was used for thickness measurements. The stylus profiler is an advanced thin and thick film step height measurement tool capable of measuring step even below 1000 A^0 [4]. Dektak 6M stylus profiler contains mechanical and optical components for sample placement, sample viewing and scanning/measurement. A camera (field of view - 1.1 to 4.6 or 70x to 280x) is attached to the scan head, viewing the sample at 45^0 viewing angle. This instrument is used to profile the surface topography and waviness as well as measuring surface roughness in a sub nanometre range. The stylus is mechanically coupled to the core of an LVDT (linear variable differential transformer). As the stage moves the sample, the stylus rides over the sample surface. Surface variations cause the stylus to be translated vertically. Electrical signals corresponding to the stylus movement are produced as the core position of the LVDT changes. The LVDT scales an ac reference signal proportional to the position change, which in turn is conditioned and converted to a digital format through a high precision integrating analog to digital converter. The digitalized signals from a single scan are stored in computer memory for display [4]. A variable intensity white light LED was used for illuminating the sample. The scan length of the instrument ranges from 50 μm to 30 mm. Scan duration (time taken to complete a given scan) in conjunction with scan length, determines the horizontal resolution of a scan. The scan duration could be set from 3 to 200 s for a maximum of 60,000 data points (points along the scan path at which data are taken) per scan. The scan resolution indicates the distance between data points and it is automatically adjusted. The stylus force can be varied from 1 to 15 mg.

2.5. Components for holographic recording

Vibration isolation table, laser sources, electronic shutter, spatial frequency filters, beam splitters, front surface mirrors, film holders and optical power meter are required for the holographic characterization of the films. Good mechanical stability during holographic recording is a must for achieving optimum results. Hence the experiments were performed on a vibration isolation table supplied by TMC. He-Ne laser (632.8 nm, Melles Griot, 25 mW, CW, linearly polarized), Ar^+ laser (488 nm, 543 series, Melles Griot, 150 mW, CW, linearly polarized) and frequency-doubled Nd: YAG Laser (532 nm, Compass 215 M-20, Coherent, 20 mW, CW, linearly polarized) were used for various characterizations. Electronic shutter controller (Thorlabs SC10) was used to control the time of laser exposure. Thorlabs SC10 is designed to control the Thorlabs SH05 shutter. The power density was measured using optical power meter (Ophir PD200). The laser beam was expanded using spatial frequency filters. Spatial frequency filter consists of a short focal length converging lens and a pinhole. Diameter of the pinhole (D) is given by,

$$D = 1.22\lambda f / d \tag{2.1}$$

where, λ denotes the wavelength of the laser beam, f, the focal length of the lens and d, the diameter of the laser beam. The lens brings the laser beam to its focus and the pinhole is placed precisely at the focal point. The lens directs the light into the pinhole and only required parallel rays get through the hole. Other rays scattered from dirt or other defects will be blocked. The experimental setup is shown in fig. 2.6.

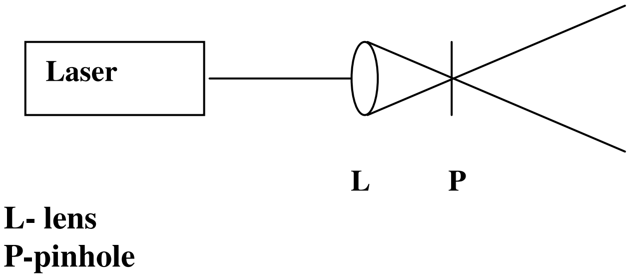

Fig. 2.6. Spatial frequency filter

To record gratings and holograms in the film using double beam interferometric technique, the laser beam has to be split into two beams. This is achieved using a beam splitter by which one reflected and one transmitted beam can be generated. In the present study, broadband non-polarizing beam splitter cube with reflectance to transmittance (R/T) ratio 50/50 was used.

2.6. Characterizations

Various characterization methods were carried out to exploit the potential of the developed film for holographic recording. The experimental setup used are described in the following sections.

2.6.1. Optical absorption studies

Optical absorption studies were carried out to determine the spectral sensitivity of the films. Absorption spectra of the films before and after laser exposure were recorded using UV-VIS-NIR spectrophotometer (JASCO V-570). When the photopolymer film is exposed to laser beam of suitable wavelength, the dye molecules in the exposed region absorbs photons and gets converted to the leucoform resulting in an absorbance modulation. Absorbance modulation was calculated as the difference between absorbance of the films before and after laser exposure.

2.6.2. Real-time transmittance measurements

Real-time transmittance measurements were carried out to determine the material's energetic sensitivity by exposing the films to suitable laser for a known time. The transmittance at regular intervals was monitored using an optical power meter. The experimental setup used is shown in fig. 2.7. Relative transmittance T/T_0 was determined, where T is the real-time transmittance of the doped films on laser exposure and T_0 is the transmittance of the undoped films.

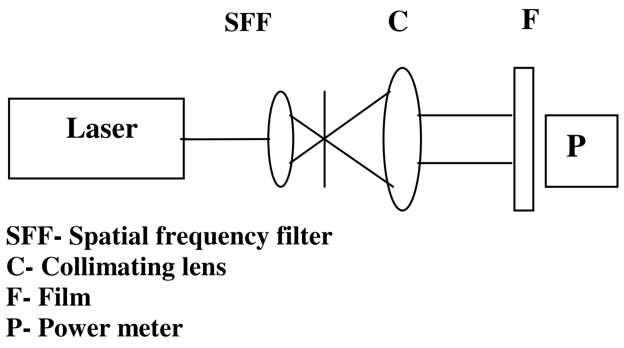

Fig. 2.7. Experimental setup for real-time transmittance measurements

As the material sensitivity increases, the transmittance increases at low exposures. This is because even at low exposure, the dye molecules are getting excited and get converted to the leucoform.

2.6.3. Recording of grating and diffraction efficiency measurements

Plane-wave transmission gratings were recorded in the films using standard holographic setup shown in fig. 2.8. The laser beam was split into two using a beam splitter cube with R/T ratio 50/50 and these beams were directed onto the film using 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 controller (Thorlabs SC10) in front of the laser.

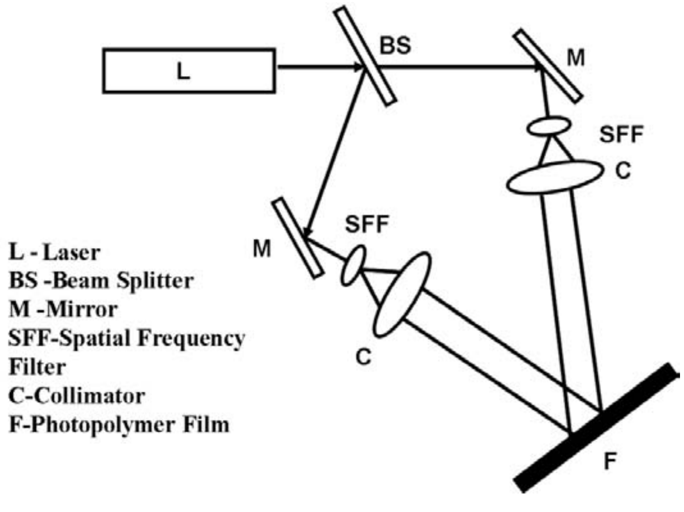

Fig. 2.8. Geometry for recording transmission grating

The diffraction efficiencies of the recorded gratings were determined by reconstructing the gratings using laser beam. The experimental setup used to measure DE is shown in fig. 2.9. The laser beam was allowed to fall on the grating recorded film kept at Bragg's angle. Neutral density (ND) filter was used to reduce the power of the reconstructing beam. Diffraction efficiency was calculated using the expression,

$$\mathrm{DE}\,(\%) = \frac{I_{\mathrm{d}}}{I_{\mathrm{i}}} \,\mathrm{x}\, 100 \qquad (2.2)$$

where, I_{d} is the intensity of the first-order diffracted beam and I_{i} is the incident probe beam intensity. The intensity was measured by an optical power meter (Ophir PD200). Incident probe beam intensity of $1\mu\mathrm{W/cm^2}$ was used for reconstructing the gratings.

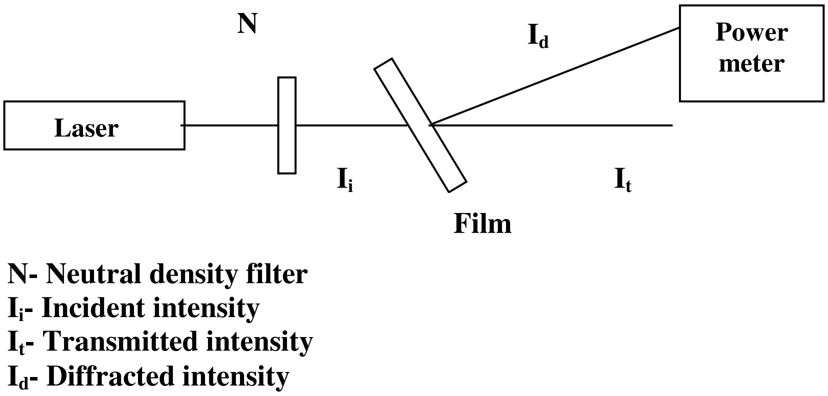

Fig. 2.9. Experimental setup for DE measurements

2.6.4. Holographic multiplexing studies

Volume holography allows multiple pages of data to be stored in the same volume of the recording material. Multiplexing is the method of manipulating the position of a hologram to fit multiple pages of data in the same volume. Multiplexing techniques such as angle multiplexing, peristrophic multiplexing, phase code multiplexing, shift multiplexing and wavelength multiplexing are commonly used [1, 5-13]. In the present study, angle and peristrophic multiplexing methods were adopted for recording multiple holographic gratings in the photopolymer film.

2.6.4.1. Angle Multiplexing

Angle multiplexing was performed by changing the interbeam angle between the recordings of individual gratings [1]. This results in the recording of gratings with different spatial resolutions in the same volume of the recording material The experimental setup is shown in fig. 2.10. The recorded gratings can be reconstructed by changing the read out laser beam angle. By varying the recording angle, a number of gratings could be recorded in the same volume of the photopolymer film.

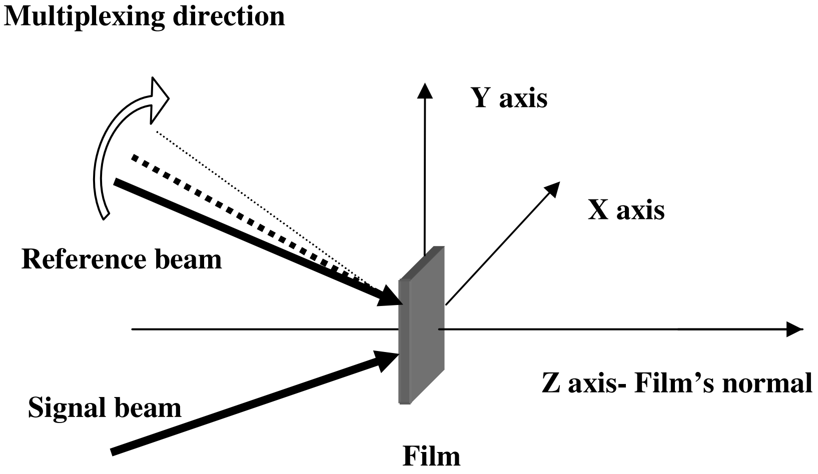

Fig. 2.10. Angle multiplexing

2.6.4.2. Peristrophic Multiplexing

Peristrophic (Greek word for Rotation) multiplexing was introduced as a solution to the bandwidth limited capacity problem [9]. Peristrophic multiplexing is a type of spatial multiplexing method. Spatial multiplexing is the method of changing the point of entry of source and reference beams into the recording medium. The reference wave is a plane wave and the addressing scheme is the relative rotational position of the storage medium and the axis of rotation is arbitrary [1]. There are mainly two types of peristrophic multiplexing techniques. They are rotation of the sample about an axis normal to the plane of incidence and the rotation of the sample about an axis in the plane of incidence. The rotation shifts the reconstructed image off the detector or the stored holograms becomes Bragg mismatched, allowing another hologram to be stored in the same location [9]. The process repeats until the maximum rotation angle of 180 degrees is reached. In this method, we have the freedom to fix the recording angle between the object and the reference beams. Certain problems arise when implementing this method of multiplexing. The rotational axis needs to be positioned in a way which does not interfere with the laser beams and bringing the recording media back to its original position for data retrieval should be very precise. To further increase the storage density, other multiplexing techniques can be combined with peristrophic multiplexing.

In the present study, peristrophic multiplexing techniques with rotation of sample normal to the recording media (Peristrophic method I) and along the plane of incidence to the recording media (Peristrophic method II) were employed to record multiple gratings in the film. For peristrophic multiplexing studies, the film was mounted on a rotational stage and was kept normal to the bisector of the recording beams. In peristrophic method I (fig. 2.11), the rotation of the film about an axis normal to the plane of incidence was performed. The film was rotated in a direction perpendicular to the plane of incidence after each recording. This rotation shifts the reconstructed image away from the detector, permitting a new grating to be recorded at the same location and viewed without interference. In the case of peristrophic method II (fig. 2.12), the rotation of the film was carried out about an axis along the plane of incidence. The film was rotated along the plane of incidence after each recording. 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. The multiplexed gratings were reconstructed using He-Ne laser (632.8 nm). Diffraction efficiency was calculated as the ratio of the intensity of the first-order diffracted beam to the incident probe beam intensity.

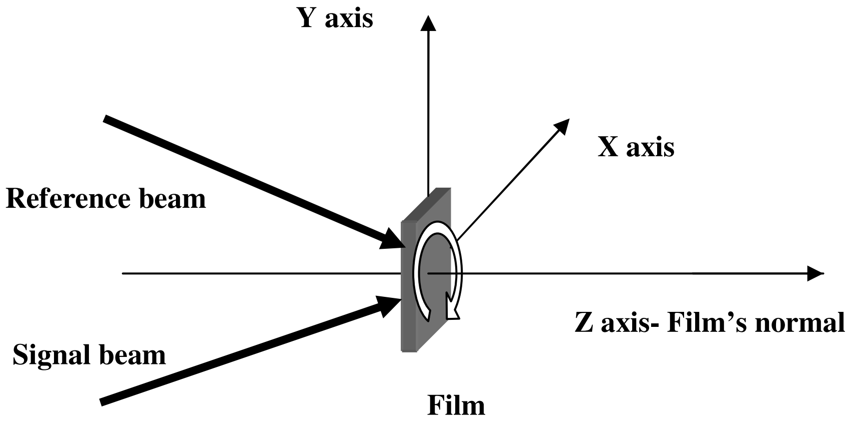

Fig. 2.11. Peristrophic method I

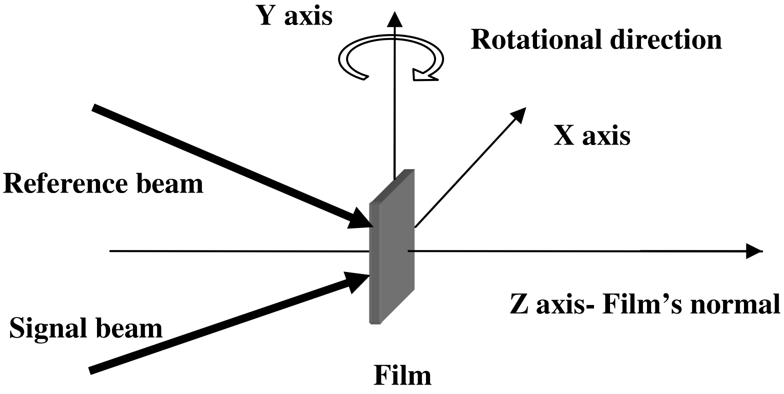

Fig. 2.12. Peristrophic Method II

2.6.5. Recording of transmission holograms

Transmission holograms were recorded in silver doped MBPVA/AA film using standard holographic recording setup shown in fig. 2.13.

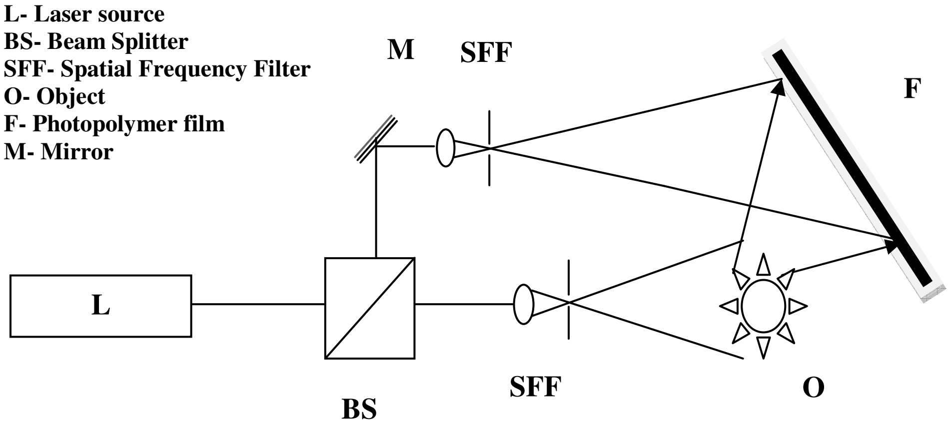

Fig. 2.13. Transmission hologram recording setup

In transmission type holograms, both the object and the reference beams interfere on the photographic plate from the same side [14]. One beam is reflected from the object and carries object information called object wave; the other one is a plane wave without information, which is called reference wave. The object wave can be regenerated from the hologram by illuminating it once again with the reference wave. The reconstructed image exhibits all the normal effects of perspective and depth of focus which the object wave would exhibit, if it were still there [14].

2.6.6. Recording of holographic data page in the film

Holographic data page was recorded in the film using the output from frequency doubled Nd: YAG laser (532 nm). Fig. 2.14 shows the schematic diagram of a 4*f* HDS system with the recording material placed at a distance of 'z' away from the back Fourier plane of the object lens; spatial light modulator (SLM) and lens (L_1, L_2) [15]. Defocusing the recording material away from the Fourier Transform (FT) plane is the simplest and the most commonly used technique to reduce the intensity variation in the hologram plane. When the recording material is placed away from the Fourier plane, one essentially records a Fresnel transform of the input data pattern. The laser beam was split into two beams and then spatially filtered, using a microscope objective lens and a pinhole. Liquid crystal programmable matrix modulator (LCD modulator SLM-M) from JENOPTIK JENA was incorporated in the path of one of the beams, inorder to spatially modulate the intensity of the light beam. The SLM-M provides a resolution of 832 x 624 pixels, each of which can be set to a relative transparency of 0 to 254. The pixel size was 27 μm x 27 μm and pixel pitch was 32 μm x 32 μm. Advanced TN-LCD technology permits a high area coverage corresponding to a maximum achievable transmission of ≥12%. The modulator consists of LCD with polarizer, analyzer and heat protecting filter, LCD controller, PC interface and power supply. The spatially modulated light beam is then directed to the recording medium by an objective lens. A reference beam mutually coherent with the image bearing beam is also incident on this medium. This creates a stationary interference pattern and is stored in the recording medium. Defocusing the recording material away from the Fourier plane distribute light more evenly over the aperture of the hologram leading to high fidelity recording.

In the reconstruction stage, the recording medium which contains the data page was illuminated with the reference beam at a low intensity so as not to deform the recorded data page since the material is sensitive at this wavelength. Another lens was placed behind the recording medium to do the inverse Fourier Transform of the diffracted beam onto the detector (CCD). Megapixel CMOS camera (PROSILICA EC1280) with high resolution (1280 x 1024), excellent image quality, high frame rates (24 fps at full resolution) and pixel size of 6.7 μm x 6.7 μm was used for capturing the reconstructed image.

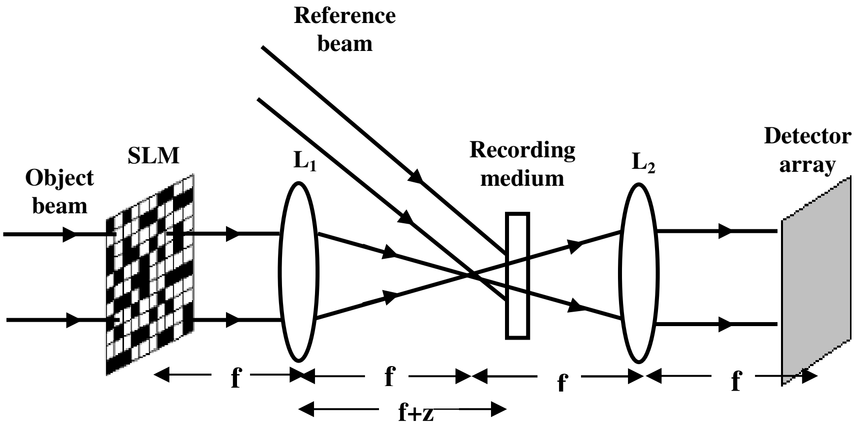

Fig. 2.14. Schematic diagram of a defocused 4*f HDS* system

2.7. Conclusions

The various constituents of the photopolymer film, methods employed for film fabrication and experimental techniques adopted for the holographic characterization of the films are described. The studies carried out to optimize the composition of silver doped photopolymer film using 632.8 nm He-Ne laser is presented in detail in the following chapter.

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3

Fabrication of silver doped MBPVA/AA photopolymer films and holographic characterization using He-Ne laser

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Preparation and characterization of silver doped MBPVA/AA photopolymer system is discussed in this chapter. Films were fabricated by gravity settling method and experiments were performed to optimize various parameters influencing the holographic performance of the films. From optical absorption studies, the films were found to have wide spectral sensitivity with peak absorption in the red region of the spectrum. Plane-wave transmission gratings were recorded in the film using 632.8 nm He-Ne laser. Silver doped films showed good energy sensitivity and gratings with diffraction efficiency above 75% could be recorded in the optimized film.

3.1. Introduction

Poly(vinyl alcohol)/acrylamide (PVA/AA) based photopolymer media with high diffraction efficiency (DE), high sensitivity and high resolution are versatile candidates for holographic recording [1-6]. The stability of gratings recorded in these films strongly depended on variations in laboratory conditions (relative humidity and temperature) and the diffraction efficiency decreased on storage [1, 5, 6]. Often, the recorded gratings were stabilized by post exposure 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 for improving their storage life, of which, incorporation of metal ions was reported to be the best, since metal ions formed ionic crosslinks with the PVA matrix, thereby inhibiting the diffusion of unreacted monomers and stabilizing the recorded grating [7-12]. Metal ion doped polymers have made significant impact in holography due to their great advantages like real-time image development, high photosensitivity and low cost.

Polymer matrices such as poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) have been doped with metallic crosslinkers like ammonium dichromate, cupric chloride and ferric chloride to realize various holographic recordings.

Dichromated PVA (DCPVA) films doped with dimethyl formamide (DMF) developed by Manivannan *et al* had peak real-time diffraction efficiency of approximately 65% at a high exposure of nearly 1000 mJ/cm^2 [8]. Fe^{+3} doped PVA holographic recording systems were developed by Changkakoti *et al* which exhibited a peak diffraction efficiency of 80% for a total beam power of 40 mW at exposure energy of 21 J/cm^2 [9]. Although high diffraction efficiency was achieved in these films, the energy sensitivity was very low. Sugegawa *et al* devised a photosensitive liquid system with a mixture of acrylamide and methylene-bisacrylamide coupled with ferric ion and tert-butyl hydroperoxide sensitive from 200 to 500 nm which exhibited a high diffraction efficiency of nearly 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 acrylamide films were developed by Beena *et al* which exhibited DE of 32% for exposure energy of 600 mJ/cm^2 [11]. Although no post processing was required for these films, the diffraction efficiency and the energy sensitivity was low. In the case of chromium doped films developed by Beena *et al*, eventhough 42% DE was achieved after self enhancement, it reduced to the initial value of 21% (exposure energy of 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 for achieving high diffraction efficiency, while those that required no post processing had poor sensitivity and diffraction efficiency. When a photopolymer is used for holographic data storage applications, the stability of the stored 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 methylene blue doped acrylamide containing photopolymer film. Silver was selected in the study because, silver halide emulsions with high sensitivity and high resolution is still the most widely used holographic recording medium. The holographic performance of the silver doped methylene blue sensitized PVA/AA photopolymer film was studied in detail and is discussed in the following sections.

