

Review of Materials for Holographic Optics

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The success of applications involving holographic optical elements depends on the performance of the recording materials used to form the elements. Selection criteria of a recording material must include not only the usual optical considerations such as achievable diffraction efficiency and optical quality, but also the environmental stability and the ease and cost of manufacture of the elements. Three materials are in widespread use and development for holographic optics applications: dichromated gelatin, photopolymer, and photoresist. Dichromated gelatin forms very high-quality holograms, but is relatively difficult to produce and must be protected from moisture. Dichromated gelatin holograms are in use as head-up display combiners, narrowband filters, and diffraction gratings. Photopolymer is generally easier to use, typically does not require wet processing, and usually has good environmental stability. Photopolymer holograms are in use or under development for several applications including laser eye protection filters, automotive lighting devices, and security holograms. Photoresist forms surface relief holograms that can be replicated by epoxy or, for large production runs, by embossing techniques. Photoresist holograms are used as diffraction gratings for scientific applications, as patterns for fabrication of photonic devices, and as master holograms for security applications such as credit card holograms.

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Introduction

Numerous recording materials have been used or evaluated as recording media for the fabrication of holographic optical elements. A large body of literature describes holographic materials and the development of those materials for a wide variety of holographic optics applications. The reader is also referred to the patent literature, for example to the U.S. Patent classifications 430/1, 430/2, and 359/3 for holographic materials developments and classification 359/15 for applications of holographic optical elements. Because of this author's experience and interest in the manufacture of holographic optics, this article's primary focus will be on materials that have been developed to the extent that they are in use in existing products or under serious investigation for new products and applications.

Following a brief review of some general materials considerations important to holographic optics, this work focuses on the mechanism, performance, and applications of three of the principal recording materials in current use. These materials (dichromated gelatin, photopolymer, and photoresist) have proved most suitable for practical holographic optics and have received the greatest amount of development and attention to date.

Hologram Types—Volume versus Surface

An important distinction in holographic materials is whether they form volume or surface holograms (see, for example, Ref. 1). The characteristics and performance of volume holograms are determined by the interactions between the incident wavefront and the recorded fringe structure within the volume, or depth, of the photosensitive

material.^{1,2} In those holograms, the fringe spacing is small relative to the thickness of the hologram so that the incident wavefront passes through many fringes in its path through the hologram. Consequently, the wavefront interacts with many fringes and interference effects between the bits of light reflected from each fringe can give rise to strong diffraction by the hologram in preferred directions and wavelengths. The effect is analogous to Bragg diffraction of x-rays by crystals and, in fact is a form of Bragg diffraction that can be described by the Bragg equation.

Because of the interference effects, typical volume phase holograms diffract light with high diffraction efficiency only for a limited range of wavelength and angles. In applications where high efficiency is needed for a broad range of angles and wavelengths, that behavior can be a limitation. In other applications, that property allows the holographic element to act as a wavelength selective, or dichroic, element, redirecting (diffracting) light incident at certain wavelengths and angles and transmitting light at others.

In surface holograms, the incident wavefront interacts with the surface profile of the hologram. The hologram material consequently can be very thin, needing only sufficient thickness to support the surface relief required to form the hologram itself. (Of course, the hologram or a supporting substrate must have sufficient thickness to provide the rigidity or flatness required by the application). The diffraction efficiency of surface holograms depends primarily on the depth and shape of the relief structure and can be as high as 100% in certain cases. At low spatial frequency, a surface hologram diffracts light into several diffracted orders. But with sufficiently high spatial frequency, the surface hologram diffracts light into a single order because the other orders are evanescent. Surface holograms are often used in reflection, in which case the incident and diffracted wavefronts do not pass through the medium or substrate. Here, the hologram

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surface is usually overcoated with a reflective layer such as aluminum to enhance reflectivity.

In addition to dividing hologram types according to whether they are volume or surface (sometimes referred to as thick or thin, respectively), they can also be divided by whether they operate by absorption effects or phase effects (or a mixture).¹ Because pure absorption holograms have low diffraction efficiencies, most if not all applications of holographic optical elements make exclusive use of materials that form phase holograms, which are capable of achieving diffraction efficiencies of up to 100%. Consequently, this review considers only phase holograms and materials that form phase holograms.

Hologram Replication

For major applications of holographic optics, optical or mechanical replication techniques are desirable for production of the holographic elements. Holograms can be copied from master holograms by optical techniques,³⁻⁹ although in many applications optical copying has not supplanted fabrication of elements on a one-by-one basis. Brumm⁴ suggested copying a volume transmission hologram by illuminating a master hologram at the Bragg angle to produce two transmitted wavefronts: first and zero orders. The two wavefronts interfere to form a new fringe pattern that can be recorded by a copy hologram. Ideally, for transmission holograms, the master hologram has a diffraction efficiency of about 50% to maximize the contrast of the fringe pattern recorded by the copy. Although the copy hologram in essence is an original two-beam hologram, its fabrication is typically simplified by placing it in contact with the master hologram to minimize space and stability requirements during exposure. An index matching fluid is normally used to provide optical contact, minimizing surface reflections that can give rise to spurious holograms.

A similar approach applies to reflection holograms, where the incident wavefront passes first through the copy.^{5,7} With the copy in front of the master, the wavefront diffracted or reflected by the master enters the copy to interfere with the incident wavefront, forming the fringe pattern. As with transmission holograms, the space and stability requirements are minimized by placing the master and copy holograms in physical and optical contact.

A recent advance in optical replication has been the development of machines for mass production of volume holograms in photopolymer films.⁷⁻⁹ Armstrong and Tipton⁷ describe a machine that makes contact copies of reflection holograms on Du Pont photopolymer: a web of photopolymer is continuously moved over a cylinder containing a master reflection hologram. As the cylinder rotates, the master and copy film move through an exposure station, after which the copy film is transported to additional process stations to complete hologram formation.

Surface holograms can be used to make embossing masters for large volume production runs.¹⁰⁻¹² After a master hologram is formed in photoresist, a metallic layer such as nickel is electroplated over the surface of the hologram. The metallic layer is subsequently removed from the photoresist and used to emboss the holographic surface pattern into thermoplastic films. A well-known application of this type of holographic replication is the security hologram found on credit cards.¹²

Dichromated Gelatin

History. Chromium compounds have been used with organic colloids since about 1830 to form photosensitive

media.¹³ A number of applications have developed from the phenomenon that colloidal coatings such as gelatin are normally soluble in water, but when sensitized with a chromate compound become insoluble in areas exposed to light. Relief patterns recorded in dichromated gelatin plates, for example, have found use as printing plates. In 1971 Meyerhofer¹⁴ reported using this phenomenon to record surface relief holograms in unhardened dichromated gelatin, although the relief height falls at high spatial frequencies. Nearly all reported DCG holography is performed with hardened gelatin, however, which is insoluble and has a high melting point.

Shankoff¹⁵ first reported holograms recorded in dichromated gelatin in 1968. During the 1970s, investigators explored the capabilities of the medium and found that while it was capable of forming superb holograms, it could be difficult to achieve those results on a consistent basis. Nevertheless, those investigations led to several important military and commercial applications of holographic optics including beam combiners for head-up displays (HUDs), holographic notch filters, and volume phase diffraction gratings.

Hologram Formation in Dichromated Gelatin.

Dichromated gelatin (DCG) films are sensitized with ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$. The exposure is believed (Ref. 13, p. 62) to reduce Cr^{6+} ions to Cr^{3+} ions that form complexes with gelatin molecules creating crosslinks between the molecules. These crosslinks harden the gelatin, rendering it less soluble in water and raising its melting point. Kosar (Ref. 13, p. 67) noted that the chemistry is complex and the exact mechanism of gelatin hardening, or crosslinking, is not well understood.

A number of authors have advanced hypotheses and observations concerning the mechanism of hologram formation in hardened dichromated gelatin.¹⁶⁻²² Curran and Shankoff¹⁶ suggested that DCG forms cracks along the fringe planes giving rise to air-filled voids that account for the high index modulation observed in DCG holograms. Meyerhofer¹⁷ proposed and Sjölander²⁰ further investigated a mechanism where isopropanol binds with both Cr^{3+} and gelatin at the crosslink sites, increasing the refractive index at those sites sufficiently to lead to high index modulation. Samoilovich, Zeichner, and Friesem¹⁸ suggested that the formation of a dichromated gelatin hologram results from the modulation of the gelatin hardness and the response of the gelatin to the development process. The authors verified that hardening reduces the extent of gelatin swelling in water. Figure 1, for example, shows their measurements of the effect of gelatin hardening on swelling in water for the case in which chrome alum was added to the coating solution to harden the gelatin and the swelling was measured by comparing the weight W of the swollen gelatin film with its initial weight W_0 . In the Samoilovich model, therefore, the initial development steps cause differential swelling, with greater swelling in the less hardened (i.e., less heavily exposed) regions. The rapid dehydration at the end of the development process is thought to freeze the density variations in place, leaving a corresponding modulation in refractive index.

The Samoilovich model is consistent with the observation that dehydration of the hologram must be rapid. In the case of slow drying, water leaves the swollen regions at a slow enough rate that the gelatin can relax to its former state, or density, with little or no observed diffraction. The relaxation occurs because water acts as a plasticizer within the gelatin,²³ allowing the molecules

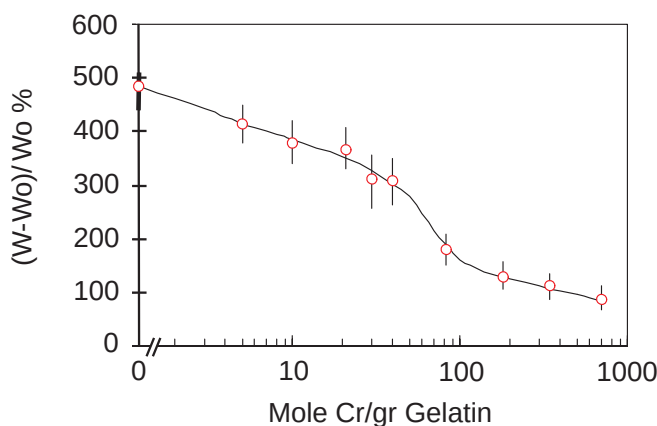


Figure 1. Effect of hardening on swelling of gelatin in water (after Samoilovich, Zeichner, and Friesem¹⁸).

to rearrange into a more compact structure. When rapid dehydration takes place in alcohol, water is removed before the gelatin molecules can rearrange, and the swollen structure remains, suggesting that the resulting density in those regions must be significantly lower than in the original film before development.

The procedure of recording holograms in dichromated gelatin typically involves sensitizing a layer of gelatin with ammonium dichromate, exposing the layer to a holographic interference pattern, and developing the hologram through a sequence of baths that begin with water and end with isopropanol. Dichromated gelatin coatings can be derived from plates and films coated with photographic emulsions,^{24–27} or prepared by coating substrates with aqueous gelatin solutions. The aqueous solution method offers more flexibility in the choice of gelatin thickness and substrate size, shape, and material. In addition, the gelatin coating solution can be sensitized either prior to or after the coating operation. In either case, the coating is sensitive to particulate contamination and must be performed at an elevated temperature at which the gelatin coating solution is liquid. Coating methods used successfully to make dichromated gelatin films include doctor blade, dip, spin, cast, and gravity settling.

An important aspect of fabricating high-quality DCG holograms is controlling gelatin hardness, both the average film and the differential hardnesses between exposed and unexposed (or more lightly exposed) fringes. Shankoff¹⁵ and Lin²⁸ noted that the processed hologram may have a milky appearance that can be eliminated by increasing the average hardness of the film prior to the development process. A harder film has a more glasslike appearance, which is often desirable, but if the average hardness of the film is too great, there may be insufficient dynamic range to establish the hardness differential required for the holographic fringes, resulting in low diffraction efficiency. The average hardness of holographic films can be increased by soaking the film in a chemical hardening agent, by exposing the sensitized film to uniform light (such as white light), and/or by baking the film at an elevated temperature (Ref. 13, p. 61). Discussions on hardening of DCG films can be found in Refs. 13, 18 through 20, and 29.