3.2. Experimental

The photopolymer film comprised of poly(vinyl alcohol) (PVA) as binder matrix, acrylamide (AA) as monomer, methylene blue (MB) and triethanolamine (TEA) as photoinitiation system and silver nitrate ($AgNO_3$) as crosslinker. 10% PVA solution was prepared by dissolving solid PVA (10 gm) in 100 ml distilled water. AA crystals were dissolved in the PVA solution and the resulting solution was sensitized with MB and TEA. The mixture was stirred well to get a homogenous solution. To this solution, silver nitrate solution prepared in distilled water was added and stirred well. The films were fabricated by depositing fixed volume of the photopolymer solution on thoroughly cleaned glass substrates kept on levelled glass trays. The films were left in the dark for two to three days for complete drying under normal laboratory conditions. Films with good optical clarity were obtained after drying and the thickness was approximately 130 μm (measured using stylus profiler).

Initially films were prepared with 10% w/v PVA solution, MB concentration of 0.21 mM, TEA concentration of 0.04 M, AA concentration of 0.25 M and Ag^+ concentration of 0.39 mM. Spectral response of the prepared films was determined by recording the optical absorption spectrum using UV-VIS-NIR spectrophotometer. The films showed wide spectral sensitivity with peak absorption in the red region of the spectrum (fig. 3.1). The optical absorption spectrum was also recorded after exposing the film to He-Ne laser (5 mW/cm^2, 10 min).

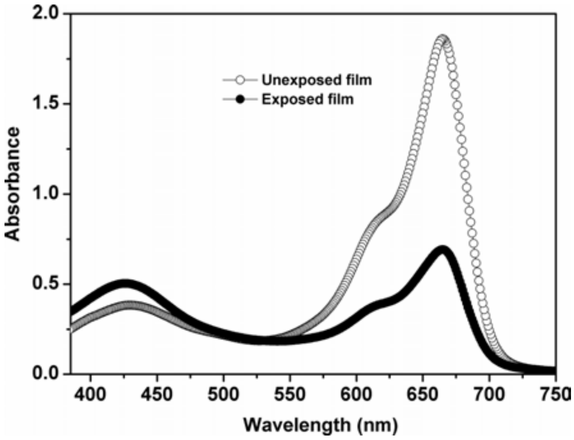

Fig. 3.1. Optical absorption spectra of unexposed and exposed films

For the unexposed film, the peak absorbance was 1.86 at 665 nm. After exposing to He-Ne laser, the peak absorbance (at 665 nm) was reduced to 0.692. When the films are exposed to laser beam, the dye molecule get excited and undergo intersystem crossing and get converted to the leucoform. Hence the absorbance decreased on laser exposure.

3.3. Recording of grating and DE measurements

Plane-wave transmission gratings were recorded in the film using He-Ne laser (fig. 2.8). The interbeam angle was 40^0 (spatial frequency~1100 lines/mm), total recording power was 4 mW and the beam intensity ratio was 1:1. The recording parameters were chosen in accordance with the earlier studies of our research group. Exposure energy was varied from 10 mJ/cm^2 to 150 mJ/cm^2. Gratings were reconstructed using He-Ne laser beam (1 μW/cm^2). The laser beam was allowed to fall on the grating kept at Bragg's angle. Diffraction efficiency was calculated as the ratio of the diffracted beam intensity to the incident intensity. Fig. 3.2 shows the variation of DE with exposure energy.

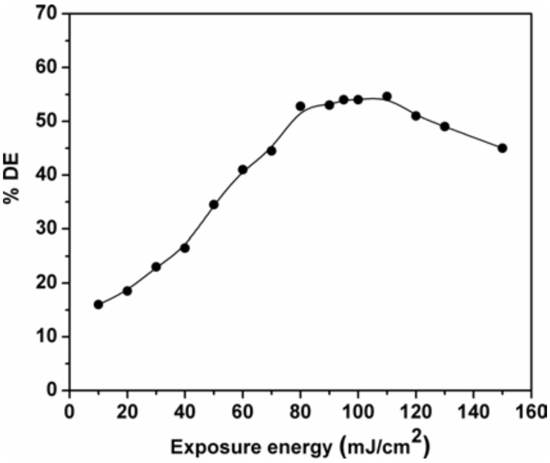

Fig. 3.2. Variation of DE with exposure energy

Peak efficiency of 55% was shown by grating recorded with exposure energy of 110 mJ/cm^2. It was observed that 50% DE could be obtained for gratings recorded with exposure energy 80 mJ/cm^2 to 150 mJ/cm^2. Diffraction efficiency was found to increase with the increase of exposure energy at first, reached its maximum value, and got saturated at a little bit low level. This may be because, with the increase of the exposure energy, the monomers getting polymerized increases, which in turn increases the refractive index (RI) modulation and DE [13]. But when the exposure energy increased further, the scattering light in the photopolymer induced by the surface deformation of the film gets large enough to result in the polymerization of the residual monomers in the dark region [14, 15]. This decreases the refractive index modulation in the sample and DE decreases a little and reached its saturation value when all the monomers in the sample got polymerized.

The refractive index modulation (Δn) was calculated using the measured DE (η) according to Kogelnik's theory [16],

$$\Delta n = \frac{\lambda \cos\theta \, \sin^{-1}\left(\sqrt{\eta}\right)}{\pi d} \tag{3.1}$$

where, λ is the reconstruction beam wavelength, d is the sample thickness and θ is the reading beam incidence angle. The variation of Δn with exposure energy is plotted in fig. 3.3.

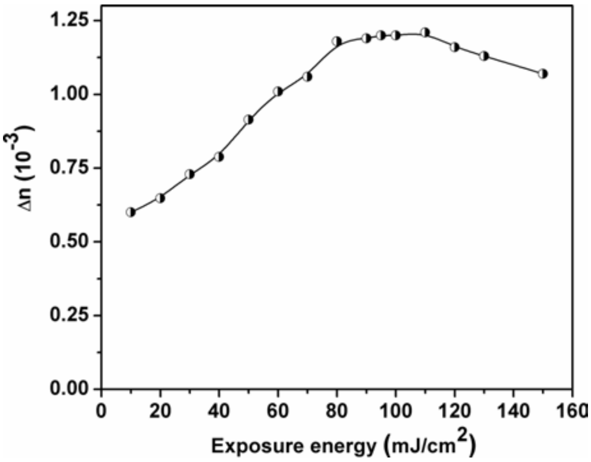

Fig. 3.3. RI modulation Vs exposure

The RI modulation was in the range 0.6 to 1.21×10^{-3}. The RI modulation increased on exposure, reached a peak value and decreased slightly on further increasing the exposure.

3.4. Mechanism of photopolymerization reaction

A possible mechanism of free radical polymerization [17-19] for the developed films is given in equations (3.2)-(3.13).When the photopolymer film is exposed to a monochromatic light of suitable wavelength, methylene blue (MB) absorbs photons and get promoted to the singlet excited state ($^1MB^*$) as can be seen in equation (3.2).

$$MB + h\nu \rightarrow {}^1MB^* \tag{3.2}$$

The singlet excited state can then undergo intersystem crossing into the more stable triplet state $^3MB^*$.

$$^1MB^* \rightarrow {}^3MB^* \tag{3.3}$$

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

$$^3MB^* + TEA \rightarrow MB^{\bullet-} + TEA^{\bullet+} \tag{3.4}$$

The TEA radical cation then loses a proton and becomes a free radical (Eq. (3.5)). The dye radical ($MB^{\bullet-}$) acquire a hydrogen molecule from the TEA free radical to form the leucoform (MBH) as shown in equations (3.6)-(3.7).

$$TEA^{\bullet+} \rightarrow TEA^{\bullet} + H^+ \tag{3.5}$$

$$MB^{\bullet-} + H^+ \rightarrow MBH^{\bullet+} \tag{3.6}$$

$$MBH^{\bullet+} + TEA \rightarrow MBH + TEA^{\bullet+} \tag{3.7}$$

The TEA free radical can initiate the polymerization reaction of acrylamide (AA) as described by equation (3.8).

$$TEA^{\bullet} + AA \rightarrow AA_1^{\bullet} \tag{3.8}$$

Equations (3.9)-(3.11) show the growth of the polymeric radical chain (propagation).

$$AA_1^{\bullet} + AA \rightarrow AA_2^{\bullet} \tag{3.9}$$

$$AA_2^{\bullet} + AA \rightarrow AA_3^{\bullet} \tag{3.10}$$

$$\cdot$$

$$\cdot$$

$$AA_i^{\bullet} + AA \rightarrow AA_{i+1}^{\bullet} \tag{3.11}$$

The termination processes [19] which give the polymeric chain (P_i) are shown in equations (3.12) - (3.13).

$$AA_k^{\bullet} + TEA^{\bullet} \rightarrow P_i \tag{3.12}$$

$$AA_k^{\bullet} + AA_l^{\bullet} \rightarrow P_i \tag{3.13}$$

3.5. Optimization of film constituents

Each constituent of the photopolymer film greatly influences its properties. The rate of conversion of monomer to polymer depends upon the concentrations of the sensitizer dye, monomer and initiator molecules, and the physical state of the recording medium [20]. Hence it is very important to optimize their concentrations inorder to ensure the best holographic performance of the material. Hence films were prepared by varying the concentrations of different constituents and gratings were recorded to determine the optimum concentration of each component required for achieving maximum diffraction efficiency.

3.5.1. Optimization of dye concentration

Inorder to optimize holographic materials for write once read many (WORM) memories, the storage capacity, the dynamic range and the energetic sensitivity of the material needs to be considered. The concentration of the sensitizer dye plays an important role in the final values of these factors. Hence the selection of proper dye concentration has great importance.

Inorder to optimize the concentration of the dye, films with different dye concentrations were prepared keeping the concentrations of other components constant (10% PVA, AA=0.25 M, TEA=0.04 M and Ag^+=0.39 mM). The dye concentration was varied from 0.007 mM to 0.21 mM. Plane-wave transmission holographic gratings were recorded in the films for interbeam angle of 40^0, total recording power of 4 mW and beam intensity ratio 1:1. The variation of DE with exposure energy for different dye concentrations is plotted in fig. 3.4. The change in efficiency with dye concentration for gratings recorded with exposure energy of 80 mJ/cm^2 is shown in fig. 3.5.

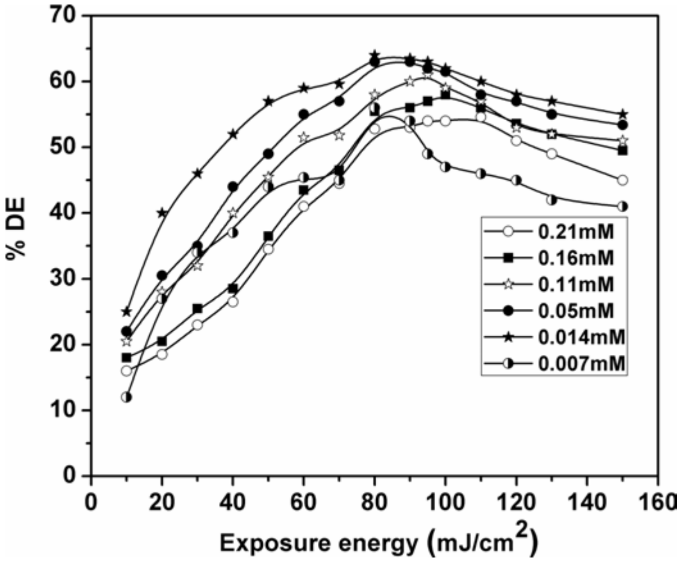

Fig. 3.4. Variation of DE with exposure energy

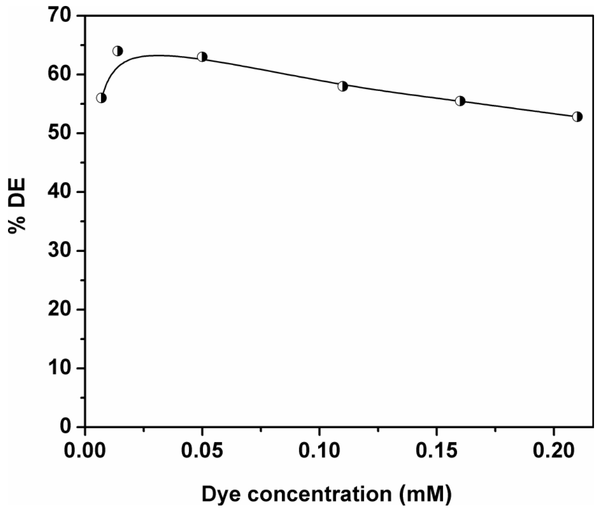

Fig. 3.5. Variation of DE with dye concentration for 80 mJ/cm^2

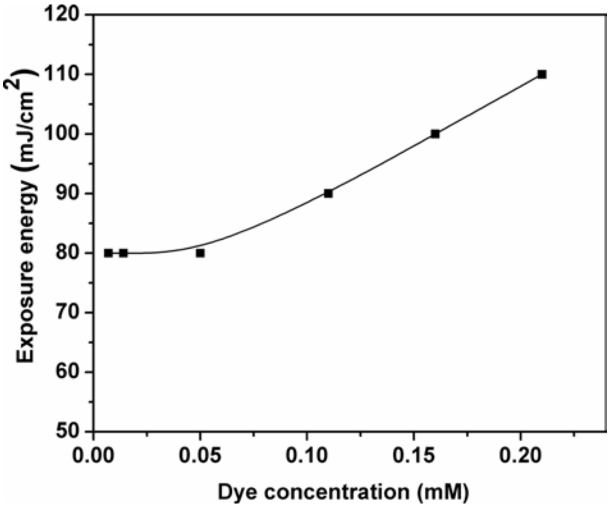

Fig. 3.6. Change in optimum exposure with dye concentration

From fig. 3.5, it can be seen that the efficiency first increased with increase in dye concentration and showed highest efficiency of 64% for 80 mJ/cm^2 (MB concentration: 0.014 mM). When the dye concentration is higher, more photons will be absorbed, thereby increasing the polymerization rate [14]. This increase in polymerization rate and absorption modulation leads to an increase in diffraction efficiency with dye concentration. For dye concentration above 0.014 mM, the efficiency was found to be decreasing. The decrease in efficiency may be due to the possible competitive polymerization mechanism that is produced when high dye concentrations are used [21]. At high dye concentrations, the dye forms dimeric state, which is involved in a polymerization termination reaction, resulting in a decrease in the overall rate of polymerization. After the consumption of the dye molecules participating in the polymerization, the dimeric molecules of the dye will decompose. The decomposition of the dimeric dye molecules influences the polymerization rate, leading to a decrease in the sensitivity of the material. Hence high exposure energy is required to achieve maximum efficiency for films with high dye concentration (fig 3.6). Since highest efficiency of 64% was shown by grating recorded in film with dye concentration of 0.014 mM, this dye concentration was selected for further studies.

3.5.2. Optimization of Ag^+ concentration

Inorder to optimize Ag^+ concentration, films were prepared with different Ag^+ concentrations. Keeping the concentrations of other constituents constant (10% PVA, MB=0.014 mM, AA=0.25 M, TEA= 0.04 M), Ag^+ concentration was varied from 0.013 mM to 0.44 mM. The films were named as Ag1, Ag2…Ag6, where the concentration of $AgNO_3$ in Ag1<Ag2……. <Ag6.

Optical absorption studies were carried out to study the effect of Ag^+ concentration on the spectral sensitivity of the films. Fig. 3.7 shows the optical absorption spectra of the films recorded before and after exposure to He-Ne laser (1mW/cm^2 for 4 min). From the optical absorption spectra, it can be seen that the absorption in the blue green region of the spectrum increases on increasing the concentration of Ag^+ in the film.

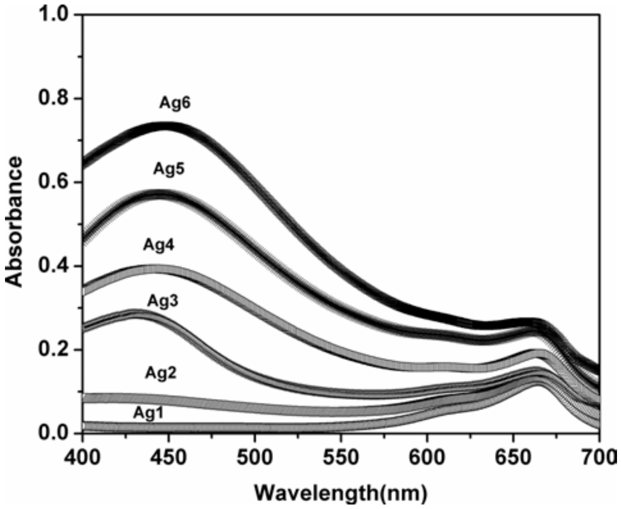

Fig. 3.7. Optical absorption spectra of unexposed films

Energetic sensitivity of the material was determined by monitoring the real-time transmittance (Section. 2.6.2). Films with different Ag^+ concentrations were exposed to He-Ne laser beam of irradiance 1 mW/cm^2 for four minutes and the transmitted power at regular intervals was monitored using an optical power meter (Ophir PD200). The relative transmittance T/T_0 was also determined, where T is the real-time transmittance of Ag^+ doped films and T_0 is the transmittance of the PVA/AA films without dye and $AgNO_3$. The relative transmittance of both undoped (films without $AgNO_3$) and Ag^+ doped films are plotted in fig. 3.8. As the material sensitivity increases, the transmittance increases at low exposures. This is because even at low exposure, the dye molecules (MB) were getting excited and got converted to the leucoform. The relative transmittance of undoped film was found to be higher than that of Ag^+ doped films. The threshold energy requirement was 0.5 mJ/cm^2. As the Ag^+ concentration increased, the relative transmittance decreased. 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.

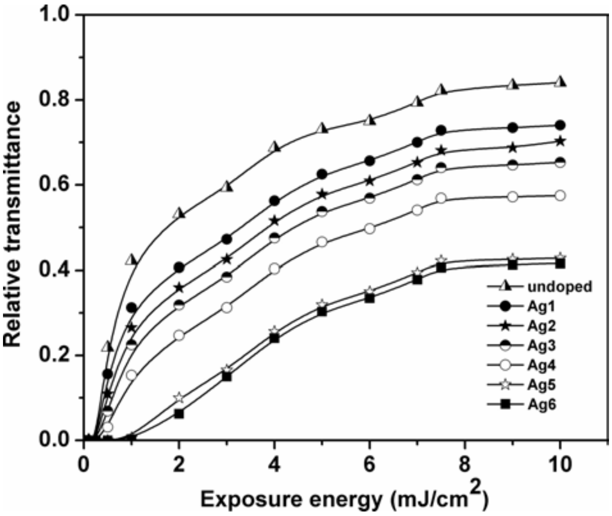

Fig. 3.8. Variation of relative transmittance with exposure energy

Plane-wave transmission gratings were recorded in the films using double beam holographic setup. The total recording beam power at the recording film was maintained as 4 mW and the exposure energy was varied from 10-150 mJ/cm^2 while recording gratings (spatial frequency~1100 lines/mm, beam intensity ratio-1:1). The diffraction efficiencies of the recorded gratings were determined by reconstructing the gratings using He-Ne laser beam (1 μW/cm^2). Fig. 3.9 shows the change in efficiency with exposure energy for various Ag$^+$ concentrations. It can be seen that gratings recorded at 80 mJ/cm^2 showed the maximum efficiency in the case of all the films. Fig. 3.10 depicts the variation of efficiency with Ag$^+$ concentration for 80 mJ/cm^2.

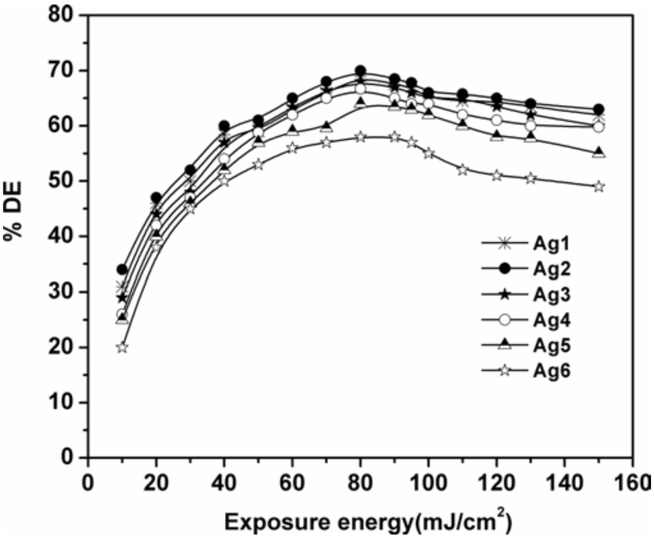

Fig. 3.9. Variation of DE with exposure energy for different Ag$^+$ concentrations

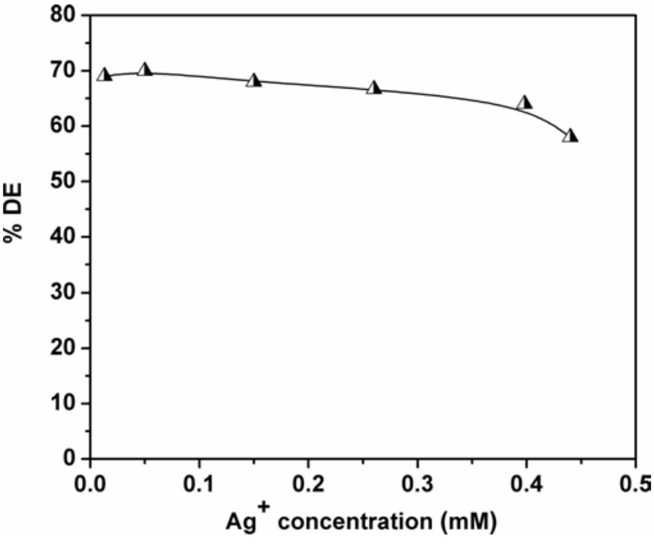

Fig. 3.10. Variation of DE with Ag$^+$ concentration for 80 mJ/cm^2

Peak efficiency of 70% was shown by the grating recorded in the film Ag2 (Ag$^+$ concentration: 0.05 mM). The diffraction efficiency 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 refractive index modulation and thus the diffraction efficiency. Grating formation in photopolymer film is mainly due to the refractive index (RI) modulation produced by the diffusion of unreacted monomers resulting from photopolymerization. The RI modulation was calculated using Kogelnik's coupled wave theory [16]. The change in RI modulation with Ag^+ concentration is plotted in fig. 3.11. Highest refractive index modulation of $1.44x10^{-3}$ was obtained for the film Ag2 which exhibited maximum efficiency.

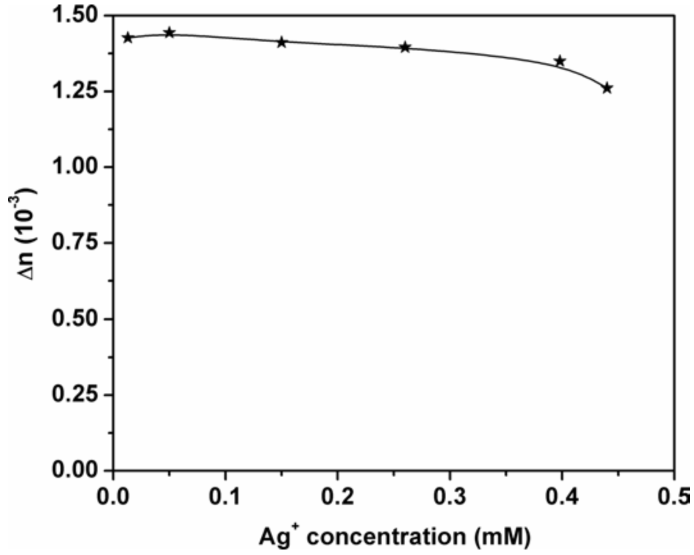

Fig. 3.11. Change in refractive index with Ag^+ concentration

3.5.3. Optimization of monomer concentration

The diffraction efficiency is affected by the thickness of the material and the index modulation. Hence, for a given thickness, it is necessary to adjust the monomer concentration to delimit the refractive index modulation. Keeping the concentration of other constituents constant (PVA=10% w/v, MB=0.014 mM, TEA=0.04 M and Ag^+=0.05 mM), films were fabricated by varying the acrylamide concentration from 0.1M to 1M. The films were coded as AA1, AA2.... AA6 and the concentration of acrylamide in the films varied as AA1<AA2...<AA6. Plane-wave transmission gratings were recorded in the films for 10 mJ/cm^2 to 150 mJ/cm^2 (beam intensity ratio: 1:1, recording power: 4 mW, spatial frequency~1100 lines/mm). The variation of efficiency with exposure energy for different acrylamide concentrations is plotted in fig. 3.12. The variation of exposure energy needed to achieve maximum diffraction efficiency is

plotted in fig. 3.13. The change in diffraction efficiency with acrylamide concentration for 80 mJ/cm^2 exposure energy is shown in fig. 3.14.