Dichromated gelatin is sensitive to wavelengths in the UV-blue-green region of the spectrum, with increased sensitivity at shorter wavelengths.³⁰ (Solano, Lessard, and Roberge,³¹ however, report a very low but nonzero sensi-

tivity at a wavelength of 633 nm.) At a wavelength of 514 nm, the exposure sensitivity is²⁵ on the order of 100 mJ/cm², but to produce a given level of hologram efficiency, the actual sensitivity depends on a number of factors including sensitizer concentration, gelatin hardness, the amount of moisture in the gelatin film, and the temperatures used in the developing baths. A considerable amount of literature exists on the use of additional sensitizers to extend the region of sensitivity to the red.^{32–34} Kubota and Ose,³⁵ for example, recorded full-color holograms in DCG sensitized with the dye methylene blue. To avoid the difficulties of sensitizing DCG to red wavelengths, the alternative is to work with a large wavelength shift. This need led to a body of literature on approaches to compensating for wavelength shifts in DCG holograms.^{36–39}

A typical development procedure is a 10 min wash in water, followed by a 5 min soak in a 50:50 mixture of water and isopropanol, and ending with a 5 min soak in 100% isopropanol. The water bath swells the gelatin and removes unreduced dichromate, rendering the material insensitive to further exposure as well as greatly reducing optical absorption by the developed hologram. The alcohol baths cause the rapid dehydration of the gelatin layer critical to the formation of the hologram. An interesting and useful characteristic of DCG holograms is that they can be put through the developing baths more than once,^{15,28} allowing the recovery of a hologram lost, for example, by exposure to high ambient humidity. More importantly, Chang⁴⁰ suggested reprocessing to adjust the index modulation of a hologram, an effective technique when achieving a particular level of modulation is important.

Many variations exist on the basic recipe for DCG holograms. One or more of the hardening steps mentioned above are usually included to optimize the performance of the completed hologram. The number and concentrations of the alcohol baths are often altered; Kubota,⁴¹ for example, uses three sequential isopropanol baths of 30%, 70%, and 100% concentration. The temperature of the processing solutions is also a variable. Higher solution temperatures produce holograms with higher diffraction efficiencies, but ultimately cause what is often referred to as cracking, where the gelatin acquires a hazy appearance and the hologram may exhibit surface defects. Achieving the maximum performance from DCG holograms often means treading a narrow line between pushing the refractive index modulation while not driving the film so hard that it exhibits signs of cracking.

McGrew³⁰ noted that depending on the processing conditions, DCG reflection holograms can be formed with relatively narrow bandwidth and thickness close to the exposure thickness or with very large bandwidth and increased thickness and Bragg wavelength. Owen⁴² noted that in the broad band region the spectral response of the hologram may be shifted by as much as 60 nm and suggested that the shift is the result of a different mechanism of hologram formation (microcracking), which produces lower gelatin hardness. Several references in the literature^{30,43–46} discuss broadband holograms, reporting bandwidths of 100 nm or more and pronounced wavelength shifts toward the red, but McGrew³⁰ and Boj, Crespo, and Quintana⁴⁶ observed that these holograms have higher levels of scattering. The large bandwidth holograms are produced by using elevated temperatures in the process baths, believed^{45,46} to cause an increase in the spacing between fringe planes from the gelatin–air surface to the gelatin–glass surface of the hologram.

The hygroscopic nature of gelatin imposes a requirement to provide a hermetic seal to keep moisture from

the hologram. Dichromated gelatin holograms left exposed to high levels of ambient humidity tend to fade with time, although recovery is often possible by putting them through the development step again. Unfortunately, the sensitivity to moisture is high enough that despite a good deal of research, DCG holograms cannot be used with plastic substrates or covers without an additional moisture barrier such as glass. The usual approach to fabricating a stable hologram is to bake it to ensure dryness and then to cement a glass cover plate to the gelatin layer with an optical adhesive. The gelatin is often recessed a few millimeters from the edge of the glass so the optical cement forms a moisture barrier at the hologram edge. DCG holograms so protected can be made to have a high degree of environmental integrity, with excellent long-term stability at any level of humidity and at temperatures to at least 100°C (Naik, Mathur, and Pappu⁴⁷ report that uncemented and uncoated DCG holograms can withstand temperatures up to 175°C).

In some applications, the substrate and cover have antireflection coatings to minimize losses caused by Fresnel reflections at glass-air surfaces. Those coatings can be important to the effectiveness of the element, but since AR coatings are usually applied at elevated temperatures that would damage gelatin, they must be applied to the glass prior to the fabrication of the hologram.

Accurate modeling of hologram behavior requires a knowledge of the refractive index of the gelatin, especially in its final form as a hologram. A number of authors have reported measured values of the index of DCG films and holograms,^{15,48-51} in which some suggest that the surface index differs from the bulk, or average, refractive index. In a thorough study of the refractive index of volume holograms, Campbell, Kim, and Kostuk⁵² described the difficulty of determining the average, or bias, refractive index of materials that have a modulated refractive index. Nevertheless, by using a method suggested by Rallison and Schicker,⁵⁰ they established that the bias index of DCG holograms is about 1.35, whereas measurements made by other techniques indicate an index of about 1.50.

Performance. Dichromated gelatin can form volume phase holographic elements of unsurpassed optical quality. High diffraction efficiencies are possible in holograms that have low levels of scatter and little or no absorption. Refractive index modulations have been reported as high as 0.08 and 0.10 and more recently 0.13 and 0.14 (Refs. 25, 49, 45, 53, respectively). High refractive index modulations provide for efficient holograms in thin gelatin films, so relatively large angular and spectral bandwidths can be achieved. DCG works over a wide range of thicknesses; at one extreme Shankoff¹⁵ used films of a few microns thickness, while Liu and colleagues⁵⁴ investigated holograms in films as thick as 84 μm and Au, Newell, and Solymar⁵⁵ discussed holograms with thicknesses in excess of 100 μm . Rallison and Schicker⁵⁶ described practical problems they encountered in working with very thick films.