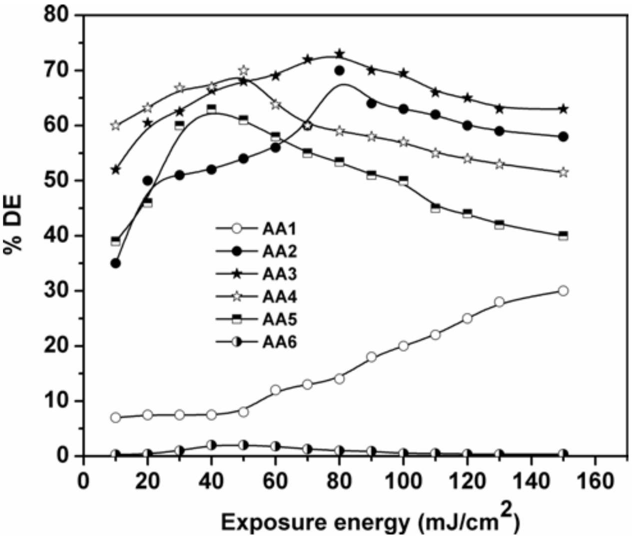

Fig. 3.12. Variation of DE with exposure energy

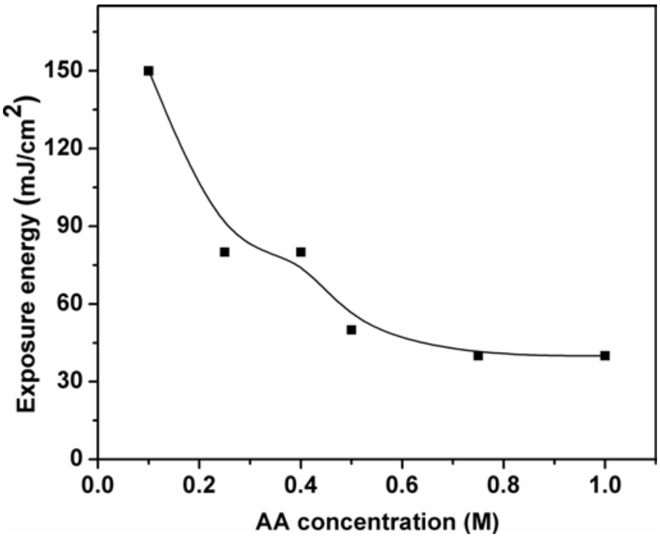

Fig. 3.13. Variation of exposure energy with AA concentration

As the acrylamide concentration is increased, diffraction efficiency also increased, reached a peak value and then decreased. This is because, as the monomer concentration increases, the number of monomers getting polymerized increases, which results in a large refractive index modulation and diffraction efficiency increases. Maximum diffraction efficiency of 73% was shown by the film AA3 with acrylamide concentration of 0.4 M. The energetic sensitivity was found to increase with increase in acrylamide concentration. Gratings recorded in films AA4 and AA5 exhibited peak diffraction efficiency for lower exposure energies. Film AA6 with acrylamide concentration of 1M had poor optical clarity and the recorded gratings had very low diffraction efficiencies. This may be because, at high concentrations, acrylamide precipitates on the surface of the film which gives rise to noise gratings [22]. Moreover, high concentration of acrylamide makes the film shrink greatly. It is impossible to increase the concentration of acrylamide indefinitely because of the limited compatibility and solubility of this monomer in the polymer solution. Acrylamide concentration of 0.4 M (AA3) which exhibited maximum diffraction efficiency was chosen as the optimum concentration.

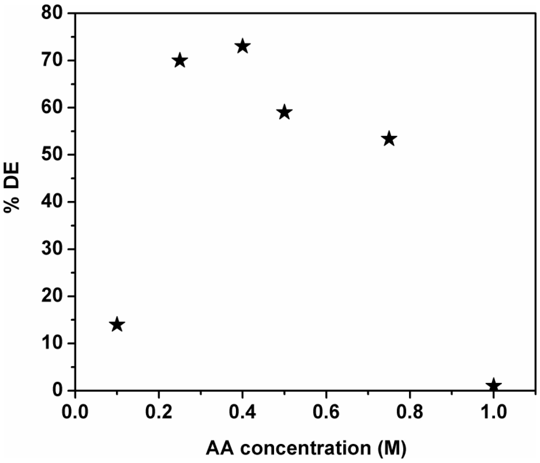

Fig. 3.14. Variation of DE with AA concentration for 80 mJ/cm^2

3.5.4. Optimization of electron donor concentration

The direct initiation of polymerization by light is very slow 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. Certain types of amines can provide electron to photoexcited MB via the transitory formation of a charge transfer complex, which is believed to be formed [23-25]. Amino groups can cause the faster photobleaching effect on MB, as they contain a nitrogen atom attached to atleast one alkyl group, the alkyl groups have an electron donating inductive effect on the nitrogen atom [22]. Of the different amines, triethanolamine has higher electron donating effect due to the lone pair of electrons on the oxygen atoms, and the electron shift is normally towards the nitrogen atom. Inorder to study the effect of electron donor (TEA) concentration on the diffraction efficiency of the recorded gratings, films were prepared by varying the concentration of triethanolamine from 0.02 M to 0.25 M. The concentration of other constituents were kept constant (PVA= 10% w/v, MB=0.014 mM, AA=0.4 M and Ag^+=0.05 mM). To determine the concentration of triethanolamine required to achieve maximum diffraction efficiency, transmission gratings were recorded in the films for exposure energies 10-150 mJ/cm^2 (beam intensity ratio-1:1, recording power: 4 mW, spatial frequency~1100 lines/mm). The variation of DE with exposure energy for different TEA concentrations is plotted in fig 3.15. Fig. 3.16 shows the change in optimum exposure energy with TEA concentration.

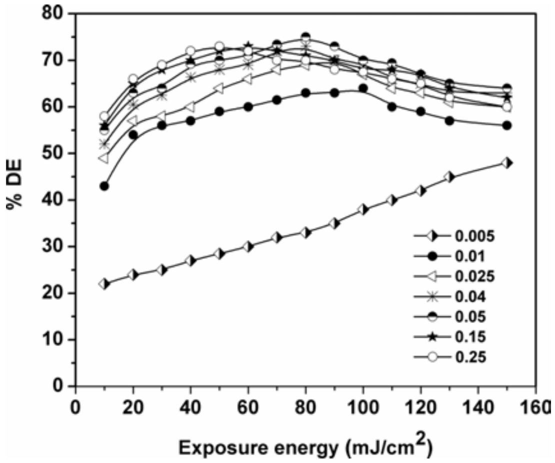

Fig. 3.15. Variation of DE with exposure energy

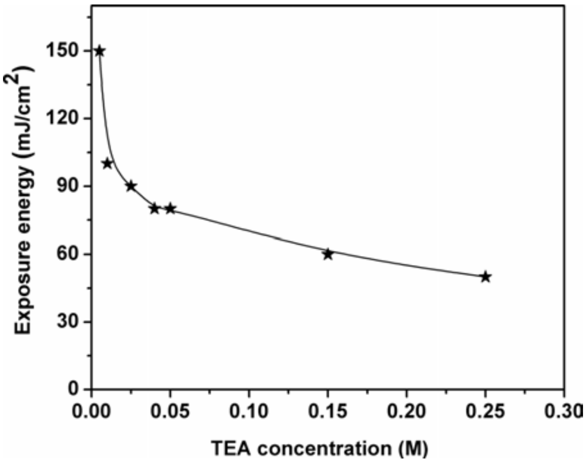

Fig. 3.16. Variation of exposure energy with TEA concentration

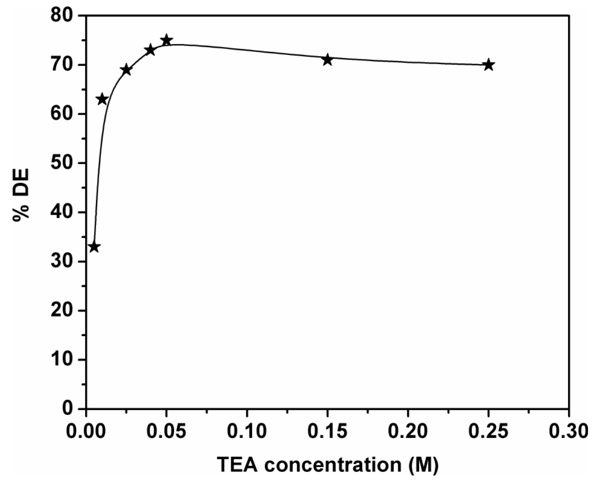

Fig. 3.17. Variation of DE with TEA concentration for 80 mJ/cm^2

Diffraction efficiency remained almost constant with the concentration of TEA, except for very low TEA concentration. But the energetic sensitivity was observed to be greatly influenced by TEA concentration. The sensitivity was higher for films with high TEA concentrations. However, films with high TEA concentrations took longer drying periods and were sticky as well. Maximum DE of 75% was exhibited by gratings recorded in films with 0.05M TEA for 80 mJ/cm^2 (fig. 3.17). Hence this concentration was chosen as the optimum. Table. 3. 1 shows the optimum film composition selected for further studies.

Table. 3.1. Optimized film composition

Constituent	**Concentration**
PVA	10% w/v
AA	0.4 M
TEA	0.05 M
MB	0.014 mM
$AgNO_3$	0.05 mM

3.6. Spatial frequency response

Depending on particular holographic application, large range of spatial frequencies can be recorded in photopolymer systems, from zero spatial frequency to more than 4000 lines/mm [26]. Inorder to determine the resolution of the developed material, gratings were recorded in the optimized film for different interbeam angles (7^0 to 140^0) maintaining the exposure energy as 80 mJ/cm^2. The spatial frequency of each grating was determined by Bragg's equation. Fig. 3.18 shows the spatial frequency response of the film.

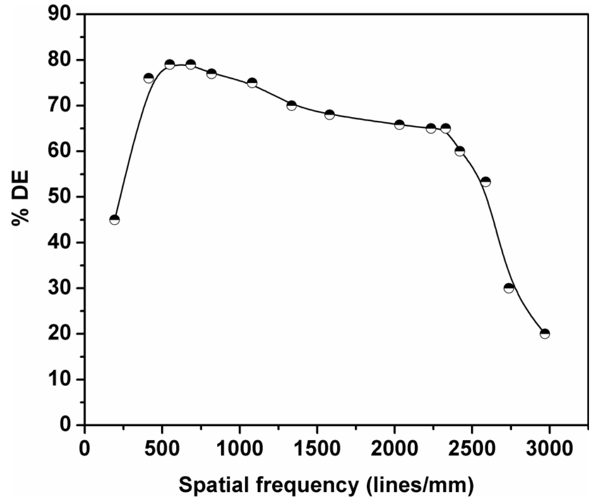

Fig. 3.18. Spatial frequency response

The peak diffraction efficiency was above 75% for gratings recorded with interbeam angles 15^0 to 40^0. This corresponds to spatial frequencies 410-1100 lines/mm. For higher spatial frequencies, DE was found to decrease gradually. For gratings with up to 2000 lines/mm, 65% DE could be obtained. It was seen that when high spatial frequencies are stored (over 2500 lines/mm), the diffraction efficiencies obtained are very low. The decrease in diffraction efficiency at high spatial frequency can be explained by using two approaches both referring to the non local response of the material [27]. This means that the response of the material at one point and time depends on what happens at other points and times in the medium. According to the non-local photopolymerization driven diffusion model (NPDD), the chains grow away from their initiation point resulting in "spreading" of the polymer. The model predicts that improvement at high spatial frequencies can be achieved if shorter polymer chains are created during the holographic recording [28, 29]. The two-way diffusion model [30, 31], which is also based on non-local response of the materials, assumes that short polymer chains diffuse away from the bright fringes thus reducing the refractive index modulation. Such processes could be responsible for the decrease in DE at high spatial frequencies at which the fringe spacing is small and there is enough time for some of the polymer chains to escape from the bright fringes before the medium becomes less permeable due to polymerization [27]. Grating recorded in the silver doped MBPVA/AA film with ~3000 lines/mm showed 20% DE, which is comparable with that of the reported materials.

3.7. Variation of beam ratio

To determine the effect of beam intensity ratio on the diffraction efficiency, gratings were recorded in the film for different intensity ratios of the recording beams maintaining the exposure energy as 80 mJ/cm^2 and spatial frequency of ~1100 lines/mm. The variation of diffraction efficiency with beam intensity ratio is plotted in fig. 3.19. Maximum diffraction efficiency was obtained for a beam intensity ratio of 1:1, where the fringe visibility is nearly unity [22]. The recording process in a photopolymer is greatly dependent on the difference between the polymerization rates at the bright and the dark regions which results in the diffusion of monomers. If the visibility is reduced, the potential of diffusion is reduced and therefore the diffraction efficiency is reduced.

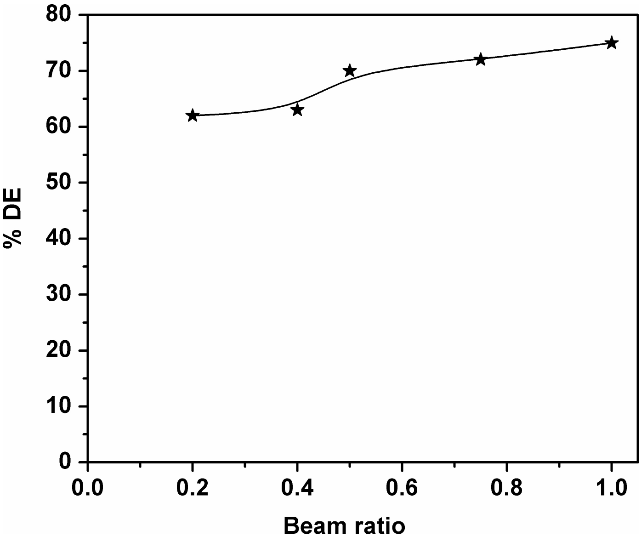

Fig. 3.19. DE versus beam intensity ratio

3.8. Storage life and pre- recorded shelf life of the film

The storage life gives an idea about how long the material can store the recorded grating or hologram. To find the storage life of the gratings recorded in the optimized film, diffraction efficiency measurements were carried out on successive days after recording. The recorded films were kept inside a dark box and no post exposure was applied. During the period of storage, the temperature of the storage place was in the range 28-30^0 C and relative humidity was 55-65%. The diffraction efficiency of the grating recorded with 1100 lines/mm was monitored on storage. Diffraction efficiency on storage is plotted in fig. 3.20. DE remained ≈70% for about three months after recording of the grating. After that, the efficiency reduced gradually and became 50% which remained stable for 6 months. Even after two years of recording, an efficiency of 40% could be attained, which is good enough for almost all of the holographic applications. As the weak ionic crosslinks formed between PVA and silver ions are labile, this results in further diffusion of the unreacted monomers from destructive to constructive interference region thereby decreasing the diffraction efficiency.

To determine the shelf life of the film, gratings were recorded in the optimized film each day after drying of the film. The films were stored in a dark box (temperature: 28-30^0 C, Relative humidity: 55-65%). It was found that gratings could be recorded in the film with DE of ≈70% for about three months. Gratings with 50% efficiency could be recorded for six months after preparation of the films. Grating recorded after 8 months showed 20% efficiency. It was observed that grating recorded in the ninth month had only a very low DE (~1%) and gratings could not be recorded in the film after ten months. DE on ageing of the film is shown in fig. 3.21. The decrease in DE on ageing of the film may be due to the polymerization of the monomer on ageing of the film [22].

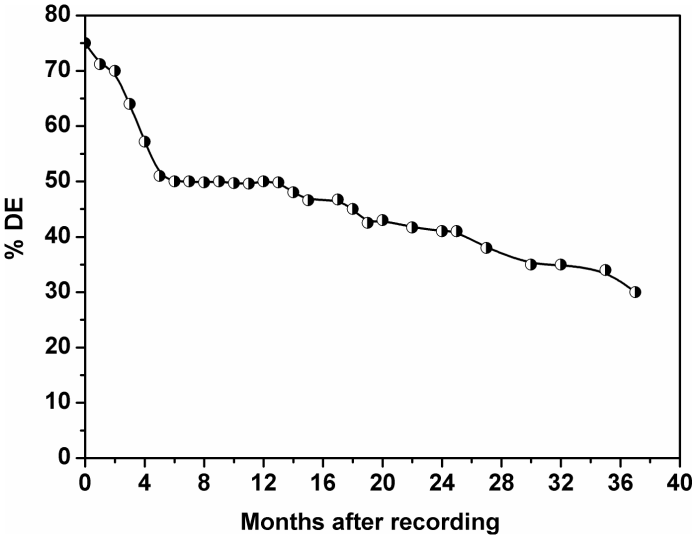

Fig. 3.20. DE on storage

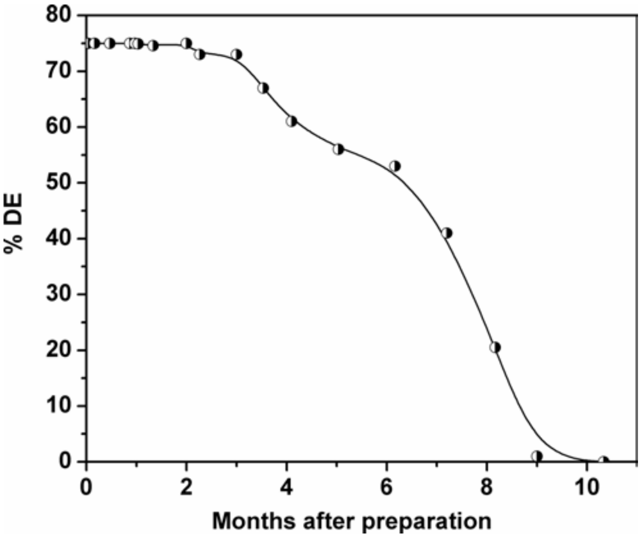

Fig. 3.21. DE on ageing of the film

3.9. Recording of transmission hologram

Volume transmission holograms were recorded in silver doped MBPVA/AA film using 632.8 nm He-Ne laser by the double beam method (Fig. 2.13). Photograph of a bright transmission hologram recorded with optimum exposure energy of 80 mJ/cm^2 is shown in fig. 3.22. The material has the great advantage of recording and reconstructing holograms in real-time.

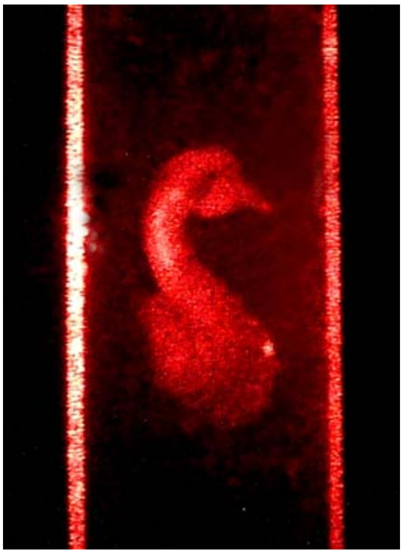

Fig. 3.22. Photograph of transmission hologram

3.10. Conclusions

Incorporation of silver ions into methylene blue sensitized poly (vinyl alcohol)/acrylamide photopolymer was observed to give better holographic performance compared to other metal ion doped photopolymer holographic recording media. Silver doped MBPVA/AA films were found to have good energy sensitivity and exhibited peak diffraction efficiency of above 75% for gratings with spatial frequencies of 410-1100 lines/mm and exposure energy of 80 mJ/cm^2. 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 three years with good diffraction efficiency. The importance of the material is that it is very cost effective and requires no post development. The feasibility of recording bright transmission holograms in the material is successfully demonstrated.

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4

Holographic characterization of silver doped MBPVA/AA films using Nd: YAG and Ar^+ lasers

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An investigation on the panchromaticity of silver doped methylene blue sensitized poly(vinyl alcohol)/acrylamide photopolymer system is presented in this chapter. Frequency doubled Nd: YAG (532 nm) and Ar^+ (488 nm) lasers were used for the characterization of the films. From studies using He-Ne laser (632.8 nm), it was observed that plane-wave transmission grating with high diffraction efficiency of 75% could be stored in the optimized film. From the present study, it was noted that transmission gratings with high diffraction efficiency could also be recorded using Ar^+ and Nd: YAG lasers thereby elucidating the possibility of using the silver doped MBPVA/AA film as a competent panchromatic recording medium.

4.1. Introduction

High-quality panchromatic holographic recording material with high diffraction efficiency, high photosensitivity, high spatial resolution and signal-to-noise ratio is one of the key factors for the successful recording of true colour holograms. Traditionally, the materials used for recording colour holograms have been silver halide emulsions, dichromated gelatin (DCG) and panchromatic photopolymers [1-10]. Commercial silver-halide materials like the Russian Sphere-S material and non-commercial materials such as the SilverCross emulsion are suitable for colour holography. Although the silver halide materials outperform the photopolymers in sensitivity in the visible and in the dynamic range, they have lower diffraction efficiency than the photopolymers and suffer from low signal-to-noise ratio due to increased light scattering in the blue spectral region. The panchromatic photopolymer material from DuPont is an alternative recording material for colour holograms [7, 9, 10]. The DuPont materials are less sensitive than the ultrafine-grain silver halide emulsions, but they have advantages of easy handling and dry processing. However, DuPont polymer materials are mainly used for DuPont's own production of holograms and only approved customers working in the field of optical security are able to obtain these materials. The photopolymer materials are in particular suitable for mass production of colour holograms. The future of colour holography is highly dependent on the availability of better panchromatic recording materials based on photopolymers. All these factors had resulted in an augmented interest for developing new panchromatic photopolymer materials. An overview on acrylamide-based panchromatic photopolymers is presented in the following section.

4.2. Acrylamide based panchromatic photopolymers

The self processing acrylamide based photopolymer systems sensitized by suitable dyes have attracted great deal of attention because of their high diffraction efficiency (DE) and low cost. Acrylamide based panchromatic photopolymers for transmission holographic recording have been developed by several research groups. Fimia *et al* have developed a liquid photopolymer system containing 1:1 mixture of 4, 5-diiodosuccinylfluorescein (2ISF), methylene blue (MB), three monomers (acrylamide (AA), N, N'- methylene bisacrylamide (BMA) and zinc acrylate) and sodium *p*-toluenesulphinate (*p*TS-Na) (co-initiator) which showed 15-20% for 15-60 mJ/cm^2 for transmission gratings recorded with He-Ne (633nm) and Ar$^+$ (514 nm) lasers [11]. Another acrylamide based photopolymer comprising of poly(vinyl alcohol) (PVA) as binder and ion pair isolated from rose bengal (RB) and MB as photoinitator system with response at 514 and 633 nm was developed by Mallavia *et al* [12]. This photopolymer system showed diffraction efficiencies of 65% at 30 mJ/cm^2 with He-Ne laser (633 nm) and 35% at 100 mJ/cm^2 with Ar$^+$ laser (514 nm), with a spatial resolution of 1000 lines/mm. The efficiency of the PVA acrylamide film containing RB-MB photoinitator system has been improved by the incorporation of BMA [13]. The efficiency obtained was nearly 80% for gratings recorded using He-Ne laser (632.8 nm), 60% for Ar$^+$ laser (514 nm) and 40% for gratings recorded using Ar$^+$ laser (488 nm). The exposure energy was nearly 120 mJ/cm^2 in all cases.

A panchromatic acrylamide-based photopolymer for multicolour reflection holography have been recently developed by Chakrapani Meka *et al* [14]. This photopolymer system consisted of acrylamide (monomer), N, N'-methylene-bisacrylamide (cross-linking monomer), PVA (binder) and triethanolamine (electron donor or coinitiator). The photopolymer was sensitized using methylene blue (MB), erythrosine B (EB) and acriflavine (ACF) dyes to record at red-green-blue (RGB) wavelengths respectively. The maximum diffraction efficiency for the reflection gratings recorded using 633 nm, 532 nm and 473 nm wavelengths were 11.5% (144 mJ/cm^2), 6% (216 mJ/cm^2) and 1.6% (180 mJ/cm^2) respectively.

Beena *et al* have studied the possibility of using acrylamide based photopolymer system with PVA binder, MB dye and triethanolamine (TEA) co-initiator as a panchromatic recording media [15]. This photopolymer film showed DE of 70% for transmission gratings recorded using 632.8 nm He-Ne (120 mJ/cm^2) and 532 nm Nd: YAG (250 mJ/cm^2) lasers, while the efficiency for grating recorded with 488 nm Ar$^+$ laser was ~50% (900 mJ/cm^2). In this case, high exposure energy was required for attaining maximum efficiency and the material had limited storage and shelf life due to the lack of a crosslinker in the system.