Major limitations of DCG are its low exposure sensitivity typically requiring long exposures with high-power lasers; limited spectral sensitivity; the need for a hermetic seal for long hologram life; and the difficulty of obtaining consistent, high-quality results with the process. The sensitized gelatin not only has a limited lifetime, but as frequently noted also undergoes slow, continuous dark reactions before and after exposure that change the properties of the material with time.^{13,25,29} Sergeant and Hurst⁵⁷ wrote with insight, however, when they noted that the

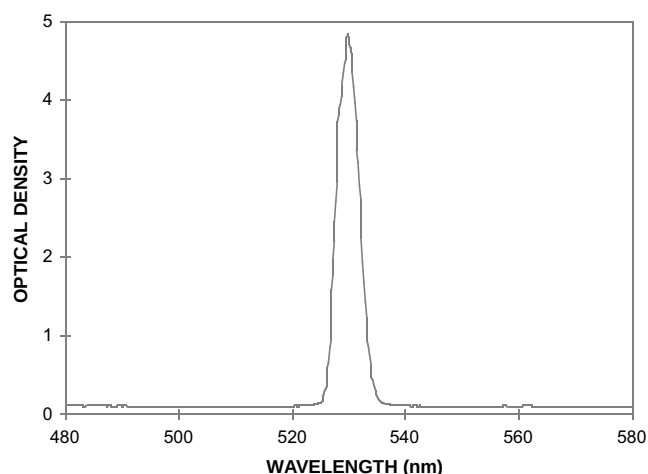


Figure 2. Optical density as a function of wavelength for a narrowband notch filter in dichromated gelatin.

complex processing of DCG makes for a flexible material with a wide range of attainable characteristics.

Applications of Dichromated Gelatin. Dichromated gelatin elements are currently in production and use as head-up display combiners,⁵⁷⁻⁶¹ narrowband rejection filters,^{21,62-65} and diffraction gratings.⁶⁶⁻⁶⁹ For head-up displays, low absorption and scatter are critical performance attributes. An important aspect of DCG holographic combiners is the design compromise between photopic (or see-through) transmission and reflectivity (or diffraction efficiency), which usually requires a gelatin thickness in the range of 8 to 12 μm and a process that provides a consistent and uniform index modulation. The challenge in manufacturing holographic combiners for military applications is meeting a stringent set of specifications, including reflectivity levels and uniformity, high transmission, lack of ghost or secondary holograms,^{70,71} and mil-spec optical quality over a relatively large area. Nevertheless, as Sergeant and Hurst⁵⁷ also noted, the success of holographic combiner production programs attests to the utility of dichromated gelatin for holographic elements.

Dichromated gelatin forms superb rejection, or notch, filters. The filters can have extremely high rejection efficiencies, narrow bandwidths, and steep sides to the rejection notch. Figure 2 is a plot of optical density (OD) as a function of wavelength for a notch filter manufactured in DCG for use in Raman spectroscopy, where OD is defined as $OD = \log(1/T)$ and T is the transmittance of the filter. An optical density of 4.0, for example, means that the transmittance is one part in 10^4 , implying a combined absorption and diffraction efficiency of 99.99%. Because the absorption and scattering are very low, most of the rejection is by means of an extremely high diffraction efficiency. Filters are routinely manufactured with a performance of OD 6 and minimal scattering. Such filters are in widespread use in Raman spectroscopy, not only for their high ODs and narrow bandwidths, but also because, as Fig. 3 demonstrates, they lack ringing or extra reflection bands outside the rejection notch, which are obtained with traditional dielectric filters.⁷²

The manufacture of DCG transmission gratings has led to the development of compact and efficient Raman spectrometers^{66,67} that exploit the high diffraction efficiency and spatial frequency capabilities of DCG. Figure 4 is a schematic diagram of an axial spectrograph configuration⁶⁶ that

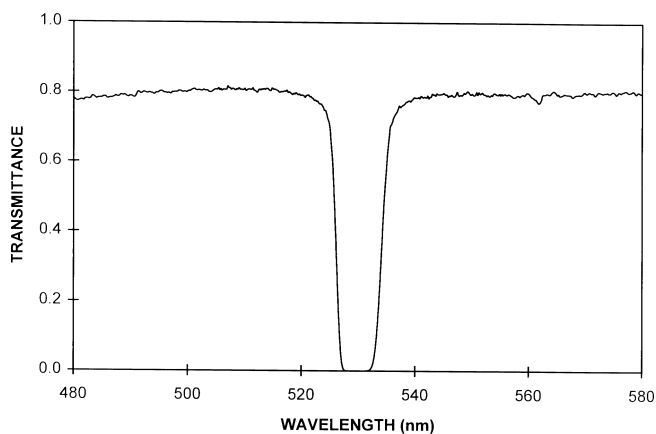


Figure 3. Transmittance as a function of wavelength for a narrowband notch filter in dichromated gelatin.

uses a high frequency transmission DCG grating. Such gratings are usually made in relatively thin layers of DCG to maximize the spectral bandwidth over which the grating performs efficiently. The 90° fold angle and the axial configuration permitted by the transmission grating leads to a compact and efficient instrument configuration. More recently Owen and colleagues⁶⁹ combined two gratings to increase the spectral coverage of a spectrometer without sacrificing spectral resolution; each grating diffracts a portion of the spectrum to a different row on a CCD detector, with both gratings utilizing the full aperture of the instrument. DCG transmission gratings offer advantages in comparison to traditional surface reflection gratings for pulse compression,^{68,73} because of their high diffraction efficiencies, buried grating surface, and the compact compressor configurations permitted. In the latter case, however, transmission through the substrate and hologram materials restricts the application to systems with pulses of moderate power levels.