Silver doped photopolymer films developed by incorporating silver ions into the methylene blue sensitized poly(vinyl alcohol) acrylamide (MBPVA/AA) films exhibited high diffraction efficiency and good energetic sensitivity [16]. Transmission grating recorded in the optimized film using He-Ne laser (632.8 nm) exhibited diffraction efficiency of 75% for 80 mJ/cm^2 exposure energy. The silver doped MBPVA/AA film exhibited good storage and shelf life as well. This chapter presents the holographic characterization of silver doped MBPVA/AA films using Ar$^+$ (488 nm) and frequency doubled Nd: YAG (532 nm) lasers. Transmission holographic gratings were recorded in the films using Nd: YAG and Ar$^+$ lasers. Efforts were made to determine the concentration of silver nitrate required to achieve maximum diffraction efficiency. Transmission holograms were recorded in the films using the lasers.

4.3. Experimental

The photopolymer films were fabricated by gravity settling method. Spectral and energetic sensitivity of the films were determined by optical absorption and real-time transmittance studies. UV-VIS-NIR spectrophotometer (JASCO V-570) was used for recording the optical absorption spectra of the films. Ar$^+$ laser (488 nm, 543 series, Melles Griot, 180 mW, CW) and frequency-doubled Nd: YAG Laser (532 nm, Compass 215 M-20, Coherent, 20 mW, CW) were used for real-time transmittance studies, recording of transmission gratings, recording of holograms and for diffraction efficiency measurements.

4.4. Results and Discussions

4.4.1. Optical absorption and real-time transmittance studies

Optical absorption studies were carried out to determine the spectral response of the silver doped MBPVA/AA film prepared with optimum composition as given in table. 4.1.

Table. 4.1. Optimum film composition

Constituent	**Concentration**
PVA	10% w/v
AA	0.4 M
TEA	0.05 M
MB	0.014 mM
$AgNO_3$	0.05 mM

The optical absorption spectra of silver doped and undoped MBPVA/AA films are shown in fig. 4.1. The absorption spectra after exposing the films to laser (1mW/cm^2 for 4 min) were also recorded. From the graph, it can be seen that, eventhough the maximum absorption is in the red region (peak at 665 nm) for both undoped and silver doped MBPVA/AA films; silver doped films showed another absorption peak in the blue region (425 nm) as well. Even for 532 nm, there is a small absorption. The broad spectral sensitivity of the silver doped film indicates the possibility of using it as a panchromatic recording material.

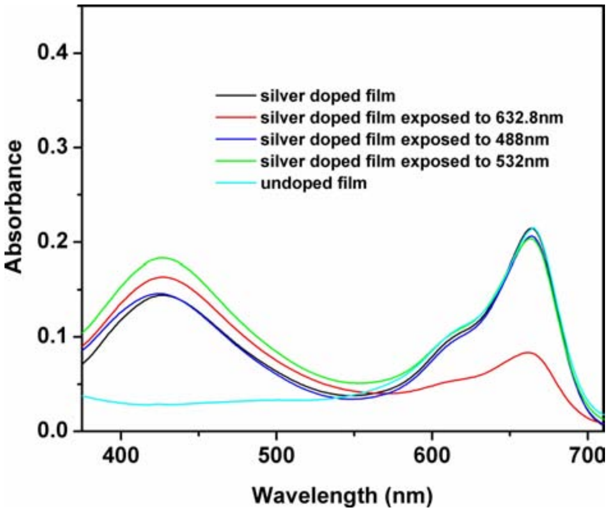

Fig. 4.1. Optical absorption spectra

Real-time transmittance on laser exposure was monitored by exposing the film to laser beam of irradiance 1 mW/cm^2 for four minutes and the transmitted power at regular intervals was monitored using an optical power meter. The relative transmittance T/T$_0$ was also determined, where T is the real-time transmittance of silver doped films and T$_0$ is the transmittance of the PVA/AA films without dye and silver nitrate. The variation of relative transmittance with exposure energy is shown in fig. 4.2.

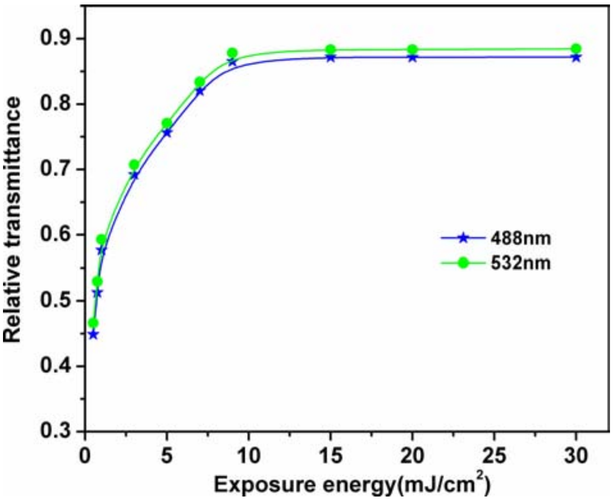

Fig. 4.2. Variation of relative transmittance on irradiation with Ar$^+$ and Nd: YAG lasers

As the material sensitivity increases, the transmittance increases at low exposures. This is because even at low exposure, the dye molecules (MB) were getting excited and got converted to the leucoform. It could be seen that the transmittance increases for low exposure energies, which indicates the good energetic sensitivity of the films. The threshold energy requirement was ~0.5 mJ/cm^2 for both wavelengths. From fig. 4.3, it can be seen that for higher exposure energies, the relative transmittance decreases in the case of irradiation with 488 nm Ar$^+$ and 532 nm Nd: YAG lasers. This may be due to scattering, since the shorter the exposure wavelength, the more is the scattering power, consistent with the classical scattering theory. On irradiation using longer wavelength (632.8 nm He-Ne laser), transmittance was found to be increasing with the increase in exposure time, and reached a final saturation value when all the dye molecules are bleached. This may be due to the less scattering in the sample at longer wavelength and as a result almost all the monomers in the dark region diffuse to the bright region to be polymerized which increases the refractive index modulation and the diffraction efficiency. But on exposure to shorter wavelengths (488 nm and 532 nm), the transmittance increased with exposure time at first (for a few seconds) due to the bleaching of the dye molecules. But with further increase in exposure time, scattering became more prominent. As a result, more monomers in the dark region got polymerized and these randomly distributed polymers acted as new scattering centres and enhanced the scattering and hence the transmittance was decreased [13].

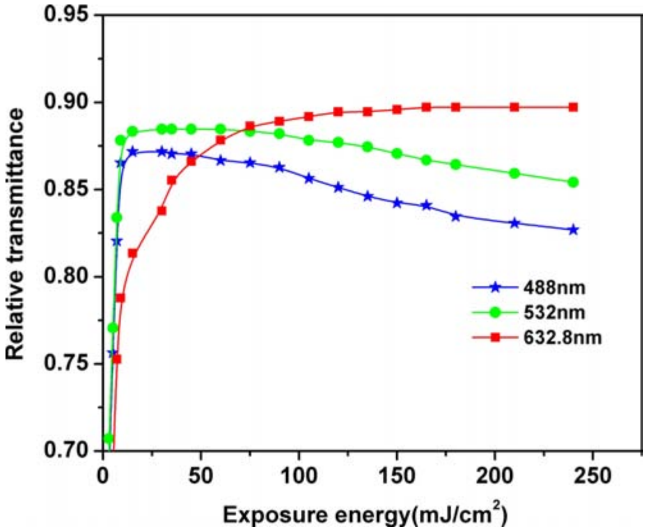

Fig. 4.3. Variation of relative transmittance on irradiation with Ar^+, Nd: YAG and He-Ne lasers

4.4.2. Recording of grating and DE measurements

Plane-wave transmission gratings were recorded in the films by double beam holographic recording setup (fig. 2.8). The exposure energy required for achieving maximum diffraction efficiency was determined by recording gratings for different exposure times keeping the total recording power as 4 mW. The interbeam angle was 40^0 and beam intensity ratio was 1:1. The spatial frequency with Nd: YAG laser was ~1285 lines/mm, while that with Ar^+ laser was ~1400 lines/mm. The gratings were reconstructed using the recording laser and diffraction efficiency was calculated as the ratio of the power of first order diffracted beam to the reading beam power. The exposure characteristic curves are shown in fig. 4.4. For both recording wavelengths, the diffraction efficiency increased with the increase of the exposure time at first, reached its maximum value and then gradually decreased. This is because with the increase in exposure time, more monomers will get polymerized which increases the refractive index (RI) modulation and hence the DE increases with exposure time [17]. But when the exposure time is further increased, the scattering light induced in the photopolymer (due to optical imperfection of the film) increases, which result in the polymerization of the residual monomers in the dark region thereby decreasing the RI modulation and consequently the diffraction efficiency decreases. Efficiency reaches its saturation value when all the monomers are polymerized. Maximum efficiency achieved with 488 nm was 57% for 125 mJ/cm^2, while with 532 nm, the peak efficiency was 65% for exposure of 100 mJ/cm^2.

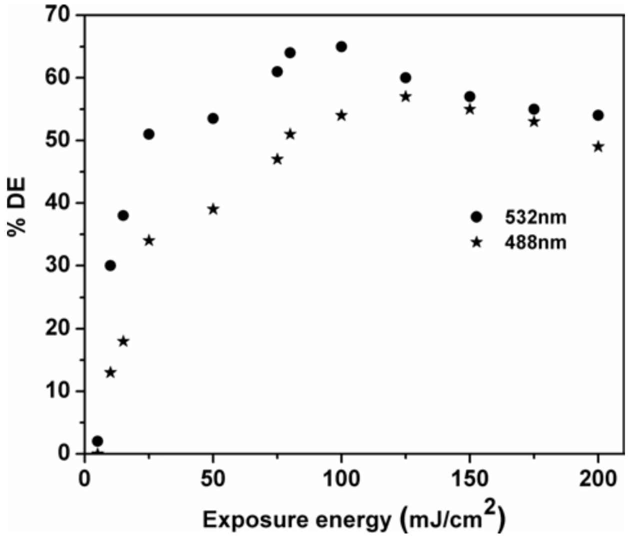

Fig. 4.4. Change in DE with exposure energy

Inorder to study the effect of total recording power on the diffraction efficiency, gratings were recorded by varying the power at the recording position. The exposure energy was maintained at the optimum value (125 mJ/cm^2 for 488 nm and 100 mJ/cm^2 for 532 nm) throughout the recording process. Fig. 4.5 shows the variation of diffraction efficiency with the recording power. For recording power in the 2.5-5 mW range, efficiency above 60% could be obtained with 532 nm, while the efficiency was above 55% for gratings recorded using 488 nm Ar$^+$ laser. There was not much variation in efficiencies while the recording power was in the range 2.5 to 4 mW. For both recording wavelengths, maximum DE was achieved when the recording power was 3 mW. For this recording power, the peak diffraction efficiency was 67% for 532 nm and 60% for 488 nm. The variation of diffraction efficiency with exposure energy for gratings recorded with 3 mW/cm^2 is shown in fig. 4.6. It was observed that even for an exposure of 25 mJ/cm^2, DE above 50% could be obtained with 532 nm, while the DE was nearly 40% for grating recorded with 488 nm Ar$^+$ laser.

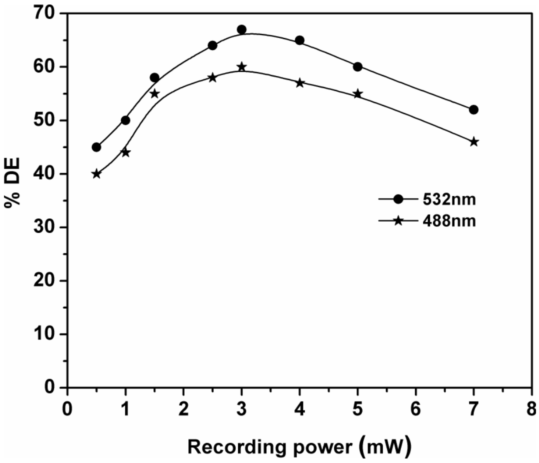

Fig. 4.5. Change in DE with total recording power

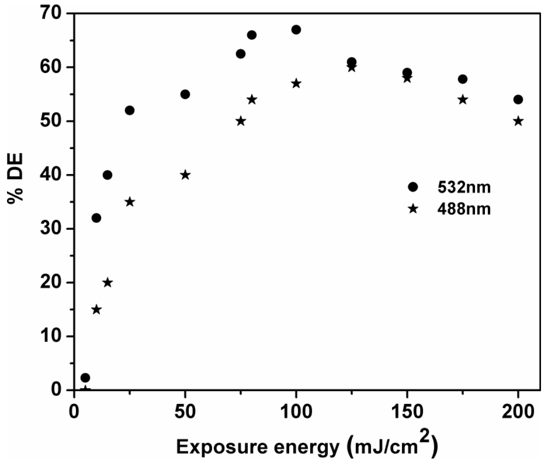

Fig. 4.6. DE variation with exposure energy

The refractive index modulation (Δn) was calculated using the measured diffraction efficiency (η) according to Kogelnik's theory [18],

$$\Delta n = \frac{\lambda \cos\theta \ \sin^{-1}\left(\sqrt{\eta}\right)}{\pi d} \tag{4.1}$$

where, λ is the reconstruction beam wavelength, d is the sample thickness and θ is the reading beam incidence angle. The variation of Δn with exposure energy is plotted in fig. 4.7. Maximum refractive index modulation was 1.17x10^{-3} for grating recorded with Nd: YAG laser (100 mJ/cm^2), while with Ar$^+$ laser, Δn was nearly 1x10^{-3} for grating recorded for 125 mJ/cm^2. The refractive index modulation increased on exposure, reached a peak value and decreased slightly on further increasing the exposure.

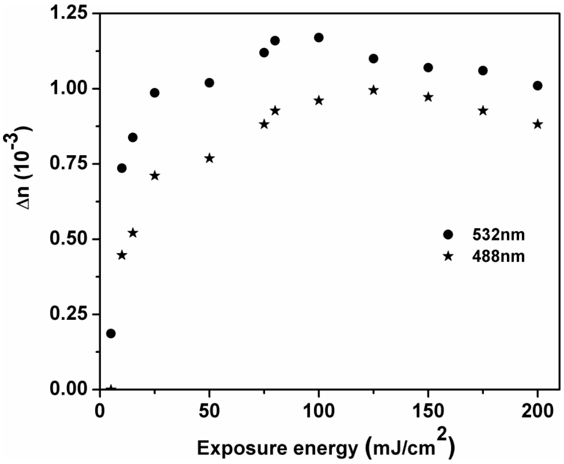

Fig. 4.7. Change in RI with exposure energy

4.5. Optimization of Ag$^+$ concentration

Inorder to study the variation of DE with Ag$^+$ concentration, films with different Ag$^+$ concentrations (0.023 mM - 0.38 mM) were prepared and transmission gratings were recorded in the films using 488 nm and 532 nm lasers. The total recording power was maintained as 3 mW and the interbeam angle was 40^0. The variation of efficiency with Ag$^+$ concentration for gratings recorded using 488 nm (exposure energy: 125 mJ/cm^2) and 532 nm (exposure energy: 100 mJ/cm^2) is shown in fig. 4.8.

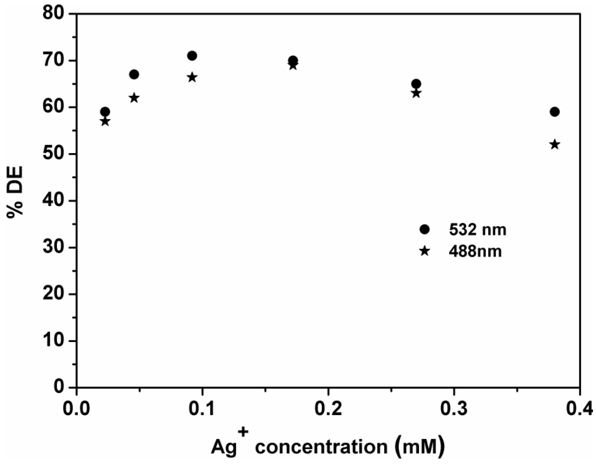

Fig. 4.8. Variation of efficiency with Ag$^+$ concentration

DE of 71% could be obtained for grating recorded using 532 nm for film with Ag^+ concentration of 0.092 mM. The maximum diffraction efficiency was 70% for grating recorded using 488 nm in film with Ag^+ concentration of 0.172 mM. Films were prepared with these optimum Ag^+ concentrations for carrying out further studies.

4.6. Spatial frequency response

The spatial resolution of the material was determined by recording transmission gratings for various interbeam angles. The interbeam angles were varied from 15^0 to 100^0 and spatial frequencies corresponding to each interbeam angle were calculated using Bragg's equation. The exposure energy was maintained at the optimum value (125 mJ/cm^2 for 488 nm and 100 mJ/cm^2 for 532 nm) throughout the recording. Fig. 4.9 depicts the spatial frequency response of the material. From the figure, it can be seen that recording with 488 nm Ar^+ laser had resulted in a diffraction efficiency > 60% for gratings with 1000-1400 lines/mm, while the diffraction efficiency was nearly 70% for gratings with 970-1300 lines/mm recorded using Nd: YAG laser.

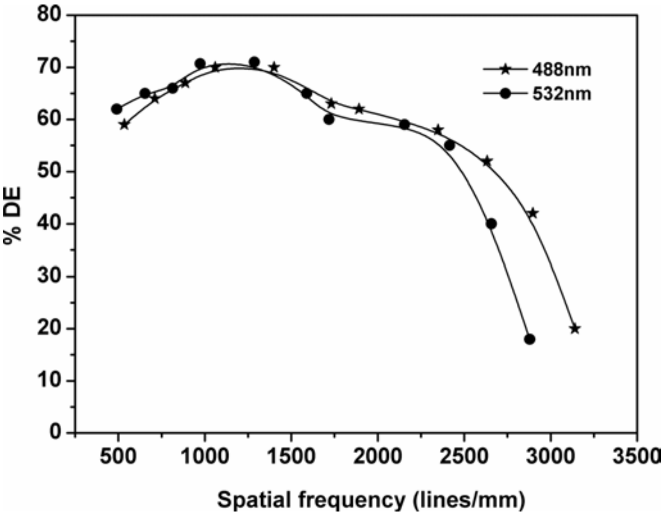

Fig. 4.9. Spatial frequency response

In both cases, more than 50% efficiency could be obtained for gratings with 2000 lines/mm. For still high resolution, the diffraction efficiency was found to be decreased. At higher spatial frequencies, the fringe spacing is very small. This results in the diffusion of short chain polymer molecules from the exposed to the unexposed regions, thereby reducing the refractive index modulation and the diffraction efficiency

[19, 20]. From the present study, diffraction efficiency of nearly 20% could be obtained even for gratings with 3000 lines/mm. This attests the good spatial resolution of the developed films.

4.7. Recording of transmission holograms

Transmission holograms were recorded in the optimized film using Nd: YAG and Ar$^+$ lasers. Standard transmission holographic recording setup (fig. 2.13) was used for recording holograms. Photographs of bright transmission holograms recorded with optimum exposure energies (125 mJ/cm^2 for 488 nm and 100 mJ/cm^2 for 532 nm) are shown in fig. 4.10 and 4.11. The developed photopolymer system has the great advantage of recording and reconstructing holograms in real-time.

Fig. 4.10. Hologram recorded with Nd: YAG laser

Fig. 4.11. Hologram recorded with Ar $^+$ laser

4.8. Conclusions

The feasibility of using the silver doped photopolymer film as a panchromatic material is demonstrated. The material is capable of recording holographic transmission grating with high diffraction efficiency using He-Ne (632.8 nm), Ar$^+$ (488 nm) and Nd-YAG (532 nm) lasers. The developed panchromatic photopolymer system is excellent on account of its wide spectral sensitivity, high diffraction efficiency, good energy sensitivity, high resolution, cost effectiveness, ease of fabrication and real-time imaging capabilities. The film is expected to have important applications in the fields of true-colour display holography, holographic storage, and holographic optical elements.

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5

Studies on Holographic Multiplexing

Angle and peristrophic multiplexing techniques were employed for recording multiple holographic transmission gratings in the same volume of silver doped MBPVA/AA photopolymer film. He-Ne laser with emission at 632.8 nm was used for recording gratings by constant and variable exposure scheduling methods. Diffraction efficiency (DE) and M number (M/#) obtained from constant and variable exposure scheduling methods were compared inorder to determine which method enabled the recording of maximum number of gratings with better homogenization of diffraction efficiencies.

5.1. Introduction

Storage requirements all over the world are mounting day by day making data storage one of the biggest challenges in the expanding multimedia market. Holographic data storage (HDS) with high storage density, fast data transfer rate and short random access time is envisioned as one of the promising technologies which can efficiently meet this challenge. In the past few years, researchers have demonstrated experimentally data storage density as high as 500 Gbits/sq. in [1] and sustained optical data transfer rate as high as 10 Gbits/s [2] separately in different optical systems. These potentialities have been achieved through the page-oriented nature of the systems and also through the application of different multiplexing techniques. Developing suitable recording media with large dynamic range is critical in achieving a practical HDS system and research is now focused on developing optimum holographic recording medium [3]. Dynamic range is the number of holograms with a diffraction efficiency of 100% which can be stored in a material with a specific thickness. It is the storage capacity of a holographic recording material and is characterized by the parameter, M number (M/#). Metal ion doped photopolymers with excellent holographic characteristics such as high refractive index modulation, large dynamic range (M/#), high diffraction efficiency, good light sensitivity, real-time image development, high optical quality and low cost are potential candidates for recording write-once-read-many (WORM) type holographic memories [4-10]. To store numerous pages of data holographically, various multiplexing techniques such as angle, peristrophic (rotational), shift and wavelength multiplexing are commonly used [11-20].

This chapter presents the studies carried out to check the capability of silver doped MBPVA/AA photopolymer film for holographic data storage applications. Holographic transmission gratings were stored in the same volume of the photopolymer film by angle and peristrophic multiplexing methods. Angle multiplexing was performed by changing the interbeam angle between the interfering beams during the recording of gratings. This results in the recording of gratings with different spatial resolutions in the same volume of the recording material. Peristrophic multiplexing makes it possible to multiplex many holograms in thin films with same spatial resolution. In this technique, after a hologram is recorded, the recording material is rotated around a certain rotational axis so as to record another hologram [16, 17]. Peristrophic multiplexing has the added advantage that it can be combined with other multiplexing methods to increase the storage density of holographic storage systems [11, 20]. Inorder to fully exploit the refractive index modulation of the recording material, it is essential to record as many holograms as possible in the same volume of the material. When a large number of holograms are to be recorded, their maximum diffraction efficiency should be as constant as possible inorder to make an efficient use of the available dynamic range [11, 20]. A brief overview on angle and peristrophic multiplexing studies in photopolymer systems is presented in the following section.

5.2. Multiplexing studies in photopolymers- A brief overview

There are several reports of multiplexing studies in photopolymer layers with different compositions and film thickness. A few of them are presented here. Curtis *et al* [21] have demonstrated the recording of multiple transmission holograms in DuPont HRF-150 photopolymer by angle multiplexing. The material was ~38 μm thick and had angular selectivity of 1^0. Ten holograms were recorded with angular separation of 2° using 488 nm and were then fixed with UV light.

By combining peristrophic multiplexing with angle multiplexing, Curtis *et al* [15] recorded 295 holograms with average diffraction efficiency of ~$4x10^{-6}$ in 38 μm thick DuPont HRF-150 photopolymer. Peristrophic multiplexing permitted almost two orders of magnitude increase in the storage capacity of the DuPont photopolymer and changed the limiting factor from the angular bandwidth of the optical system to the dynamic range of the material.

Pu *et al* [16] introduced an iterative method for determining the exposure schedule for multiplexing holograms in photopolymers. The method was designed to share all or part of the available dynamic range of the recording material among the holograms to be multiplexed. Thousand holograms were multiplexed at a single location in the 100 μm thick DuPont HRF-150 photopolymer using an exposure schedule making use of a combination of angle and peristrophic multiplexing methods. It was also determined that about 2000 holograms could be multiplexed in HRF-150-38 photopolymer with a diffraction efficiency of $\sim 10^{-6}$ per hologram.

Jang *et al* [22] proposed a structure of a holographic recording system by combined use of peristrophic, angle and spatial multiplexing techniques. In this system, both peristrophic and angle multiplexing methods were obtained by controlling the reference beam directly by the use of a pair of wedge prisms, while the method of spatial multiplexing was achieved by shifting the recording medium. The medium used was 38 μm thick DuPont photopolymer film and upto 18 holograms could be recorded in the test system. The mean diffraction efficiency obtained was roughly of the order of 10^{-5}. The exposure time was controlled by using the method proposed by Pu *et al* [16] to get uniform diffraction efficiencies.

Hsu *et al* [23] demonstrated multiple storage of digital data pages in phenanthrenequinone doped poly(methyl methacrylate) (PQ: PMMA) photopolymer cube. Multiple storage and reconstruction of two hundred and fifty Fresnel holograms of a chessboard pattern in a 1x1x1 cm^3 cube was experimentally demonstrated. Typical angle-multiplexing system with 90^0 geometry was used for multiplexing holograms. The reconstructed images had good image fidelity. From the holographic recording characteristics, the criterion for evaluating the dynamic range (M/#) of the polymer was described. M/# ~2 was obtained for 1 mm thick layers.

Lin *et al* [24] developed Irgacure 784 doped PMMA photopolymer material and recorded two hundred plane-wave holograms at one location of the material using 532 nm laser. For a film thickness of 2 mm, M/# of the Irgacure 784/PMMA sample was 3.26 and that of PQ/PMMA sample was 1.7.

Acrylate Oligomer-based photopolymers for optical storage applications were developed by Schilling *et al* [25]. Multiple holograms were recorded in the same volume of the photopolymer sample using frequency doubled Nd: YAG laser by rotating the sample with respect to the recording arms. Twenty five holograms were recorded by rotating the sample in 2^0 increments in majority of the samples.

Dye sensitized acrylamide-based photopolymer systems have attracted great deal of attention because of their high diffraction efficiency and low cost. The capability of yellowish eosin sensitized poly(vinyl alcohol)-acrylamide photopolymer materials to obtain angularly multiplexed holographic gratings was demonstrated by Ortuno *et al* [26]. A method for preparing photopolymer layers of thickness of approximately 1 mm was developed. Argon laser (514 nm) was used to store diffraction gratings in the material. Optimization of the material resulted in a diffraction efficiency of 70% and energetic sensitivity of 50 mJ/cm^2. Seven diffraction gratings were recorded in the same volume of a 700 μm thick recording material using angular multiplexing technique. Dynamic range (M/#) as high as 25.91 was obtained.

Sherif *et al* [12] studied the suitability of a moderately thin acrylamide based photopolymer layer for holographic data storage utilizing angular multiplexing. An Nd: YVO_4 laser beam (532 nm) was used for recording holographic transmission gratings. Storing multiple gratings in the same volume entailed rotating the photopolymer layer by an angle of 1.5^0 between recordings. Series of 18-30 gratings were angularly multiplexed in the same volume of the photopolymer layer with a spatial frequency of 1500 lines/mm. An exposure scheduling method was used to exploit the entire dynamic range of the material and allow equal strength holographic gratings to be recorded. M/# of 3.6 was obtained in 160 μm thick photopolymer layer.

The effect of incorporation of N, N' methylene-bis-acrylamide (BMA) crosslinker on multiplexing of holograms in a yellowish eosin doped acrylamide photopolymer was analyzed by Ortuno *et al* [27]. Slanted diffraction gratings were multiplexed at constant and variable exposure scheduling methods. By exposure scheduling method, 50 holograms were stored in 700 μm thick photopolymer film using Argon laser (514 nm). For the photopolymer with crosslinker, M/# of 3.58 was obtained, while for the photopolymer without crosslinker, M/# was 1.88.

Fernandez *et al* [11] used a combination of peristrophic and angular multiplexing methods to record 60 holograms in a poly(vinyl alcohol)-acrylamide photopolymer sensitized by yellowish eosin. An exposure schedule method was used to optimize the capability of the photopolymer material and to obtain holograms with higher and more uniform diffraction efficiencies. Holographic gratings were recorded using the output from a diode-pumped frequency-doubled Nd: YAG laser. Dynamic range (M/#) equal to 8.7 was obtained with a mean diffraction efficiency of 2% in 800 μm thick photopolymer layers. Ninety holograms were stored at the same location of a yellowish eosin sensitized poly(vinyl alcohol)-acrylamide photopolymer material by Fernandez *et al* [19]. Peristrophic and a combination of angular and peristrophic multiplexing methods were used for storing gratings in 700±10 μm thick photopolymer layer. An exposure schedule method was adopted in both cases to calculate the exposure times necessary to obtain uniform diffraction efficiencies. In the case of peristrophic multiplexing, dynamic range (M/#) equal to 12 was obtained with a mean diffraction efficiency of 2.1%, while in the case of combination of angular and peristrophic multiplexing, the M/# was 8 and the mean diffraction efficiency was 1%.

Nine holograms were recorded in a 900 μm thick yellowish eosin sensitized acrylamide based photopolymer material by Ortuno *et al* [13]. Nd: YAG laser (532 nm) was used as the recording beam. Mean diffraction efficiency equal to 12% and M/# of 3 was obtained while recording nine transmission holograms.

Gallego *et al* [14] have analyzed the recording of multiplexed holograms in 770 μm thick yellowish eosin sensitized acrylamide based photopolymer film. The experimental utility of the exposure schedule model was checked inorder to predict the multiplexing process of many holographic gratings in a PVA/acrylamide photopolymer. Holographic gratings were recorded using a diode pumped frequency-doubled Nd: YAG (532 nm) laser. Gratings were stored using two approaches, firstly using similar exposure times to record a small number of gratings with large diffraction efficiency, and secondly using iterative algorithms to store many holograms with a diffraction efficiency of around 2%.

In the present study, multiple transmission gratings were stored in silver doped MBPVA/AA photopolymer film using angle and peristrophic multiplexing techniques. Both constant and iterative exposure energy scheduling schemes were employed for recording gratings. The storage capacity of the material was determined by calculating the M number (M/#). The results obtained from different methods were compared inorder to determine the suitable multiplexing method.

5.3. Experimental

Silver doped photopolymer films with optimum composition shown in table. 5.1 were used for multiplexing studies. The films were fabricated by gravity settling method. The films had a thickness of approximately 130 μm (measured using Dektak

6m stylus profiler). He-Ne laser with emission at 632.8 nm (Melles Griot) was used for recording and reconstruction of the gratings.

Table. 5.1. Optimum film composition

Constituent	Concentration
PVA	10% w/v
AA	0.4 M
TEA	0.05 M
MB	0.014 mM
$AgNO_3$	0.05 mM

5.4. Results and discussion

5.4.1. Angular selectivity of the material

In holographic multiplexing, multiple holographic gratings are recorded in the same volume of the recording material. From the angular selectivity (the angular bandwidth of the main lobe of the stored grating), it is possible to determine the angular separation necessary between the gratings to prevent them from overlapping during storage [11].

To calculate the angular selectivity of the material, a grating with spatial frequency of ~1100 lines/mm was stored in the film for exposure energy of 5 mJ/cm^2. The film was then mounted on a rotation stage and the intensity of the diffracted beam was measured for different reconstruction angles by rotating the stage. For each reconstruction angle, diffraction efficiency was calculated as the ratio of the intensity of the diffracted beam to the reading beam intensity. The variation of diffraction efficiency with deviation from Bragg angle is plotted in fig. 5.1. The angular bandwidth of the stored grating was approximately 1°. Therefore, while recording multiple gratings, they need to be separated by this angular distance to prevent overlapping between them. The angular selectivity indicates how many holograms can be multiplexed within the same volume of material. The selectivity increases with spatial frequency and material thickness. In the present study, an angular distance of 5^0 was chosen for recording multiple holographic gratings inorder to prevent overlapping between the recorded gratings.

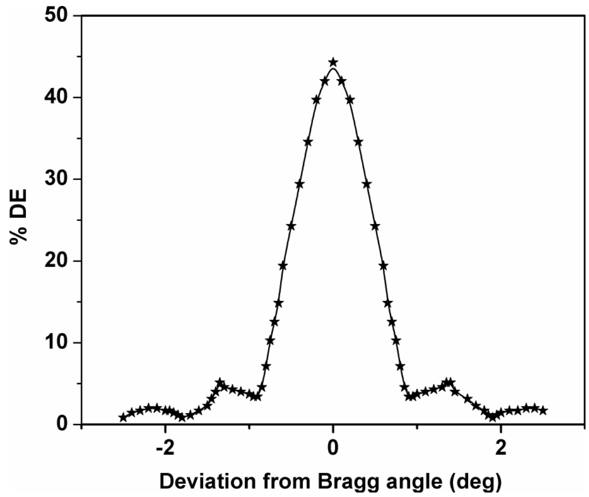

Fig. 5.1. Angular selectivity curve

5.4.2. Angle multiplexing studies

Angle multiplexing was performed by varying the interbeam angle between the recording beams (fig. 2.10). Gratings were recorded using constant and variable exposure scheduling methods. In constant exposure method, gratings were recorded for constant exposure energy, whereas in variable exposure scheduling, gratings were recorded for different exposure energies. The results obtained from both methods are presented in the following sections.

5.4.2.1. Constant exposure method

Plane-wave transmission grating recorded in the optimized film using 632.8 nm He-Ne laser showed high diffraction efficiency of 75% for exposure of 80 mJ/cm^2 and recording power of 4 mW. Hence this exposure energy and recording power were chosen for recording multiple gratings in the photopolymer film. The interbeam angle was varied from 20^0 to 40^0. Five transmission gratings were recorded with an angular separation of 5^0 by this method. The gratings were reconstructed using He-Ne laser (2 mW, 632.8 nm). The diffraction efficiency of the gratings recorded with a constant exposure schedule is shown in fig. 5.2.

Recording with a constant exposure schedule resulted in gratings with non-uniform diffraction efficiencies. The first recorded grating had high diffraction efficiency while the other gratings had very low diffraction efficiency values. Efficiency of the first grating was 45% while that of the fifth one was only 0.003%. The mean diffraction efficiency (DE$_m$) was calculated using the expression

$$DE_m = \frac{1}{N}\sum_{i=1}^{N}\eta_i \tag{5.1}$$

where, η_i represents the maximum diffraction efficiency of each grating and N, the total number of gratings recorded. The mean diffraction efficiency was 10%. Maximum efficiency was seen to decrease as the number of recorded gratings increases which may be due to the consumption of the dynamic range of the photopolymer film as each new grating was recorded [13].

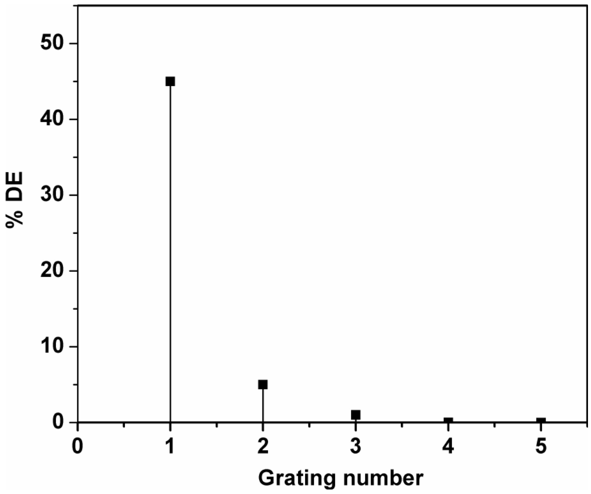

Fig. 5.2. DE of five gratings recorded with constant exposure

5.4.2.1 (a). Determination of M/#

One of the parameters that characterizes a material in terms of its suitability as a holographic memory is the "M-number" (M/#), which indicates the dynamic range of the material or its capacity to store holograms by means of multiplexing. It predicts the overall diffraction efficiency of the photopolymer for N number of gratings. The suitability of the photopolymer for the holographic storage system is characterized by a high M/#.

The M/# is given by the expression (5.2) in which η_i is the maximum diffraction efficiency of each of the gratings recorded and N is the number of gratings recorded [20].

$$M/\# = \sum_{i=1}^{N}\eta_i^{1/2} \tag{5.2}$$

The dynamic range (M/#) used to record the gratings by constant exposure scheduling was equal to 1. M/# is equivalent to the maximum cumulative grating strength when plane waves are recorded using multiplexing. The cumulative grating strength (A) is the dynamic range used before each hologram is recorded and is calculated according to expression

$$(A)_n = \sum_{i=1}^{n} (\eta_i)^{1/2} \tag{5.3}$$

where, η_i is the maximum diffraction efficiency of each of the gratings recorded, $n \leq N$, the total number of gratings recorded [13]. The recording behaviour of the photopolymer can be best characterized by plotting the cumulative grating strength (A) as a function of exposure energy (fig. 5.3). If the cumulative grating strength increases linearly with exposure energy, it indicates that we are far from the saturation zone of the photopolymer throughout the recording process. From the figure, it can be seen that the cumulative grating strength grows quasi-linearly with exposure energy and then saturates.

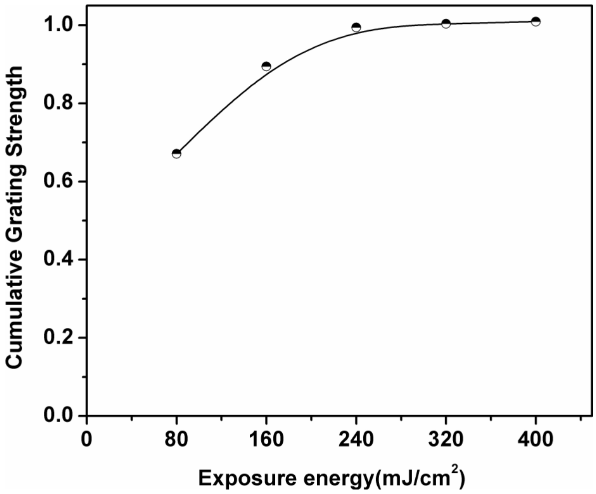

Fig. 5.3. Cumulative grating strength as a function of exposure energy

Inorder to achieve an efficient use of the available dynamic range, gratings or holograms recorded by multiplexing should have homogeneous diffraction efficiency, since reading problems may arise if a hologram has diffraction efficiency lower than the mean. Therefore, when a specific number of holograms are to be recorded, their maximum diffraction efficiency should be as constant as possible inorder to make good use of the available dynamic range. However, from multiplexing studies at constant exposure energy, it was seen that this type of multiplexing will not result in gratings with homogeneous diffraction efficiency. This may be because, when gratings are recorded in the photopolymer film, the monomer and dye are being consumed and therefore the material becomes less sensitive [13, 19]. Hence it is necessary to increase the exposure time for the last gratings so that they also attain the same diffraction efficiency as the first recorded gratings.

5.4.2.2. Variable exposure scheduling method

Photopolymer is a saturable material and so its dynamic range is not shared equally among the gratings recorded with equal exposure energy within the photopolymer layer. As a result, each additional grating recorded has less potential for modulating the photopolymer's refractive index. The diffraction efficiency of the multiplexed holographic gratings is expected to scale as $1/N^2$, where N is the number of gratings multiplexed [16, 28]. Therefore, as the number of holographic gratings stored in the photopolymer increases, appropriate exposure scheduling becomes increasingly important. For this reason, an exposure scheduling method was used for recording multiple gratings in the film, enabling the dynamic range to be equally shared between all the recorded gratings. The exposure scheduling method was designed so as to allocate the available dynamic range of the recording material among the gratings to be multiplexed. In this case, ten gratings were recorded with an angular separation of 5^0 and the interbeam angle was varied from 20^0 to 65^0. The total power at the recording plate was maintained as 4 mW throughout the recording process and the beam intensity ratio was 1:1. Exposure energy was increased in steps by increasing the exposure time while recording gratings. Several exposure scheduling schemes were used for recording gratings. The exposure scheduling scheme which showed better result is shown in fig. 5.4.

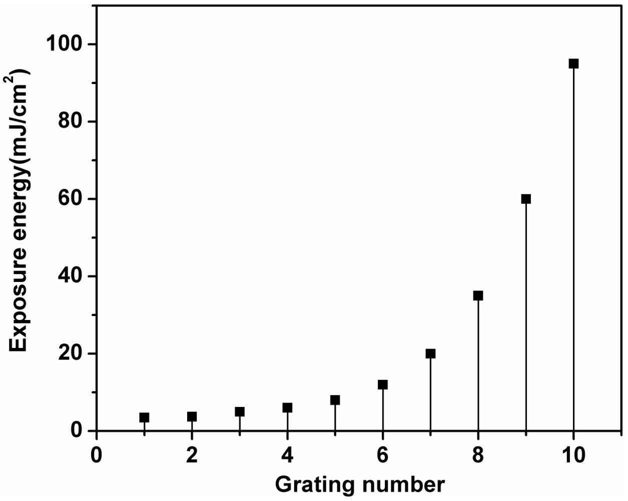

Fig. 5.4. Exposure scheduling scheme for 10 gratings

The variation of diffraction efficiency with grating number for 10 multiplexed gratings is shown in fig. 5.5. The range of diffraction efficiency was 0.5 to 2% and the mean DE was 1.2%. From the diffraction efficiencies obtained, the cumulative grating strength was calculated and plotted as a function of exposure energy (fig. 5.6). It can be seen that, the cumulative grating strength increases with exposure energy and then saturates. The dynamic range (M/#) was obtained as 1.1. From the dynamic range and the number of holographic gratings to be recorded, it is possible to determine the mean theoretical diffraction efficiency that could be reached for each of the recorded gratings.

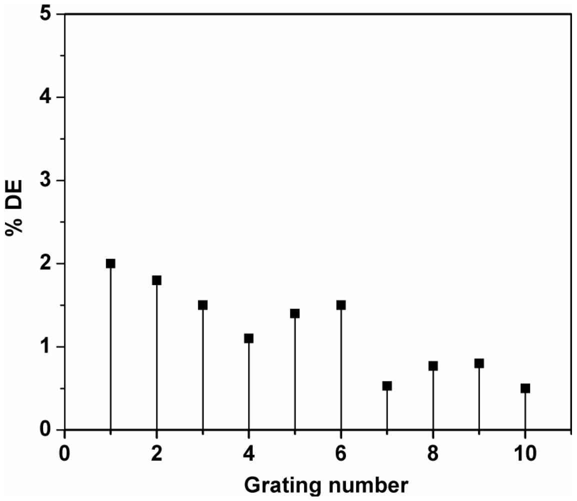

Fig. 5.5. Variation of efficiency with grating number

To calculate the mean diffraction efficiency (η_{avg}), the dynamic range M/# was divided by the number of gratings (N) and the result obtained was squared,

$$\eta_{avg} = \left(\frac{M/\#}{N} \right)^2 \tag{5.4}$$

When M/# = 1.1 and 10 gratings are recorded, a mean theoretical diffraction efficiency of 1.21% could be achieved, as was obtained experimentally.

The dynamic range obtained from the exposure scheduling method is larger than that obtained from constant exposure energy scheduling method. This indicates that variable exposure energy scheduling makes better use of the dynamic range of the photopolymer material. Recording with a variable exposure schedule resulted in more uniform gratings than multiplexing at constant exposure energy.

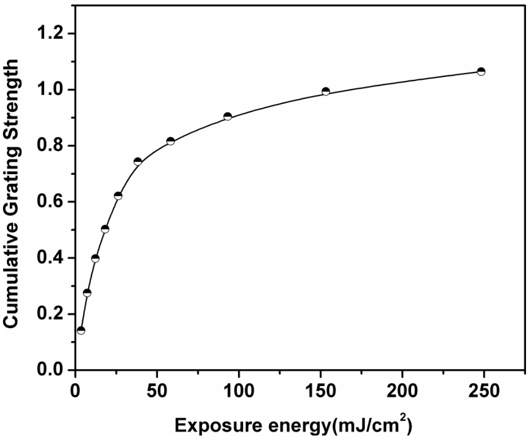

Fig. 5.6. Cumulative grating strength as a function of exposure energy

5.4.3. Peristrophic multiplexing studies

Peristrophic multiplexing technique with rotation of the film in a plane normal to the bisector of the incident beams was employed for recording plane wave transmission gratings at the same location of the silver doped MBPVA/AA photopolymer film (fig. 2.11). Here also, both constant and variable exposure scheduling methods were adopted for storing gratings using 632.8 nm He-Ne laser.

5.4.3.1. Peristrophic multiplexing at constant exposure energy

In this case, transmission gratings were recorded in the film with exposure energy of 80 mJ/cm^2 per grating. The total recording power was 4 mW and the interbeam angle was 40^0 (spatial frequency ~1100 lines/mm). The beam intensity ratio was maintained as 1:1. Ten gratings were recorded with an angular separation of 5^0. The variation of efficiency of the gratings recorded with constant exposure of 80 mJ/cm^2 is shown in fig. 5.7.

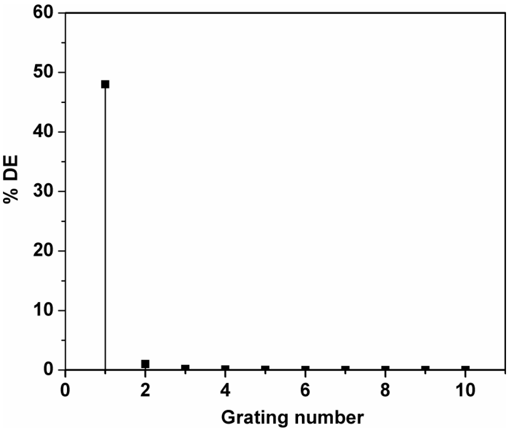

Fig. 5.7. DE of peristrophically multiplexed gratings with 80mJ/cm^2 exposure

The first grating had DE of 48%, while the tenth one showed only 0.001%. The mean DE was 4.9%. The plot of cumulative grating strength as a function of exposure energy for 10 multiplexed gratings is shown in fig. 5.8. The cumulative grating strength increases with exposure and then saturates.

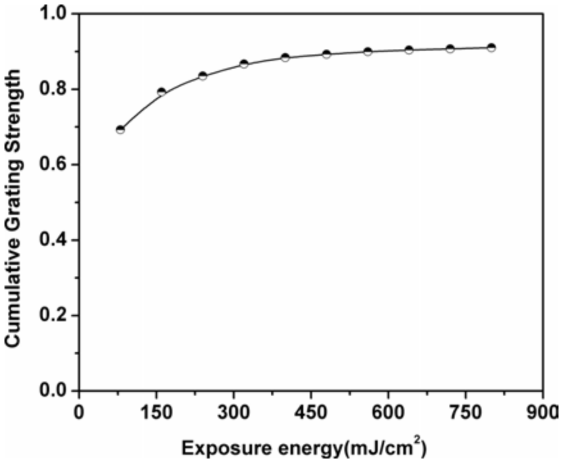

Fig. 5.8. Cumulative grating strength as a function of exposure energy

The M/# was obtained as 0.91. Inorder to equalize the efficiency of the recorded gratings, attempts were made to record gratings making use of variable exposure scheduling method.

5.4.3.2. Peristrophic multiplexing at variable exposure energy

Exponential growth energy scheduling was implemented to record 10 gratings in the photopolymer film. The exposure scheduling scheme is shown in fig. 5.9.

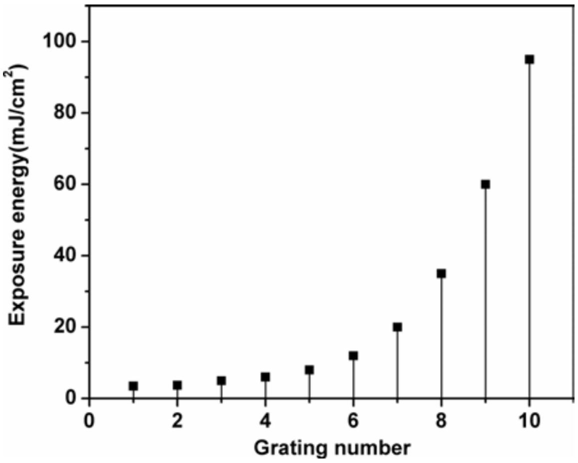

Fig. 5.9. Variable exposure scheduling scheme

The change in diffraction efficiency with grating number for the gratings recorded using the exposure scheduling method is shown in fig. 5.10. Multiplexed gratings had DE between 0.8% and 2.5% and the mean DE was 1.4%. The plot of cumulative grating strength as a function of exposure energy for 10 multiplexed gratings is shown in fig. 5.11. The M/# was 1.15 (calculated using expression (5.2)). Variable exposure method resulted in the recording of gratings with more uniform efficiencies and larger M/# value.