A number of other applications using dichromated gelatin elements are under development or have been investigated. These include laser scanners,^{19,74,75} solar collector elements,⁷⁶⁻⁷⁸ solar control films,^{43,45} wavelength division multiplexing (WDM) devices for optical communications,⁷⁹⁻⁸² optical interconnects,⁸³⁻⁸⁵ fan-out elements,⁸⁶ polarization-selective elements,^{51,87-89} and holographic diffusers.⁹⁰⁻⁹²

Photopolymer

History. Since the late 1960s, a variety of photopolymer materials have been used to fabricate holograms. Photopolymers are of interest because they form phase holograms with potentially high diffraction efficiencies, generally have low scatter noise, and usually do not require wet processing. Photopolymer materials for holography can be broadly classified into those where exposure leads to the polymerization of one or more monomers and those where exposure causes molecules to form crosslinks. Photopolymers of the first type have been used in liquid form, but more typically are used in dry-film form. A multitude of papers have been published on the development of photopolymers, including a Volume from the SPIE Milestone Series of Selected Reprints⁹³ containing a collection of seminal papers on investigations of photopolymers for holography and related fields.

The earliest reported photopolymer materials for holographic recording were liquid formulations of acrylamide materials.^{94,95} In the early 1970s, a photopolymer compo-

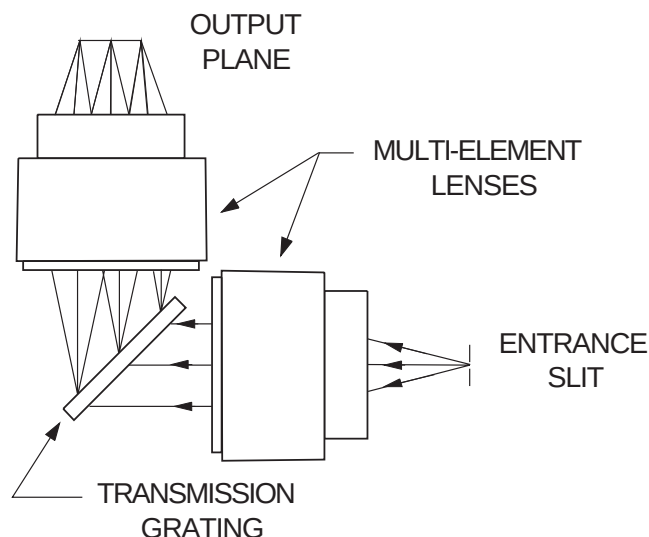


Figure 4. Spectrograph configuration using a DCG transmission grating (after Battey et al)⁶⁶.

sition in dry-film form was reported,⁹⁶⁻⁹⁸ that was a forerunner to the material now supplied by Du Pont. Continued materials research led to the introduction in the 1980s of new and improved photopolymer compositions.⁹⁹⁻¹⁰² Crosslinking photopolymers have been developed,^{103,104} but never received the level of interest shown in photopolymerizing materials. Because of the dominance of the polymerizing materials, we consider only photopolymers of that type here.

Hologram Formation in Photopolymer. In photopolymers of the solid, or dry-film, type, a polymeric binder provides a solid, or dry, support for the liquid monomer(s), and the material can thereby be coated onto substrates of different sizes and shapes. Because the monomer component is a liquid, materials referred to as dry films often have a surface which is not completely dry but one that is invariably described as tacky. Consequently, the films may be protected with cover sheets until the hologram is formed and most or all of the monomer has been converted to polymer. Nonetheless, those materials are much more convenient to use than liquid compositions, which must be held between transparent plates during exposure.

Hologram formation in monomer-binder photopolymers is based on a combination of photopolymerization and monomer diffusion, illustrated in Fig. 5. The photopolymer compositions typically include a photosensitizer dye, an initiator, one or more monomers, and a polymeric binder. The dye-initiator system forms free radicals upon exposure, which begin polymerization of the monomer molecules. Polymerization occurs more rapidly in the bright fringes of the interference pattern, partially depleting those regions of monomer. The resulting concentration gradient of monomer between lightly exposed, or unexposed, regions (more residual monomer) and more heavily exposed regions (less monomer) causes the relatively small monomer molecules to diffuse from the lightly exposed to the heavily exposed regions. A subsequent exposure to uniform illumination (for example, to the reference beam alone) polymerizes the remaining monomer, forming a stable hologram with a monomer-derived polymer distribution that corresponds in some manner to the intensity distribution of the interference pattern.

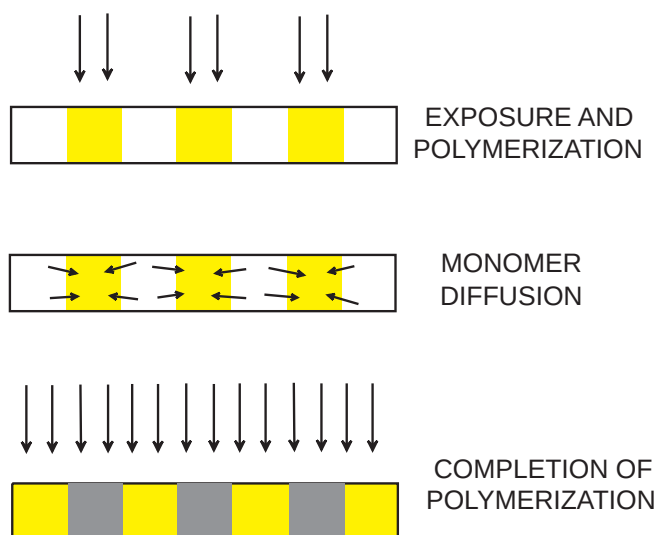


Figure 5. Process of hologram formation in monomer-binder photopolymer materials.

One of the conveniences of photopolymer holography is that as the hologram forms, diffraction can usually be observed in real-time by interrogation with a weak probe beam, preferably one at a wavelength that does not cause photopolymerization.^{95,102} Real-time monitoring in this way not only provides information about the state of hologram formation, but also insights into the behavior of the material under various exposure conditions and rates. For materials with low sensitivity to red wavelengths, the probe beam is typically an unexpanded He-Ne laser beam incident at the Bragg angle. While this works well for transmission holograms, it is less convenient for monitoring the formation of reflection holograms, because for a given reconstruction wavelength, hologram shrinkage caused by polymerization changes the Bragg angle continuously during hologram formation. However, Yamamoto and colleagues¹⁰⁵ were able to monitor the formation of reflection holograms in photopolymer with a white-light probe beam by sampling the spectrum of the reflected light every second, acquiring information not only about the hologram efficiency but also about its bandwidth, wavelength shift, and sidelobe structure.