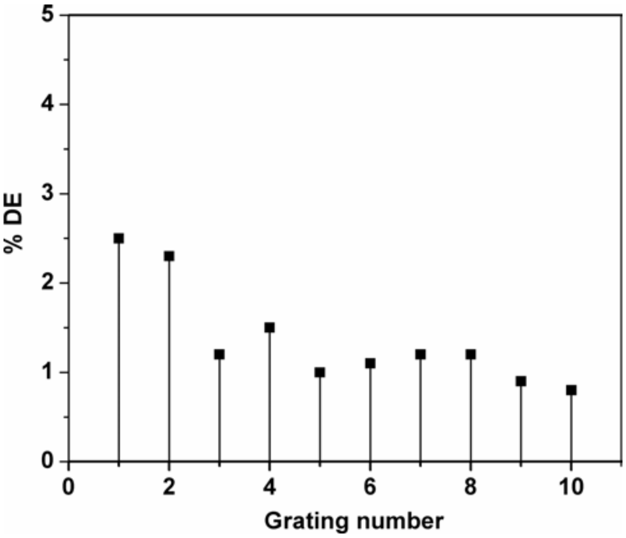

Fig. 5.10. Variation of DE with exposure energy

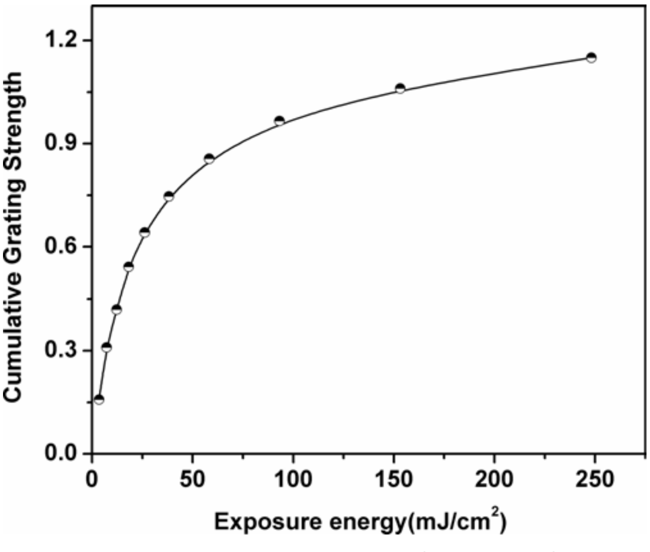

Fig. 5.11. Cumulative grating strength as a function of exposure energy

5.5. Multiplexing gratings at lower recording power

From multiplexing studies carried out at a total recording power of 4 mW, it was found that the first recorded grating had very high DE, while the other ones had very low DE values. This may be because, at this high recording power, most of the monomer and dye molecules will be utilized during the recording of the first grating itself and hence the first recorded grating showed high DE. This results in less number of monomers and dye molecules available for further grating recording and hence the other gratings showed lower DE. Inorder to fully exploit the dynamic range of the material, as many gratings as possible need to be stored. Hence, with the aim of recording more number of gratings, the total recording power was reduced to 0.4mW and gratings were stored in the film by angle and peristrophic multiplexing methods.

5.5.1. Angle multiplexing

Multiple transmission gratings were recorded by constant and variable exposure scheduling methods using angle multiplexing technique.

5.5.1 (a). Angle multiplexing at constant exposure energy

Fifteen gratings were recorded with a constant exposure of 1 mJ/cm^2. The interbeam angle was varied from 10^0 to 80^0 and the angular separation was 5^0. The variation of diffraction efficiency with grating number is plotted in fig. 5.12. The range of diffraction efficiency was 0.02 to 21% with mean efficiency of 2.45%. The plot of cumulative grating strength as a function of exposure energy for 15 multiplexed gratings is shown in fig. 5.13. The M/# was 1.5, which is greater than that obtained for multiplexing with high recording power of 4 mW.

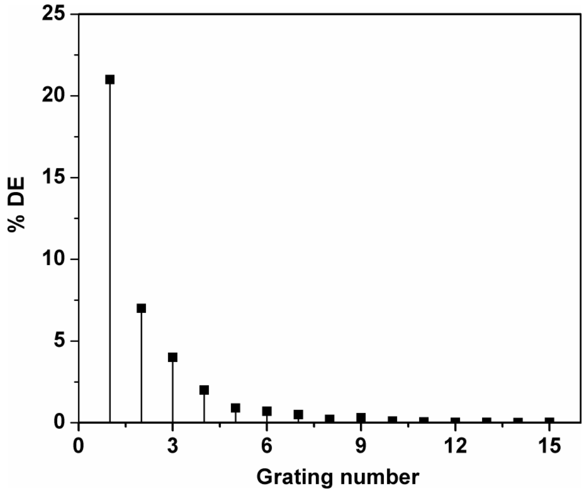

Fig. 5.12. Variation of DE with grating number

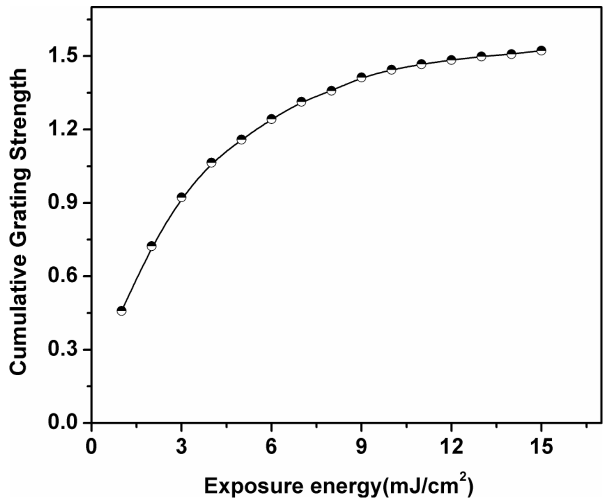

Fig. 5.13. Cumulative grating strength as a function of exposure energy

5.5.1 (b). Angle multiplexing at variable exposure energy

By variable exposure method, fifteen gratings were recorded in the film. The exposure scheduling scheme is shown in fig. 5.14 and the variation of diffraction efficiency with grating number is shown in fig. 5.15.

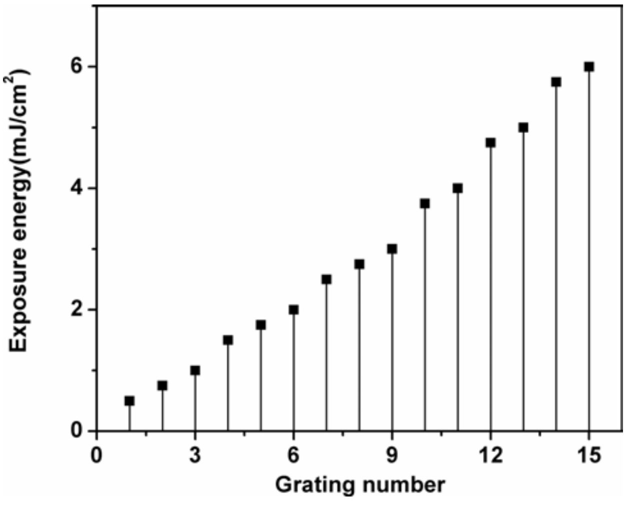

Fig. 5.14. Exposure scheduling scheme

The range of diffraction efficiency was 0.5 to 4% and the mean diffraction efficiency was calculated to be 1.33%. The variation of cumulative grating strength with exposure energy for 15 multiplexed gratings is shown in fig. 5.16. The M/# was obtained as 1.7. The M/# was slightly larger than that obtained from constant exposure method.

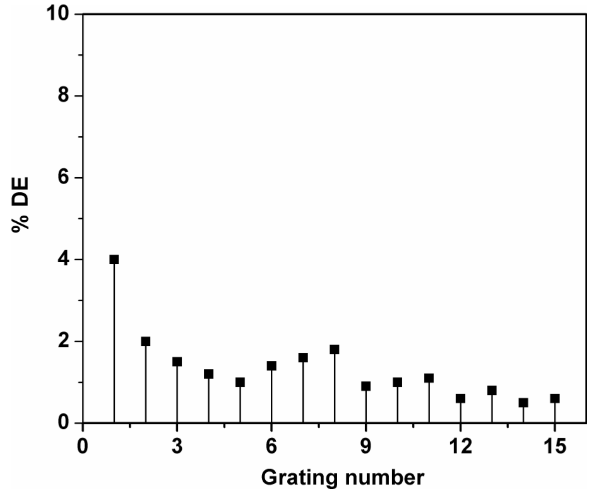

Fig. 5.15. Change in DE with grating number

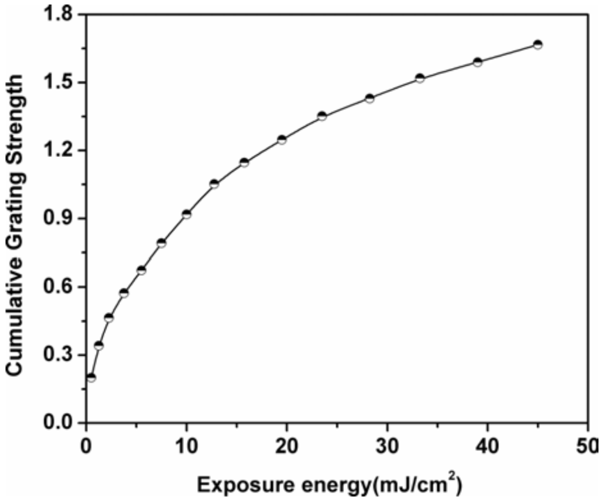

Fig. 5.16. Cumulative grating strength as a function of exposure energy

5.5.2. Persitrophic multiplexing

Two types of peristrophic multiplexing methods were adopted for storing gratings. Here also, gratings were multiplexed by constant and variable exposure scheduling methods.

5.5.2.1. Peristrophic method I

In peristrophic method I (fig. 2.11), the rotation of the film about an axis normal to the plane of incidence was performed. The film was rotated in a direction perpendicular to the plane of incidence after each recording. This rotation shifts the reconstructed image away from the detector, permitting a new grating to be recorded at the same location and viewed without interference.

5.5.2.1 (a). Multiplexing at constant exposure energy

In constant exposure method, gratings were recorded in the photopolymer film with 1 mJ/cm^2 incident exposure energy per grating. The recording beams had an incident angle of 20^0 with respect to the normal on the photopolymer surface and the beam intensity ratio was 1:1. Twenty plane wave gratings were recorded with an angular separation of 5^0 in the film by this method. The stored holographic gratings were reconstructed using He-Ne laser (2 mW, 632.8 nm). DE of 20 peristrophically multiplexed plane-wave gratings recorded with a uniform exposure schedule is shown in fig. 5.17. The variation of cumulative grating strength with exposure energy for 20 multiplexed gratings is shown in fig. 5.18.

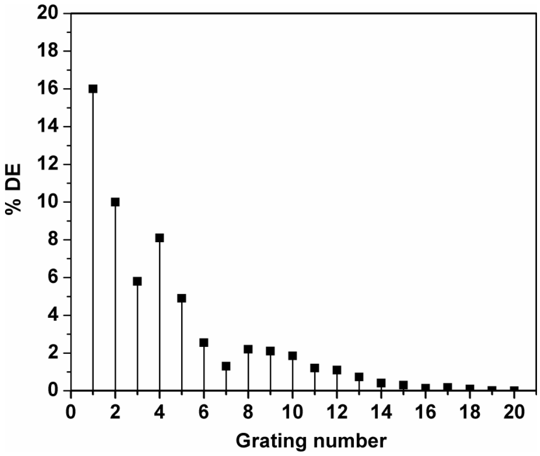

Fig.5.17. DE of 20 plane wave gratings recorded with a constant exposure of 1mJ/cm^2

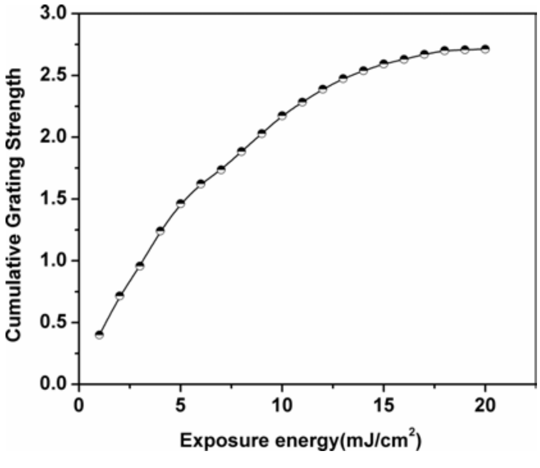

Fig. 5.18. Variation of cumulative grating strength with exposure energy

The diffraction efficiency of the first grating was 16% while that of the twentieth one was 0.002%. The mean diffraction efficiency was calculated using the expression (5.1) and was equal to 3%. The dynamic range (M/#) used to record the gratings by constant exposure scheduling was equal to 2.7.

5.5.2.1 (b). Peristrophic multiplexing at variable exposure energy

Efforts were made to equalize the diffraction efficiency of the multiplexed gratings by adopting proper exposure scheduling method. In this case also, gratings were recorded with an angular separation of 5^0 and spatial frequency of ~1100 lines/mm. The total power at the recording plate was maintained as 0.4 mW throughout the recording process and the beam intensity ratio was 1:1. Exposure energy was increased in steps by increasing the exposure time while recording gratings.

Sets of 20-30 gratings were recorded in the film by adopting variable exposure scheduling methods. The diffraction efficiencies of the recorded gratings were determined by reconstructing the gratings by He-Ne laser beam (2 mW). The variation of diffraction efficiency with grating number for 20 multiplexed gratings is shown in fig. 5.19. The exposure scheduling scheme used is shown in inset. The range of diffraction efficiency was 2.9 to 6% and the mean diffraction efficiency was 4.5%. The variation of cumulative grating strength with exposure energy is shown in fig. 5.20. The dynamic range (M/#) used to record the gratings was obtained as 4.2.

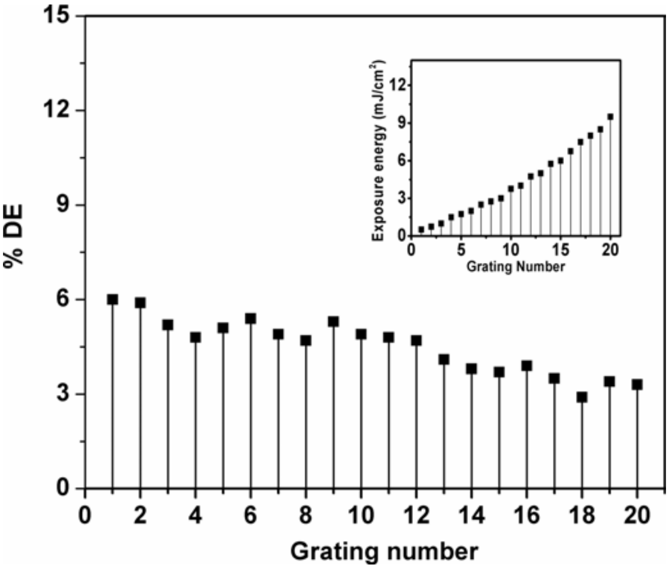

Fig. 5.19. Diffraction efficiency as a function of grating number for 20 gratings

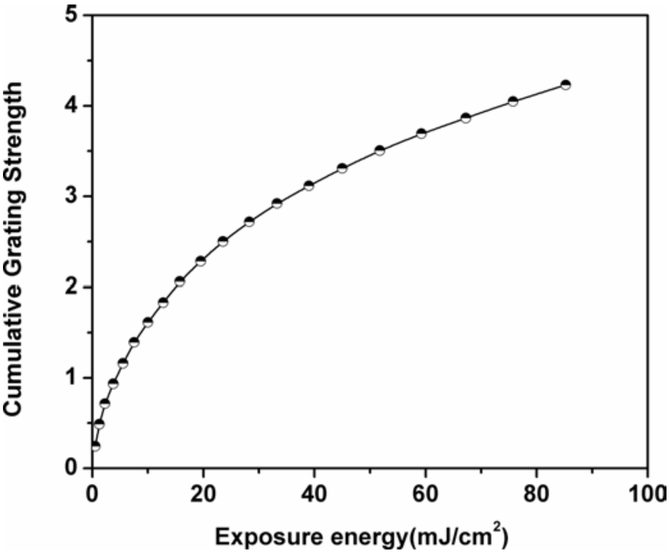

Fig. 5.20. Variation of cumulative grating strength with exposure energy

The diffraction efficiency of 30 peristrophically multiplexed plane wave gratings recorded with a variable exposure schedule is shown in fig. 5.21. Recording with a variable exposure schedule resulted in nearly uniform gratings. The range of DE was 0.9 to 5.5% and the average DE was 2.7%. The variation of cumulative grating strength with exposure energy is shown in fig. 5.22. The dynamic range (M/#) was equal to 4.7. The range of DE and M/# values is summarized in table 5.2.

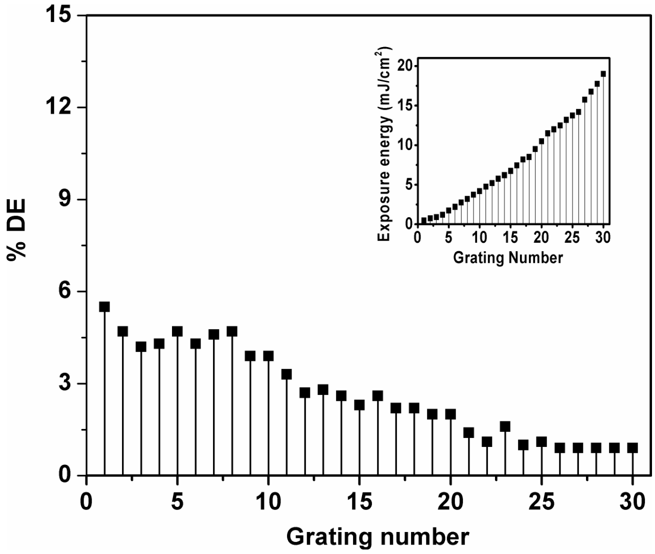

Fig. 5.21. Diffraction efficiency as a function of grating number for 30 gratings

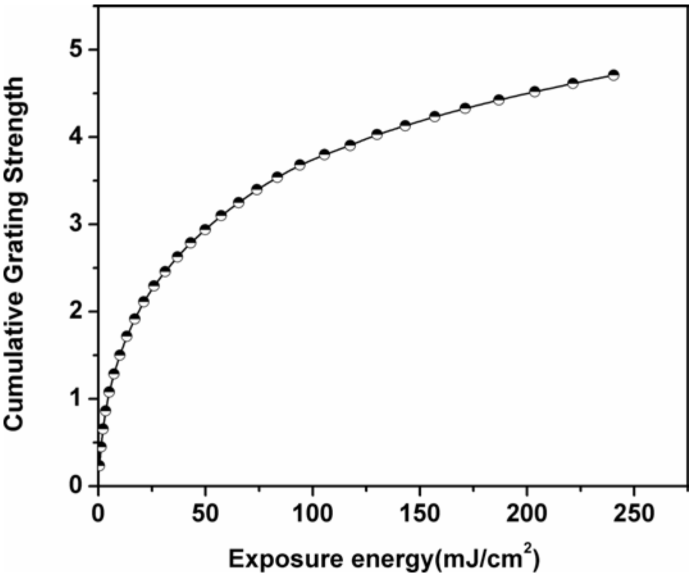

Fig. 5.22. Variation of cumulative grating strength with exposure energy

Table. 5.2. DE and M/# values

No. of multiplexed gratings	Range of DE (%)	M/#
20	2.9 - 6	4.2
30	0.9 -5.5	4.7

In the case of set of 20 gratings, the recorded gratings were found to be more uniform than the set of 30 multiplexed gratings. But M/# value was larger for the set of 30 gratings because as the number of recorded gratings increases, there will be maximum utilization of the available dynamic range. Variable exposure method resulted in larger M/# value and more uniform gratings than constant exposure scheduling which clearly indicate that variable exposure energy scheduling makes better use of the dynamic range of the photopolymer material. The M/# obtained while recording 30 gratings in the 130 μm thick silver doped MBPVA/AA photopolymer material is assumed to be larger than the reported values for acrylamide based composition with similar layer thickness [29]. Sherif *et al* has achieved M/# of 3.6 while recording 30 holograms in a 160 μm thick acrylamide-based photopolymer film with slightly different composition [12]. From the table 5.2, it can be seen that the multiplexed gratings have high diffraction efficiency values. Since typically one can work with holographic diffraction efficiencies of the order of 10^{-6}, we have sufficient dynamic range to record more number of gratings [15]. Ortuno *et al* have recorded 9 holograms with uniform efficiency having an M/# of 3 using 900 μm thick eosin sensitized acrylamide polymer films [13]. Fernandez *et al* have developed 700 ± 10 μm thick acrylamide-based photopolymer layer and peristrophically multiplexed 90 gratings which gave M/# of 12 [19]. Hence, it is expected that more number of gratings can be multiplexed in the developed silver doped photopolymer film by increasing the film thickness.

5.5.2.2. Peristrophic method II

In the case of peristrophic method II (Fig. 2.12), the rotation of the film was carried out about an axis along the plane of incidence. The film was rotated along the plane of incidence after each recording. 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. All the grating recording parameters were the same as that used in the case of peristrophic method I. The angular distance between successive gratings was 5^0. Gratings were recorded in the film by variable exposure scheduling method. Fig. 5.23 shows the variation of diffraction efficiency with grating number and the corresponding exposure scheduling scheme is shown in inset. The range of diffraction efficiency was 0.6 to 2% and M/# was calculated as 2.5 [30]. The mean diffraction efficiency was 1.6%. The variation of cumulative grating strength with exposure energy is shown in fig. 5.24.

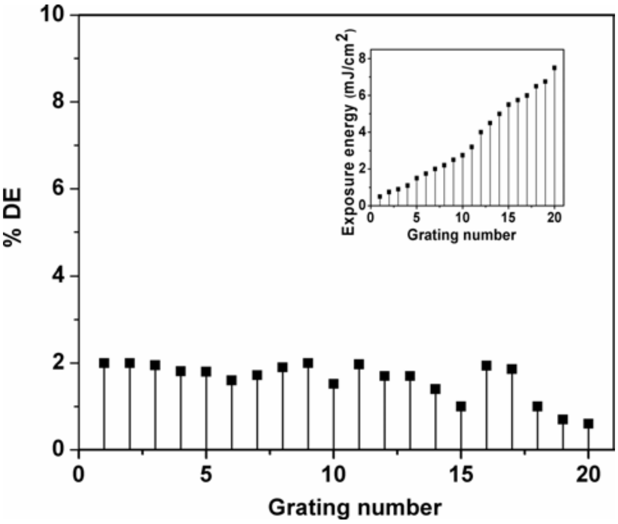

Fig. 5.23. Variation of diffraction efficiency with grating number

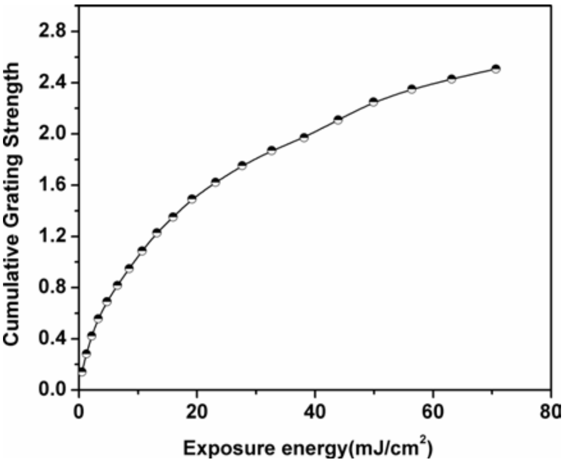

Fig. 5.24. Variation of cumulative grating strength with exposure energy

Unlike peristrophic method I, only 180^0 rotation of the film was achievable by this method, since the rotation was about an axis parallel to the angle of incidence. Also for larger rotation angles (angular distances), one of the interfering beams was observed to be elongated. Hence the number of recorded gratings was limited to twenty. In this case, the recorded gratings were found to have more uniform diffraction efficiency, but the M/# value is smaller than that obtained from peristrophic method I. In the case of peristrophic method I, recording of 20 gratings had resulted in M/# of 4.2. Thus peristrophic method I is more suitable for data storage applications since it makes better use of the available dynamic range of the recording material.

5.6. Conclusions

Angle and peristrophic multiplexing techniques were employed for storing multiple transmission gratings in silver doped MBPVA/AA photopolymer film using He-Ne laser. Peristrophic multiplexing with rotation of the film normal to the plane of incidence resulted in the recording of nearly uniform gratings with higher DE and dynamic range (M/#). Variable exposure scheduling resulted in a larger M/# value of 4.7 while peristrophically multiplexing 30 gratings in the 130 μm thick photopolymer layer. This clearly indicates that variable exposure energy scheduling makes better use of the available dynamic range of the photopolymer material. The M/# value obtained for 30 gratings in this 130 μm thick acrylamide based photopolymer layer is assumed to be larger than the reported values for multiplexing equal number of gratings in acrylamide based photopolymer materials with similar composition and layer thickness.

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6

Fabrication of films by spin coating technique and recording of data pages

Uniformity over the entire film surface is an essential requirement for achieving better holographic performance. In the present study, efforts were made to develop uniform photopolymer films by spin coating technique. Plane-wave transmission gratings were recorded in the films by 632.8 nm He-Ne laser. Bright transmission holograms were also recorded in the films using He-Ne, Nd: YAG and Ar^+ *lasers. The feasibility of recording data page with good image fidelity is also demonstrated.*

6.1. Introduction

Photopolymer materials are attractive candidates for write-once-read- many (WORM) times data storage applications because they can be designed to have large modulations in their refractive index and high photosensitivity, record permanent holograms, and are capable of real-time recording [1-15]. Among the different photopolymer materials, those based on poly(vinyl alcohol)/acrylamide has generated a great deal of interest because of their many attractive features which makes them potential candidates for holographic data storage applications [9-15]. The fabrication of dye doped photopolymer film involves the deposition of the respective dye sensitized polymer solution on a suitable substrate and allowing the solvent to evaporate slowly. Dip coating, doctor blading, gel casting, gravity settling and spin coating are the methods commonly used for coating the polymer solution on the substrates. From the studies on films prepared by gravity settling method, it was found that the films had thickness non-uniformity particularly in the portion near the edges. Since structural uniformity over the entire film surface is an essential prerequisite for achieving better holographic performance, it is needed to prepare uniform films making use of suitable fabrication technique. Spin coating is an excellent technique for preparing uniform films since it is possible to obtain a highly uniform film over a large area with a highly controllable and reproducible film thickness. Spin coating is widely employed for the fabrication of thin film coatings over large areas with high structural uniformity. Hence in the present study, attempts were made to fabricate uniform photopolymer films by spin coating method. Parameters like speed, quantity of solution and time were optimized so as to prepare uniform films with good holographic properties. Holographic characterization of the films was carried out in detail and is presented in the following sections. The capability of the film for holographic data storage applications was studied by recording checker board pattern.

6.2. Methodology

The films were fabricated by spin coating unit SPIN 150 (SPS Europe). The spin coating process involves the deposition of the solution onto a substrate and then spinning the substrate at a required speed. In the present study, initially films were fabricated using photopolymer solution prepared with optimum film composition as shown in table. 6.1.

Table. 6.1. Concentration of the photopolymer constituents

Constituent	**Concentration**
PVA	10% w/v
AA	0.4 M
TEA	0.05 M
MB	0.014 mM
$AgNO_3$	0.05 mM

A fixed volume of photopolymer solution (6 ml) was deposited on the centre of glass substrate (6 cm x 6 cm x 2 mm) kept over the vacuum chuck (bearing area (size)- 50 mm, vacuum diameter - 10 mm). Films were prepared by spinning the substrate for different speeds (300 rpm, 600 rpm) for 2 s. The film fabricated at a speed of 600 rpm was coded as S1, while that fabricated at a speed of 300 rpm was coded as S2. After the spin process is over, the films were taken carefully from the chuck and were kept on a levelled glass tray for drying. The trays were covered properly. After drying, the thickness of the films was measured using stylus profiler (Dektak 6m). The spin parameters and thickness of the films are shown in table. 6.2.

Table. 6.2. Spin parameters and thickness of S1 and S2

Speed (rpm)	**Time (s)**	**Volume (ml)**	**Thickness (μm)**	**Sample name**
600	2	6	20	S1
300	2	6	32	S2

6.3. Recording of grating and DE measurements

Plane-wave transmission gratings were recorded in the films S1 and S2 using He-Ne laser (Fig. 2.8). The interbeam angle was 40^0, total recording power was ~4 mW and intensity ratio of the recording beams was kept as 1:1. The exposure energy was varied from 5 mJ/cm^2 to 100 mJ/cm^2. Fig. 6.1 shows the variation of diffraction efficiency with exposure energy.

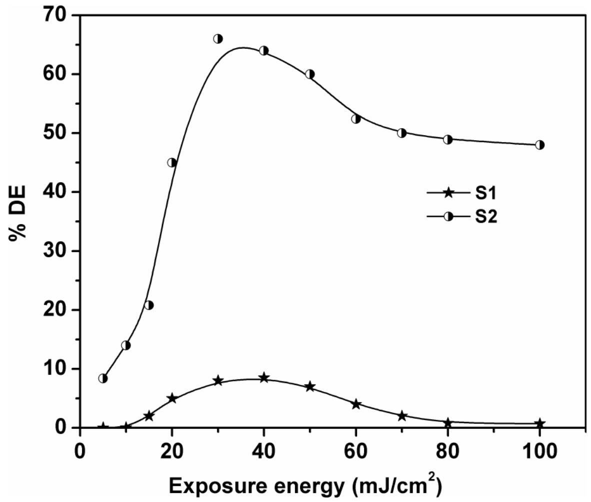


Fig. 6.1. Variation of DE with exposure energy

The gratings recorded in the film S1 showed very low DE values. Maximum diffraction efficiency was only 9% for exposure of 40 mJ/cm^2. But in the case of film S2, maximum efficiency was 66% for 30 mJ/cm^2. Eventhough the film S2 showed high DE and high energy sensitivity, the film thickness was only 32 μm. For data storage applications, thick films are very essential and hence attempts were made to enhance the film thickness. For fabricating thicker films, high material viscosity is needed.

Hence films were fabricated using PVA solution with high viscosity (15% w/v), keeping the concentrations of all other components same as that of the samples, S1 and S2. The same spin parameters were used for film fabrication. The film fabricated at a speed of 600 rpm was coded as S3, while that fabricated at a speed of 300 rpm was coded as S4. After drying, the thickness of the films was measured using stylus profiler (Dektak 6m). Table. 6.3 shows the spin parameters used and the thickness of films S3 and S4. These films had thickness above 100 μm.

Table. 6.3. Spin parameters and thickness of S3 and S4

Speed (rpm)	**Time (s)**	**Volume (ml)**	**Thickness (μm)**	**Sample name**
600	2	6	108	S3
300	2	6	126	S4

Transmission gratings were recorded in the films by He-Ne laser making use of the same recording parameters used in the case of the films S1 and S2. The exposure energy was varied from 5 mJ/cm^2 to 100 mJ/cm^2. Fig. 6.2 shows the variation of diffraction efficiency with exposure energy for gratings recorded in the films S3 and S4.

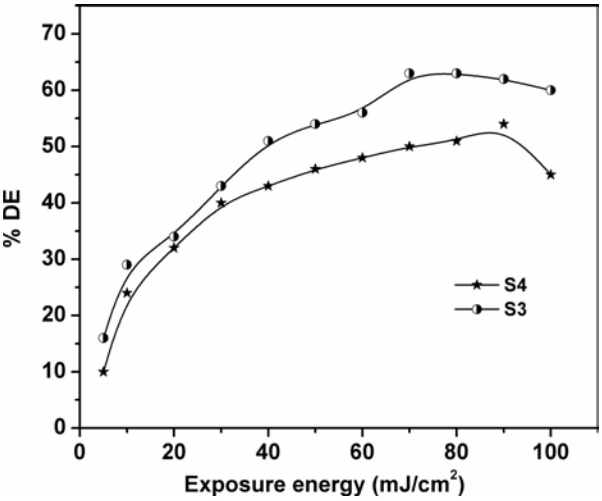


Fig. 6.2. DE variation with exposure energy

Maximum DE obtained was 63% for 70-80 mJ/cm^2 for grating recorded in S3, while grating recorded in S4 showed peak efficiency of 54% for 90 mJ/cm^2. The film S3 was selected for further studies and efforts were made to optimize the composition of the film S3. Films were prepared by varying the concentrations of different constituents as shown in table. 6.4.

Table. 6.4. Variation of film composition

Constituent	Concentration
PVA	15% w/v
AA	0.47-0.9 M
MB	0.014-0.06 mM
TEA	0.05-1 M
$AgNO_3$	0.05-0.09 mM

Inorder to determine the concentration of each constituent required for achieving maximum DE, gratings were recorded in the films using the same recording parameters as that of film S3. The exposure energy was varied from 5 mJ/cm^2 to 150 mJ/cm^2. Gratings were reconstructed using He-Ne laser and the DE values were calculated. Fig. 6.3 shows the variation of DE with exposure energy for the gratings recorded in the optimized film. High DE of 80% was exhibited by grating recorded with an exposure of 50 mJ/cm^2. Even for an exposure of 10 mJ/cm^2, DE above 70% could be obtained, which clearly indicate the high energy sensitivity of spin coated films. The efficiency was above 70% for exposures 10-150 mJ/cm^2. The optimum film composition which exhibited maximum DE and energy sensitivity is shown in table. 6.5.

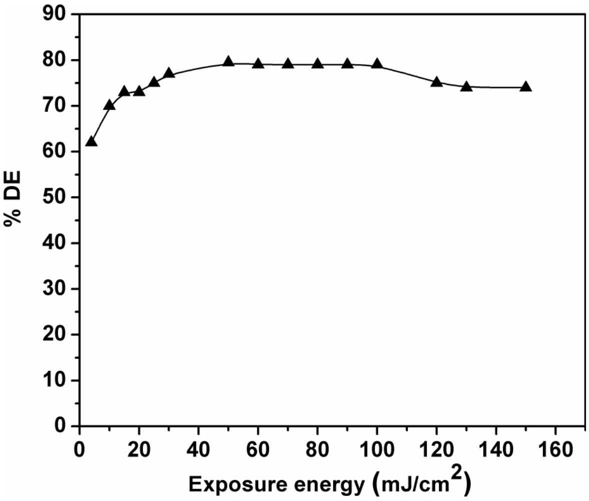


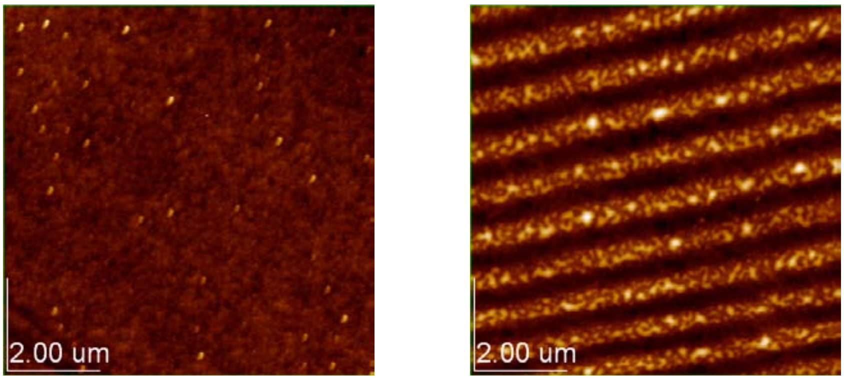
Fig. 6.3. Change in DE with exposure energy

Table. 6.5. Optimum film composition

Constituent	Concentration
PVA	15% w/v
AA	0.84 M
MB	0.04 mM
TEA	0.09 M
$AgNO_3$	0.06 mM

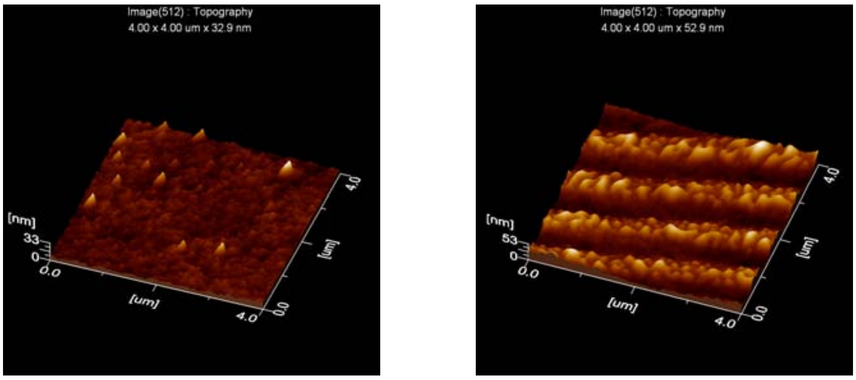
6.4. AFM analysis

The surface topographical change of the photopolymer layer after recording of grating was observed by atomic force microscope (AFM) (JEOL, JSPM 5200). AFM images (fig. 6.4) shows the surface topography of the spin coated photopolymer film before and after laser exposure. It is clear that significant change in the surface morphology is taking place after laser irradiation which culminates in the formation of a grating with period of ~1 micron. On comparing the height of the surface features, it is seen that the features in fig. 6.4 (b) are of more height than that in fig. 6.4 (a). This supports the fact that mass transport takes place in the sample during laser exposure which eventually results in the formation of a transmission grating. 3D AFM images for the same set of samples are depicted in fig. 6.5 and 6.6. The images reveal that coalescence of individual clusters takes place during the mass transport on laser exposure.



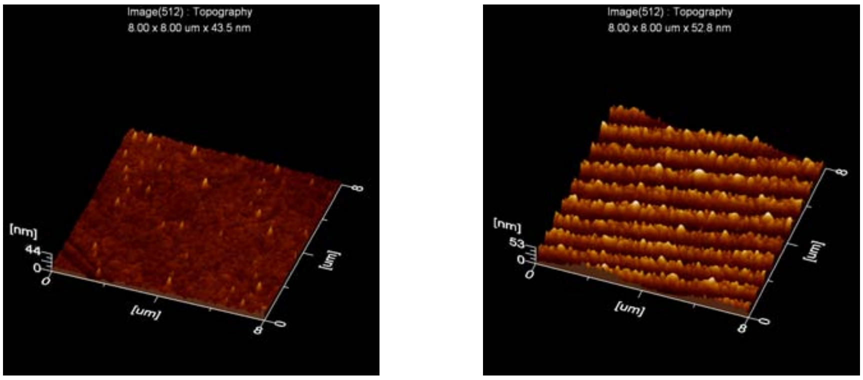
(a) (b)

Fig. 6.4. Surface topography of spin coated film (a) before and (b) after laser exposure. The image size is 8x8 μm^2 and z height is 44 nm in (a) and 53 nm in (b).



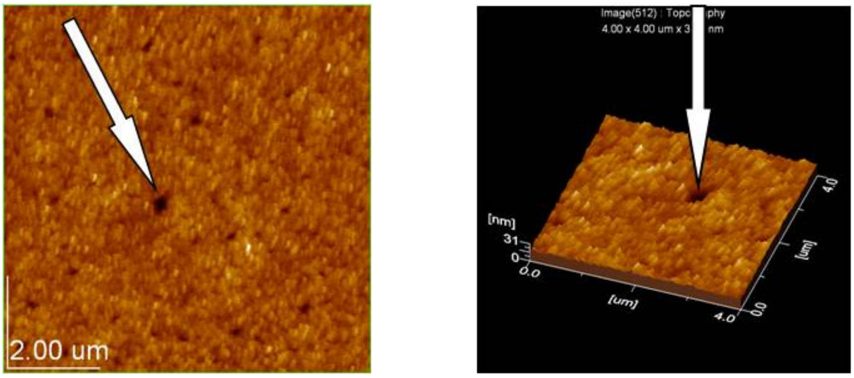
(a) (b)

Fig. 6.5. 3-D AFM images (a) before and (b) after laser exposure. The image size is 4x4 μm^2 and z height is 33 nm in (a) and 53 nm in (b).



(a) (b)

Fig. 6.6. 3D AFM images (a) before and (b) after laser exposure. The image size is 8x8 μm^2 and z height is 44 nm in (a) and 53 nm in (b).



(a) (b)

Fig. 6.7. Surface topography of gravity settled silver doped MBPVA/AA film (a) 2D image and (b) 3D image

Fig. 6.7 shows the AFM images of the gravity settled silver doped MBPVA/AA photopolymer film with same composition as that of the spin coated film. Arrows indicates the pin holes on the film surface. No such pin holes were observed in the case of spin coated films (Fig. 6.4 (a) and Fig 6.5 (a)). Hence it can be seen that the spin coated films exhibits high surface homogeneity when compared to the films prepared by gravity settling method.

6.5. Spatial frequency response

Inorder to determine the resolution of the film, gratings were recorded in the optimized film for different interbeam angles (from 10^0 to 140^0) maintaining the exposure energy as 50 mJ/cm^2. The spatial frequency of each grating was determined by Bragg's equation. Fig. 6.8 shows the spatial frequency response of the film. Peak DE was above 75% for gratings recorded with interbeam angles 15^0 to 40^0. This corresponds to spatial frequencies 410-1100 lines/mm. For higher spatial frequencies, DE was found to decrease gradually. At higher spatial frequencies, the fringe spacing is small which lead to the diffusion of short polymer chains away from the exposed region. This decreases the refractive index modulation which in turn decreases the DE. Grating with spatial resolution of 2000 lines/mm exhibited 65% DE. For still higher spatial frequencies (~3000 lines/mm), 25% DE could be obtained, which indicates the high spatial resolution of the film.

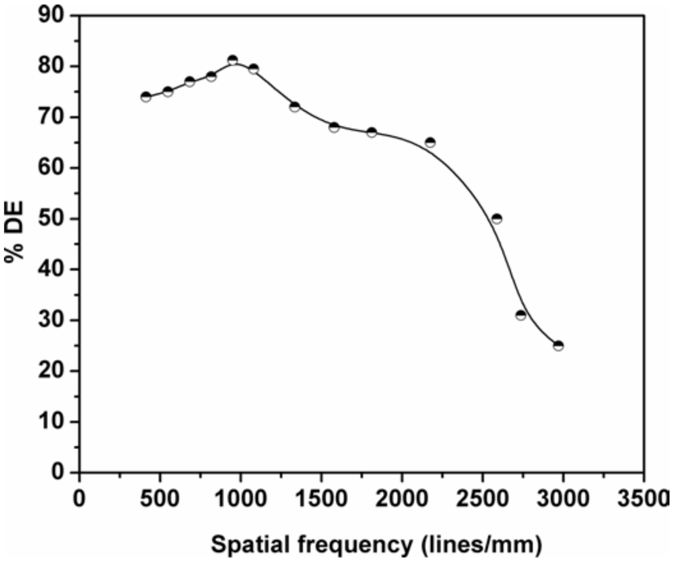


Fig. 6.8. Change in diffraction efficiency with spatial frequency

6.6. Storage life and pre- recorded shelf life

Inorder to determine the storage life of the grating recorded in the optimized film (spatial frequency: 1100 lines/mm, exposure: 50 mJ/cm^2), diffraction efficiency was measured on successive days by reconstructing the gratings using He-Ne laser beam (1μW). During the period of storage, the temperature of the storage place was in the range 28-30^0 C and relative humidity was 55-65%. A stable diffraction efficiency of ~80% could be attained for five months. After that a gradual decrease in diffraction efficiency was observed. Variation of diffraction efficiency of the recorded grating on storage is shown in fig. 6.9. It could be seen that after 9 months of storage, the diffraction efficiency reduced to 50% and this value is still retained.

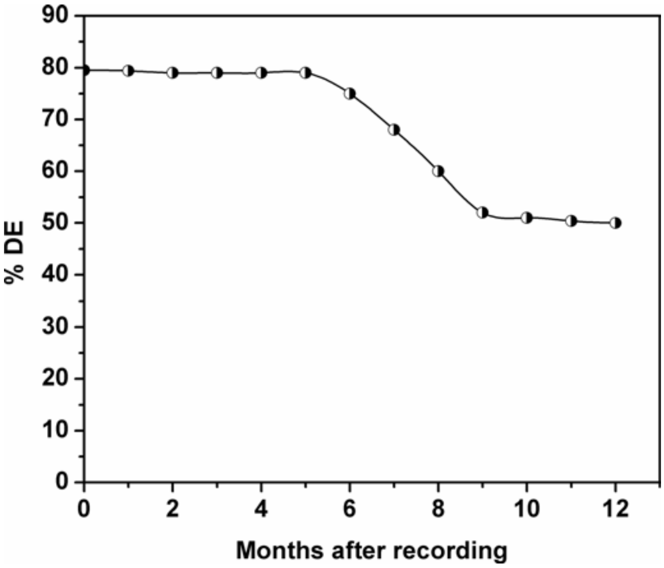


Fig. 6.9. Change in efficiency on storage

Inorder to check the pre-exposure shelf life of the optimized film, gratings were recorded in the film on successive days after preparation of the film. The films were stored in a dark box (temperature: 28-30^0 C, Relative humidity: 55-65%). The variation in diffraction efficiency with days after preparation is shown in fig. 6.10. It was seen that gratings with 60% diffraction efficiency could be stored for two weeks after preparation of the film. After that, a gradual decrease in DE was observed. Gratings could be recorded in the film with very feeble efficiency for three months.

From the shelf life studies on gravity settled films (fig. 3.21), it was observed that the gratings could be recorded in the film with diffraction efficiency of ≈70% for about three months. Gratings with 50% diffraction efficiency could be recorded in the films even after six months after preparation.

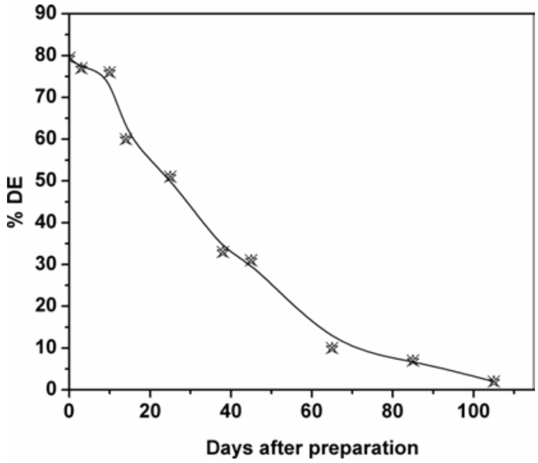


Fig. 6.10. Diffraction efficiency on ageing for the unsealed film

With the aim of improving the shelf life of the spin coated film, the film was covered by a glass plate and the edges were sealed using cyanoacrylate. Gratings were recorded in the sealed film by He-Ne laser (power at recording position~4mW, exposure energy: 50 mJ/cm^2, spatial frequency~1100 lines/mm, beam ratio-1:1). The variation of efficiency on ageing for the sealed photopolymer film is shown in fig. 6.11.

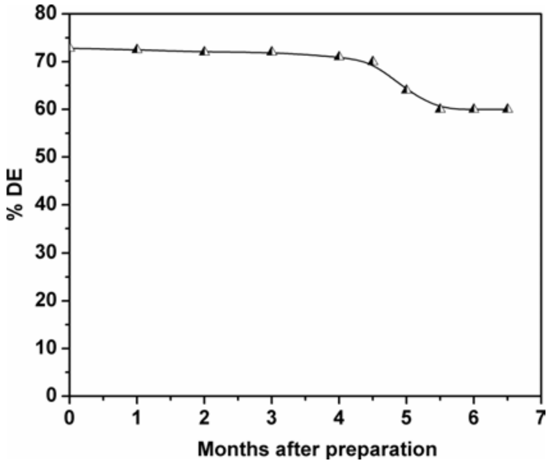


Fig. 6.11. DE on ageing for the sealed film

DE obtained was slightly low (72%) when compared to that of unsealed films. But it was observed that sealing has significantly improved the shelf life of the film. Gratings with 70% diffraction efficiency could be recorded for more than four months after film preparation. Even after six months of preparation, gratings could be recorded with an efficiency of 60%. Inorder to determine the storage life of the grating recorded in the sealed film, the diffraction efficiency was measured on successive days by reconstructing the grating using He-Ne laser beam. During the period of storage, the temperature of the storage place was in the range 28-30^0 C and relative humidity was 55-65%. Variation of diffraction efficiency on storage is shown in fig. 6.12. It was observed that a stable diffraction efficiency of ~70% could be attained for more than six months. In the case of unsealed film also, a diffraction efficiency of ~75% was obtained after six months of recording.

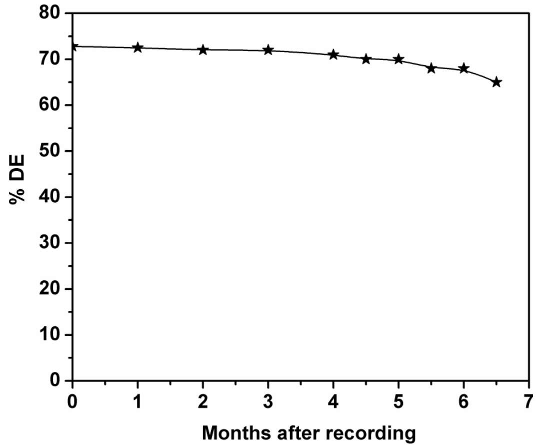


Fig.6.12. Variation of DE on storage for the sealed film

A comparison on the holographic properties of the spin coated and gravity settled films for gratings recorded using He-Ne laser is presented in table. 6.6. It could be seen that the spin coated photopolymer films exhibited high diffraction efficiency and energetic sensitivity than the gravity settled films. Grating recorded in the spin coated film prepared with optimum film composition showed a peak DE of 80% for 50 mJ/cm^2 exposure energy. High diffraction efficiency of 70% could be attained even for gratings recorded with an exposure of 10 mJ/cm^2. Whereas, in the case of gravity settled films, grating recorded using He-Ne laser showed peak DE of 75% for an exposure of 80 mJ/cm^2 and the DE obtained for 10 mJ/cm^2 was only 55%. Eventhough the spin coated films had poor shelf life than that of gravity settled films, shelf life could be improved by sealing the film. The spin coated film could be sealed properly and gratings with 60% DE could be recorded for more than six months after film preparation. Grating recorded in the sealed film showed DE of ~70% for more than six months after recording.