Du Pont Photopolymer. Although a variety of photopolymer materials exist, a family of dry-film photopolymers developed by Du Pont^{96–98,100–102} has received a great deal of attention because of commercial availability and ease of use. Early forms of the photopolymer investigated in the 1970s were limited in index modulation and were not suitable for reflection holograms.^{96–98} Recent developments in materials^{100–102} have led to higher index modulations and to compositions that can be optimized for either transmission or reflection holograms or both.

Du Pont's photopolymer formulations in general include six components¹⁰⁶: photosensitizing dye, initiator, chain transfer agent, plasticizer, acrylic monomer(s), and polymeric binder. Because the initiator is sensitive to UV light, dye is added to extend the range of photosensitivity to wavelengths in the visible portion of the spectrum. Exposure to the holographic interference pattern creates free radicals in the dye-initiator system in the bright fringe regions, which, with the aid of the chain transfer agent, begin polymerization of the monomer molecules. Because monomer diffusion slows as the film matrix becomes more

rigid with increasing photopolymerization, a plasticizer is added to reduce the rigidity of the matrix, facilitating monomer diffusion, and thereby increasing the achievable index modulation. In addition, for most of Du Pont's compositions, a final step of heating the hologram after the uniform exposure further enhances the index modulation.^{100–102}

Du Pont's photopolymer materials are a family of compositions that vary in their specific constituents depending on the wavelength and hologram type of interest. In particular a number of monomers and binder polymers are available; these are selected to optimize the formulation for specific configurations and applications. Smothers, and colleagues¹⁰⁶ and Monroe¹⁰⁷ reported that both monomers and binders are available in either aliphatic or aromatic form and the highest index modulations in photopolymer holograms are obtained by combining aliphatic monomers with aromatic binders or aromatic monomers with aliphatic binders. This result is consistent with the observation that aliphatic monomers and binders are lower in refractive index than their aromatic forms. Those regions rich in monomer-derived polymer (corresponding to bright fringes in the exposure) have a refractive index closer to that of the polymerized monomer, and binder-rich regions (corresponding to dark fringes from which the monomer diffused) have a refractive index closer to the binder; this difference is the basis of the index modulation that forms the hologram. Consequently, the highest index modulations occur when the monomer and binder have the largest difference in refractive index and when the greatest amount of diffusion has occurred. Monroe¹⁰⁷ noted that the highest index modulations occurred with a formulation containing an aliphatic binder and an aromatic monomer that was a mixture of a liquid monomer and a solid monomer with a still higher index. Furthermore, in discussing the mechanism of hologram formation in photopolymer, Monroe suggested that in addition to monomer diffusion some migration of binder may occur in the early stages of hologram formation.

The exact process of hologram formation is a complicated interaction between photopolymerization and monomer diffusion. The rate of monomer diffusion depends on the film composition and extent of polymerization. Zhao and Mouroulis¹⁰⁸ developed a model of hologram formation that shows that maximum index modulation is achieved if the diffusion rate is high compared to the rate of polymerization. Smothers and colleagues¹⁰⁰ point out that the heating step may increase the index modulation by enhancing diffusion and causing further reaction of film components. Furthermore, the diffusion distance is thought to be greater for compositions optimum for transmission holograms and shorter for reflection hologram compositions. As with diffusion, the rate of polymerization must also be a function of the composition, depending on the relative concentrations of the initiator constituents and the monomer, the rate of monomer diffusion, and the intensity of the exposure. Piazzolla and Jenkins¹⁰⁹ recently published a model describing the formation of transmission gratings based on the diffusion of monomer, in which they assume the rate of diffusion is faster than that of grating formation. The authors also showed that the index modulation δn at the completion of grating formation depends on the beam intensity ratio K as

$$\delta n = \delta n_M \left(\frac{2\sqrt{K}}{K+1} \right),$$

where δn_M is the maximum available index modulation.

Although photopolymer can be coated from solution, Du Pont typically supplies its photopolymer coated on a film of polyethylene terephthalate (Mylar) with a cover sheet of the same material to protect the tacky surface of the unexposed photopolymer. For exposure the cover sheet is removed and the photopolymer is laminated to a glass substrate with the original supporting film left in place as a protective layer during the subsequent operations. Following exposure to the holographic interference pattern, most or all of the remaining monomer is polymerized by exposure to uniform UV illumination, and the index modulation is increased¹¹⁰ by baking the hologram in an oven at a temperature of 100°C to 150°C.

The Du Pont photopolymer shrinks on polymerization, which, because it affects the Bragg performance of the hologram, may require compensation by an adjustment to the exposure geometry or wavelength. The shrinkage is minimized by leaving the Mylar film in place to cover the hologram during the bake operation, which presumably prevents the evaporation of volatile components from the photopolymer.^{100,101} For a given angle of illumination, the effect of material shrinkage on reflection holograms is to shift the Bragg wavelength toward the blue by an extent dependent on the amount of shrinkage. Masso and Ning¹¹¹ reported that the amount of the shrinkage also depends on the slant angle of the fringes relative to the hologram surface. Zager and Weber¹¹² describe a color tuning film that can be used to swell the hologram during the bake step; the tuning film contains monomers that at elevated bake temperatures diffuse into the hologram and subsequently polymerize, forming a stable, thickened hologram that has an increased Bragg wavelength. With the color tuning film, the shrinkage that occurs during hologram formation can be compensated, and, if necessary, the hologram thickness can be increased to more than its original value.

Gambogi, Weber, and Trout¹¹³ reported the Du Pont photopolymer can be sensitized to wavelengths from the UV to the near IR (690 nm), has an exposure sensitivity on the order of 5 to 100 mJ/cm², and forms holograms with index modulations as high as 0.06. Although haze in photopolymer is somewhat higher than in DCG holograms and some coloration from residual dye occurs, the optical quality of holograms in Du Pont photopolymer is still very good.⁴⁹ Holograms fabricated in Du Pont photopolymer are much less sensitive to the effects of moisture than DCG holograms and, as a result, can be used with plastic (e.g., polycarbonate) substrates and covers.

Polaroid Photopolymer. In the 1980s Polaroid Corporation announced a photopolymer system DMP-128 based on a vinyl monomer.^{99,114} The composition of DMP-128 includes polymeric binders, an aqueous acrylate as monomer, a dye to initiate photopolymerization, and a crosslinking agent.¹¹⁵ On exposure to a holographic interference pattern, the material undergoes the expected polymerization and diffusion of monomer from dark to bright regions. A subsequent exposure to uniform white light polymerizes the remaining monomer to fix the monomer-derived polymer distribution in the hologram. The polymerization and diffusion produce weak refractive index modulation intensified by processing the hologram in one or more chemical baths, followed by a rinse to remove residual processing fluids and then a drying step.

Ingwall and Troll^{114,116} determined that the processing baths remove soluble constituents and create a fringe

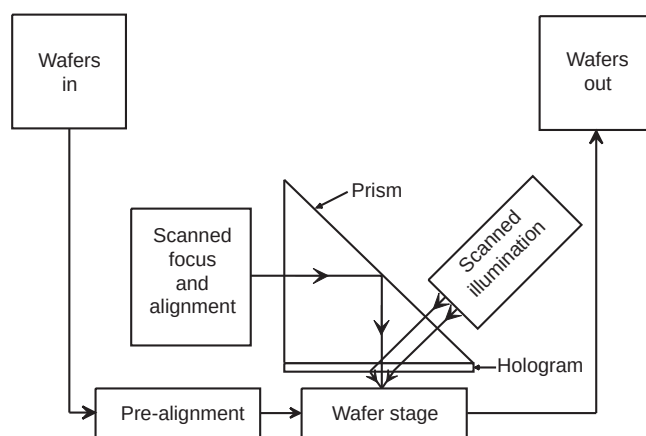


Figure 6. Schematic diagram of holographic mask aligner using a TIR hologram recorded in Du Pont photopolymer (after Clube, et al.).¹³¹

structure in the material of alternating solid and porous layers. The porous layers contain voids normally filled with air that significantly lower the average refractive index of those layers relative to the solid layers, thereby creating a large modulation in refractive index. The voids are connected by a pore structure that allows liquid penetration. By selecting a liquid of the appropriate refractive index, one can fine tune the diffraction efficiencies of transmission gratings or adjust the spectral response of a reflection hologram. The authors also suggest that the environmental stability of the hologram can be enhanced by filling the pores with a liquid monomer subsequently polymerized in place.

DMP-128 is relatively sensitive for a nonsilver material, with reported sensitivities of 4 to 8 mJ/cm² for transmission holograms and 15 to 30 mJ/cm² for reflection holograms.¹¹⁷ Dyes are available to sensitize the material to the blue, green, or red portions of the spectrum. Coatings ranging in thickness from 3 to 20 μ m can be prepared on glass- or film-based substrates. High levels of refractive index modulation can be achieved with reported values of 0.08 and 0.08 to 0.13 (Refs. 117 and 115, respectively).

Applications of Photopolymer. Photopolymer holograms are in use or have been evaluated for a wide variety of applications, including holographic scanners,^{118,119} laser eye protection devices,⁴⁹ helmet-mounted displays,⁵⁷ optical interconnects,¹²⁰⁻¹²² elements for LCD displays,^{123,124} automotive lighting,¹²⁵ security holograms,^{126,127} holographic diffusers,^{9,128,129} and waveguide couplers.¹³⁰ Clube and colleagues¹³¹ recently reported development of a holographic mask aligner for photolithography of microelectronic devices, illustrated by the schematic diagram in Fig. 6. Using total internal reflection holography in a layer of Du Pont photopolymer, the aligner achieves very high resolution over large device dimensions. In still another application, Loiseau and colleagues¹³² fabricated photopolymer transmission holograms that use a chirped spatial frequency to form an improved pulse stretcher grating for ultrafast laser systems.

The development of machines for replication of photopolymer holograms⁷⁻⁹ should foster the growth of applications requiring large-scale production of holograms. The machine developed by Du Pont^{7,8} copies master reflection holograms onto a photopolymer film in continuous motion around a cylindrical drum, as indicated

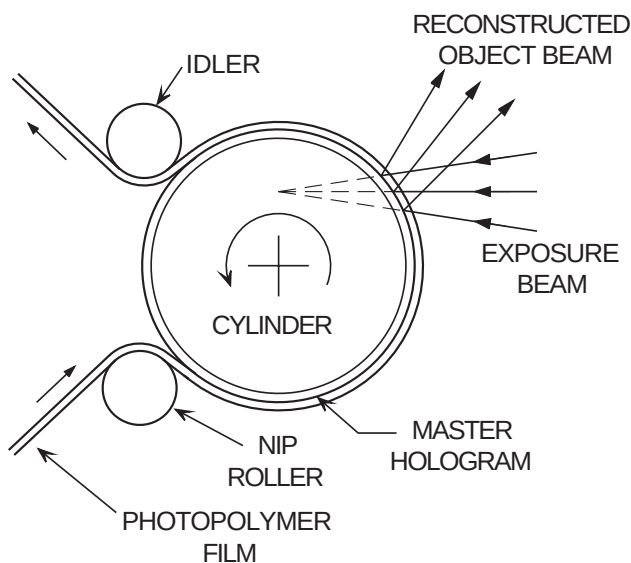


Figure 7. Configuration of exposure station of machine for continuous copying of reflection holograms onto a photopolymer film (after Armstrong and Tipton).⁷

in Fig. 7. In addition to the exposure station shown, the machine includes stations for adding an index-matching liquid, exposing the film to uniform UV illumination, and permitting visual inspection of the copy holograms.