Table. 6.6. Comparison of gravity settled and spin coated films

Silver doped MBPVA/AA film	**DE (%)**	**Exposure energy (mJ/cm^2)**	**Spatial frequency (lines/mm)**	**DE on storage (After 6 months)**	**DE on ageing (After 6 months)**
Gravity settled	**75%**	**80**	**1100**	**50%**	**50%**
	55%	10			
Spin coated (unsealed)	**80%**	**50**	**1100**	**75%**	Grating could not be recorded
	70%	10			
Spin coated (sealed)	**72%**	**50**	**1100**	**70%**	**60%**

The gravity settled films had thickness non-uniformity especially towards the edges of the film and hence the films could not be sealed properly. In the case of gravity settled films, it was noted that the diffraction efficiency of the stored grating reduced to 50% after six months of recording. Gratings with 50% DE could be recorded in the gravity settled films after six months of preparation.

6.7. Recording of transmission holograms

Transmission holograms with good image quality were recorded in the films using He-Ne (632.8nm), frequency doubled Nd: YAG (532 nm) and Ar$^+$ (488 nm) lasers. Standard holographic recording geometry (fig. 2.13) was used for recording holograms. The photographs of the reconstructed holograms are shown in figures 6.13(a), 6.13(b) and 6.13(c).

Fig. 6.13 (a). Hologram recorded using He-Ne laser

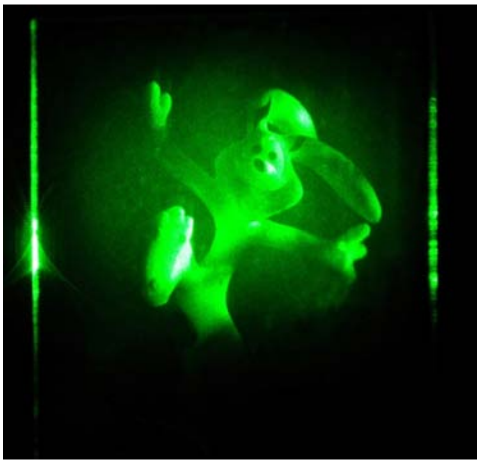


Fig. 6.13(b). Hologram recorded using Nd:YAG laser

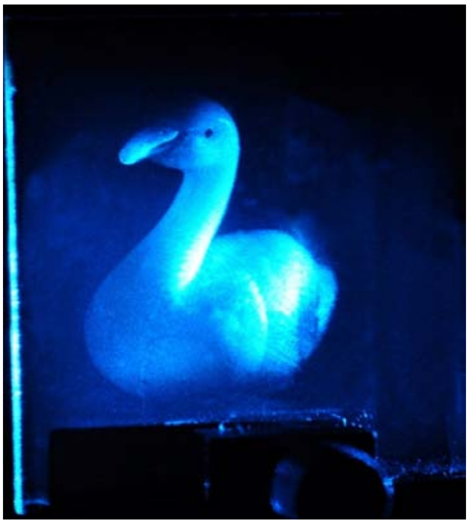


Fig. 6.13(c). Hologram recorded using Ar^+ laser

6.8. Recording of holographic data page

Two dimensional data pages are stored as Fourier Transform (FT) holograms in a holographic data storage system. A typical holographic data storage system consists of the following components:

- **A coherent source** (array) or collection of sources that provide object, reference and reconstruction waves. The laser beam produces a light beam of high spatial and temporal coherence, which is expanded, collimated and split into two parts. The first part called the signal arm is spatially modulated by a page of information after passing through a spatial light modulator (SLM). The second optical arm of the storage system called the reference arm defines the address where the information is to be stored.

- **A Spatial Light Modulator** (SLM) for preparing the data to be stored as two dimensional images. The SLM is a planar array of thousands of pixels. Each pixel is an independent optical switch that can be set either to block or pass light.
- **A detector** (array) and subsequent electronics for data readout, post detection signal processing and error correction. The output devices can be a charge coupled device (CCD) camera or CMOS pixel array.
- **Optics** for routing and imaging the wave fields within the system and system for multiplexing
- **A storage medium** to record the data as holograms.

The 4-f architecture [16] with the recording medium placed at the Fourier plane of the objective lens is one of the most commonly used geometries for recording data pages. However in this geometry, a high-intensity DC peak occurs in the Fourier plane of an amplitude modulated data page. These high-intensity peaks require a very large dynamic range from the holographic recording material and result in the saturation of the recording material like photopolymers. This saturation results in non-linear grating formation and an increase in the noise level of the reconstructed data page. Several methods exist to diffuse the high-intensity peaks and redistribute the energy into higher spatial frequencies inorder to increase the fidelity of the reconstructed data page [17]. Of these, moving the recording material away from the Fourier plane is the simplest and the most commonly used technique as it does not require any additional optical component as some of the other methods require. Defocusing the recording material away from the Fourier plane distribute light more evenly over the aperture of the hologram leading to high fidelity recording. In the present study, a defocused 4*f* HDS system was employed to record the image of a checker board pattern in the film using the output from frequency doubled Nd: YAG laser (532 nm).

The laser beam was split into two beams and then spatially filtered, using a microscope objective lens and a pinhole. Liquid crystal programmable matrix modulator (LCD modulator SLM-M) was incorporated in the path of one of the beams, inorder to spatially modulate the intensity of the light beam. The SLM-M provides a resolution of 832 x 624 pixels, each of which can be set to a relative transparency of 0 to 254. The pixel size was 27 μm x 27 μm and pixel pitch was 32 μm x 32 μm. The spatially modulated light beam was then directed to the recording medium by an objective lens. A reference beam mutually coherent with the image bearing beam was also incident on the recording medium. This creates a stationary interference pattern and is stored in the recording medium within a spot area of 0.5 cm^2. Fig. 6.14 shows the schematic diagram of a 4*f* HDS system with the recording material placed at a distance of 'z' away from the back Fourier plane of the object lens; spatial light modulator and lens (L_1, L_2) [17].

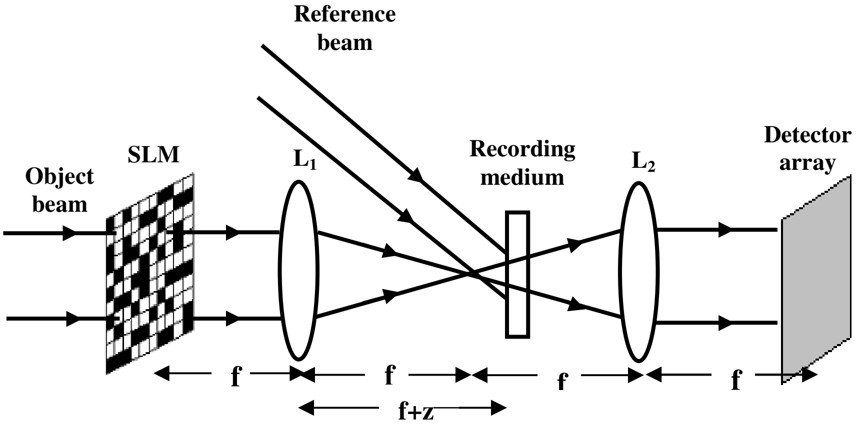
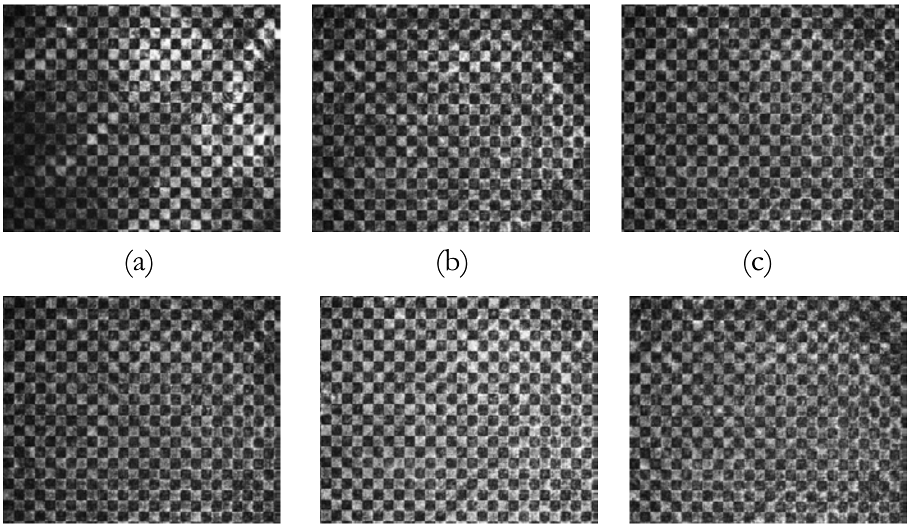


Fig. 6.14. Schematic diagram of a defocused 4*f HDS* system

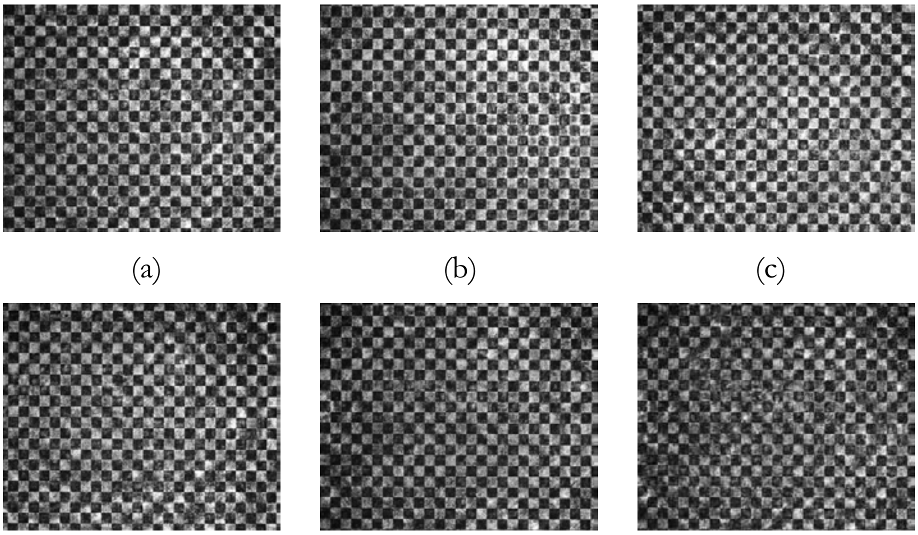
In the reconstruction stage, the recording medium which contains the data page was illuminated using a low power reference beam (0.15 mW) so as not to deform the recorded data page since the material is sensitive at this wavelength. Another lens was placed behind the recording medium to do the inverse Fourier Transform of the diffracted beam onto the detector (CCD). Megapixel CMOS camera with high resolution (1280 x 1024) was used for capturing the reconstructed image.

Parameters like defocusing distance (z), beam intensity ratio (R) and exposure energy were varied to record data page with good image fidelity. Initially, the exposure time was varied from 60 s to 320 s keeping the recording power as 0.3 mW. This corresponds to exposure energies of 18 to 96 mJ/cm^2. The beam ratio (R) was 1:1 and defocused distance (z) was 2 cm. The reconstructed images for different exposure energies are shown in fig. 6.15. Better image quality was shown by the data page recorded for an exposure time of 300 s (90 mJ/cm^2). Hence this exposure was chosen for further studies. Inorder to study the effect of beam ratio, images were recorded by varying beam ratio from 1 to 25. The exposure energy was kept as 90 mJ/cm^2 and the defocused distance (z) was 2 cm. Fig. 6.16 shows the reconstructed images for different beam ratios.


(a) (b) (c)

(d) (e) (f)

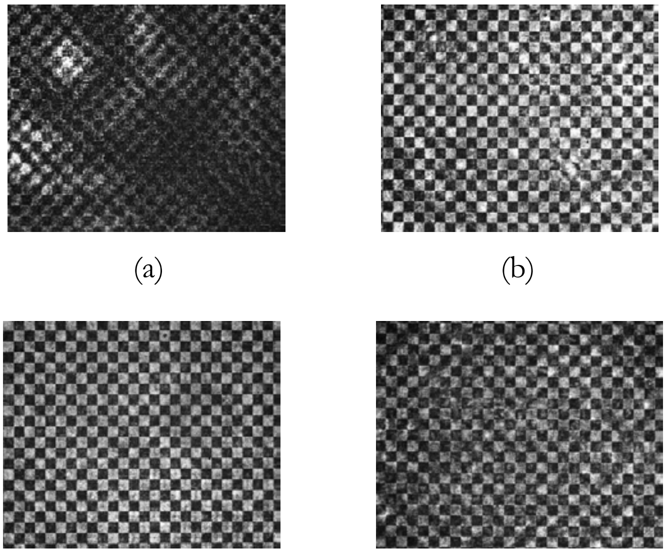
Fig. 6.15. Reconstructed images for different exposure energies (a) 60 s (b) 120 s (c) 180 s (d) 240 s (e) 300 s and (f) 320 s


(a) (b) (c)

(d) (e) (f)

Fig. 6.16. Reconstructed images for different beam ratios (a) R=1 (b) R=2 (c) R=3 (d) R=4 (e) R=10 and (f) R=25

It was observed that beam ratios 2 and 3 resulted in better image quality compared to others. In the present study, beam ratio 2 was selected for studying the effect of variation of defocusing distance on the image quality. Keeping exposure energy as 90 mJ/cm^2, defocusing distance (z) was varied from 1 cm to 4 cm. The reconstructed images obtained for different distances are shown in fig. 6.17. It could be seen that image quality is better for the defocused distance, z = 3 cm.



(a) (b)

(c) (d)

Fig. 6.17. Reconstructed images obtained for different defocused distances (a) z=1 cm (b) z=2 cm (c) z=3 cm and (d) z=4 cm

Image of a checker board pattern was recorded in the spin coated silver doped MBPVA/AA film using frequency doubled Nd: YAG laser (532 nm). Parameters like exposure energy, beam intensity ratio and defocusing distance was varied inorder to study their effect on the quality of the reconstructed image. Figures 6.15, 6.16 and 6.17 clearly depict the good image fidelity of the reconstructed images. It was noted that better image fidelity was shown by the image recorded with an exposure energy of 90 mJ/cm^2, beam ratio (R) equal to 2 and defocused distance (z) of 3 cm. Figures 6.18 and 6.19 shows the original and reconstructed images of checker board pattern recorded using these parameters. Efforts can be made to determine the bit error rate (BER), which provides a quantitative measure of the image quality of the reconstructed images [15, 17, 18].

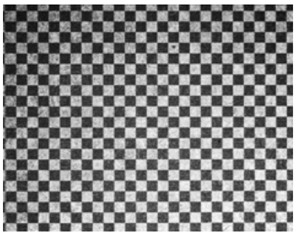


Fig.6.18. Original image

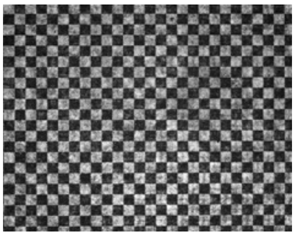


Fig. 6.19. Reconstructed image

6.9. Conclusions

Holographic transmission gratings with 80% diffraction efficiency could be stored in the optimized film using 632.8 nm He-Ne laser. Bright transmission holograms could be recorded in the film. The image of a checker board pattern recorded in the film using optimum recording parameters could be reconstructed with good image fidelity. Hence from the present study, the suitability of the developed film for holographic data storage could be successfully demonstrated.

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7

Summary and Outlook

The main focus of the present study was to develop competent metal ion doped photopolymer material with enhanced holographic properties. Efforts were made to develop silver doped photopolymer system and to study its suitability for holographic applications. This chapter summarizes the research work and verify whether the proposed objectives have been achieved. Major achievements of the present study and scope for future work are also outlined here.

7.1. Summary of the work

Holography is one of the remarkable achievements of modern science and technology. With its widespread applications, holography has the potential to stretch boundaries and impact the society profoundly. Fields of applications include interferometric measurement techniques, image processing, holographic optical elements, holographic memories, security holograms and so on. One of the major challenges in the area of holographic technology has been the development of suitable recording materials. Advances in media and recording methods can further enhance the prospects for holography to become a realizable next-generation storage technology. While many materials have been developed as media for holographic storage, most suffer from disadvantages that prevent their use in practical systems. Photopolymer materials are attractive candidates for write-once read-many (WORM) data storage applications because they can be designed to have large modulations in their refractive index and high photosensitivity, record permanent holograms and are capable of real-time image development [1]. Research work on photopolymer materials are also on the rise and efforts are made by scientists worldwide to improve the properties of existing materials and also to develop new materials with better properties. The present study focussed on the development of metal ion doped photopolymer recording media with improved holographic properties. Efforts were made to optimize the composition of the photopolymer material and to investigate its suitability for holographic applications.

Silver doped photopolymer system consisting of poly(vinyl alcohol) as the binder matrix, acrylamide as monomer, methylene blue and triethanolamine as photoinitiation system and silver nitrate as crosslinker was developed. The films were fabricated by gravity settling and spin coating methods and experiments were carried out to optimize the film composition so as to ensure the best holographic performance. Incorporation of silver ions into methylene blue sensitized poly(vinyl alcohol)/acrylamide photopolymer was observed to give better holographic performance compared to other metal ion doped photopolymer holographic recording media [2]. Silver doped MBPVA/AA films were found to have good energetic sensitivity and transmission gratings recorded in the film using He-Ne (632.8 nm), frequency doubled Nd: YAG (532 nm) and Ar^+ (488 nm) lasers exhibited high diffraction efficiency of above 70%. The recorded gratings could be stored for more than three years with good diffraction efficiency. The feasibility of recording bright transmission holograms in the material could be successfully demonstrated. The developed panchromatic photopolymer system is excellent on account of its wide spectral sensitivity, high diffraction efficiency, good energy sensitivity, high resolution, cost effectiveness, ease of fabrication and real-time imaging capabilities.

Holographic multiplexing studies were carried out to check the suitability of the film for holographic data storage applications. Angle and peristrophic multiplexing techniques were employed for storing multiple transmission gratings in the films. Gratings were multiplexed by constant and iterative exposure scheduling methods. The storage capacity of the film was determined by calculating the dynamic range (M/#). Diffraction efficiency and M/# obtained were compared to determine which method enabled the greatest number of gratings to be recorded with uniform diffraction efficiencies. By peristrophic multiplexing method, 30 nearly uniform plane wave gratings with M/# equal to 4.7, could be recorded in the developed photopolymer film. The M/# value obtained while recording 30 gratings in this 130 μm thick acrylamide based photopolymer layer is assumed to be larger than the reported values for multiplexing equal number of gratings in acrylamide based photopolymer materials with similar composition and layer thickness [3].

Photopolymer films were fabricated by spin coating technique and holographic transmission gratings with 80% diffraction efficiency could be recorded in the optimized film with 632.8 nm He-Ne laser. The image of a checker board pattern was recorded in the film with frequency doubled Nd: YAG laser (532 nm). The reconstructed image captured using CCD camera showed good image fidelity. Hence from the present study, the suitability of developed film for holographic data storage applications could be successfully demonstrated.

7.2. Major achievements

- Silver doped photopolymer films were introduced as a novel holographic recording material
- Demonstrated the potential of the developed film as a competent panchromatic recording medium
- Multiple holographic gratings were recorded in the same volume of the material
- Bright transmission holograms were recorded in the material
- The feasibility of recording data page with good image fidelity could be demonstrated

7.3. Outlook

This thesis has discussed the development of a new metal ion doped panchromatic photopolymer for various holographic applications. High-quality panchromatic holographic recording material with high diffraction efficiency, high photosensitivity and high spatial resolution is one of the key factors for the successful recording of true colour holograms. The capability of the developed material for multi-colour holography can be investigated.

In the present work, multiplexing studies were carried out using He-Ne laser (632.8 nm). Multiplexing can be done using low wavelength lasers like Ar^+ ion (488 nm) and frequency doubled Nd: YAG (532 nm) lasers, so as to increase the storage capacity. The photopolymer film studied had a thickness of only 130 μm. Films with high thickness (~500 μm) is highly essential for competitive holographic memories [4]. Hence films with high thickness can be fabricated and efforts can be made to record more holograms or gratings in the material.

In the present study, attempts were made to record data page in silver doped MBPVA/AA photopolymer film. Image of a checkerboard pattern was recorded in the film, which could be reconstructed with good image fidelity. Efforts can be made to determine the bit error rate (BER) which provides a quantitative measure of the image quality of the reconstructed image [4]. Multiple holographic data pages can also be recorded in the material making use of different multiplexing techniques [5].

Holographic optical elements (HOEs) are widely used in optical sensors, optical information processing, fibre optics, optical scanners and solar concentrators [6]. The suitability of the developed film for recording holographic optical elements like lenses, beam splitters and filters can be studied.

The suitability of a reflection hologram recorded in acrylamide based photopolymer for visual indication of environmental humidity is reported [7]. Studies can be done to optimize the film composition for recording of reflection holograms.

An improvement in the spatial resolution of PVA/acrylamide based photopolymer by using a low molecular-weight poly (vinyl alcohol) binder was recently reported [8]. Effect of the molecular weight of the binder matrix on the holographic properties of the developed photopolymer system can be investigated.

Incorporation of nanoparticles into photopolymer system is reported to enhance the resolution and improve the dimensional stability of the system [9, 10]. Hence efforts can be made to incorporate silver nanoparticles into the photopolymer and its influence on the holographic properties can be studied.

This thesis was a small venture towards the realization of a big goal, a competent holographic recording material with excellent properties for practical holographic applications. As a result of the present research, we could successfully develop an efficient panchromatic photopolymer system and could demonstrate its suitability for recording transmission holograms and holographic data page. The developed photopolymer system is expected to have significant applications in the fields of true-color display holography, wavelength multiplexing holographic storage, and holographic optical elements. Highly concentrated and determined effort has yet to be put forth for this expectation to become a reality.

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Abbreviations

AA	Acrylamide
ACF	Acriflavine
AFM	Atomic force microscopy
BER	Bit error rate
BMA/MBA	N, N'- methylenebisacrylamide
CCD	Charge coupled device
CGH	Computer generated hologram
CMBPVC	Complexed methylene blue sensitized poly(vinyl chloride)
CROP	Cationic-ring opening
CTA	Chain transfer agent
CW	Continuous wave
DCG	Dichromated gelatin
DCPVA	Dichromated poly(vinyl alcohol)
DE	Diffraction efficiency
DEA	Diethanolamine
DETN	Diethylamine
DHEBA	N, N'- dihydroxyethylenebisacrylamide
DMAA	Dimethylacrylamide
EA	Ethanolamine
EB	Erythrosine B
EGDMA	Ethylene glycol dimethacrylate
HABI	Hexaarylbiimidazole
HBPs	Hyper branched polymers
HDS	Holographic data storage
HEMA	2-hydroxy ethyl methacrylate
HMA	N-hydroxy methyl acrylamide
HOE	Holographic optical element
HUD	Head-up display
LVDT	Linear variable differential transformer
M/#	M-number
MB	Methylene blue
MBPVA	Methylene blue sensitized poly(vinyl alcohol)
MBPVA/AA	Methylene blue sensitized poly(vinyl alcohol)/Acrylamide
MDEA	Methyldiethanolamine
MOBZ	Mercapto-benzoxazole
MTF	Modulation transfer function
ND	Neutral density
NPDD	Non-local photopolymerization driven diffusion
NPs	Nanoparticles
PA	Poly(acrylamide)
PAA	Poly(acrylic acid)
PAP	Photoaddressable polymer
PETA	Pentaerythritol triacrylate
PMMA	Poly(methyl methacrylate)
PQ	Phenanthrenequinone

PR	Photorefractive
PRF	5’-riboflavin monophosphate
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
RB	Rose bengal
RGB	Red-geen-blue
RH	Relative humidity
RI	Refractive index
SHPE	Silver halide photographic emulsion
SLM	Spatial light modulator
TEA	Triethanolamine
TETN	Triethylamine
TN-LCDs	Twisted-Nematic liquid crystal displays
WORM	Write-once-read-many
YE	Yellowish eosin
2ISF	4,5-diiodosuccinylfluorescein
3D	Three dimensional