Photoresist

History. Photoresist was first used for holographic optics in the late 1960s. An early and successful application was interferometrically formed diffraction gratings,^{133,134} that avoided the periodic errors inherent in gratings made by mechanical ruling processes. Labeyrie and Flamand¹³³ studied the performance of diffraction gratings fabricated in photoresist and overcoated with aluminum, reporting efficiencies as high as 68% for gratings that had line spacings comparable to or smaller than the wavelength of the incident light. Rudolph and Schmahl¹³⁴ reported diffraction from holographic gratings free of ghosts and with low stray light.

Other early work included Sheridan's disclosure¹³⁵ in 1968 of a hologram recording configuration that produced blazed diffraction gratings which, with aluminum overcoating, had diffraction efficiencies as high as 73%. Gerritsen, Hannan, and Ramberg¹³⁶ recorded two-dimensional gratings in photoresist for use in a multibeam hologram recording configuration. In 1970 Bartolini and colleagues¹⁰ described holograms in Shipley AZ1350 photoresist that served as embossing masters for a video storage system, a replication process that ultimately led to a major commercial application of holography. At about the same time, Beesley and Castledine¹³⁷ also recorded holographic gratings in Shipley AZ1350 photoresist and described a method to monitor the photoresist development in real time to optimize the groove depth of the developed grating. In 1970 Dakss et al.¹³⁸ used photoresist gratings to couple a laser beam to a thin film optical waveguide. Although they did not discuss holograms, in 1975 a group under Dill published a model of exposure and development of AZ1350J photoresist that described the material in some detail.^{139,140} To date the major uses of photoresist as a holographic medium have been to form holographic diffraction gratings, that is, classical diffraction gratings formed

by exposure to an interference pattern; gratings transferred by chemical or ion-etching processes into other materials; and master holograms for replication by embossing techniques.

Hologram Formation in Photoresist. Unlike the volume phase materials discussed thus far, photoresist forms holograms as surface relief patterns. Hologram formation is relatively simple: a thin coating of photoresist is exposed to an interference pattern and developed in a solvent. The developer removes material from the exposed regions in positive working resists and from the unexposed regions in negative working resists. The hologram formed is a surface phase hologram used in transmission or reflection. Because the reflectivity of the photoresist material itself is relatively low, a coating of a highly reflective material such as aluminum is deposited on the surface of photoresist holograms intended for reflection applications.

In general, the groove depth in the developed photoresist depends on the exposure irradiance in a nonlinear fashion. Bartolini¹⁴¹ analyzed the recording process of photoresist, paying particular attention to the nonlinearities inherent in phase holograms as well as to the dependence of the relief depth on the exposure irradiance. Experimental investigations showed that choice of developer can affect linearity and apparent sensitivity of photoresist holograms. A pre-exposure to uniform illumination may reduce the distortion of the groove profiles from the expected sinusoidal shape,¹³⁷ although in some cases the exact shape of the groove does not seem to matter a great deal. Wilson, McPhedran, and Waterworth¹⁴² suggested that when inverted (as in an epoxy replica) the distorted groove shape typically obtained actually performs better than a strictly sinusoidal profile. Austin and Stone^{143,144} later developed an empirical model of grating formation in photoresist to predict and control groove profiles.

Most if not all photoresist holograms reported were formed in positive resists, perhaps because as Bartolini and colleagues¹⁰ observed, the development step removes only the exposed portion of positive resists, leaving more material to adhere to the substrate than in the case of negative resists. Although other materials have been evaluated, the materials most widely reported are the Shipley AZ1350, AZ1400, and AZ1450 families of photoresists. Currently, Shipley provides an AZ1800 family of resists with improved environmental properties.

The preferred method of coating photoresist for holography is spin coating, with typical thicknesses^{145,146} in the range of 0.1 to 1.5 μm . The coating thickness is adjusted by selecting the speed of the spin coater and by diluting the resist with a thinning solvent. Prior to coating, the substrate is usually baked to ensure complete dryness. After coating, but prior to exposure, another bake eliminates residual solvent, which, if present, can cause nonuniformities in the sensitivity of the resist.¹³⁷ Because thin coatings tend to have flat substrate surfaces and do not undergo the swelling or shrinking of DCG and photopolymer holograms, photoresist holograms are often preferred in applications requiring high wavefront quality.^{133,147,148}

Most photoresists used for holographic recording are sensitive to the UV-violet portion of the spectrum. Consequently, despite the higher power of argon ion lasers at a wavelength of 488 nm, photoresist holograms are typically exposed at a wavelength of 459 nm where the increased sensitivity more than offsets the lower laser power at that wavelength. Still shorter wavelengths are often used for writing photoresist holograms: Bartolini^{10,141} used a He-Cd

laser at a wavelength of 442 nm to expose holograms in Shipley AZ1350 photoresist and Yen et al.¹⁴⁹ used the 325-nm line of the He-Cd laser. Hutley¹⁵⁰ reported exposing photoresist gratings with the 351-nm line of the krypton-ion laser. After exposure, the hologram is developed in a solution that removes the exposed material (for positive resists), with typical development of 30 s to several minutes; the hologram is then rinsed and dried. The developer solution can be obtained from the photoresist manufacturer and may be diluted to improve control of the process. Depending on the application, the hologram may be baked after development to harden the photoresist. Although exposed as transmission holograms, photoresist elements are often coated by vacuum deposition with a thin layer of a reflective material for use as reflection elements.

Performance. Photoresist holograms can have high diffraction efficiencies with excellent optical quality. The grainless nature of the material keeps scattered light to a minimum. Diffraction efficiencies have been reported as high as 90% in photoresist transmission gratings^{151,152} and more than 95% in metallized reflection gratings.¹⁵³ As for volume phase materials, achieving high diffraction efficiencies in photoresist is dependent to an important extent on the hologram configuration. For highly efficient photoresist holograms, the fringe spacing must be comparable in size to the wavelength of the illuminating light or the grooves must have a blazed profile. In addition to excellent hologram performance, photoresist is relatively easy to use. The flexible medium is capable of forming a wide range of optical elements, directly as holograms, with or without additional reflective coatings, or as patterns for subsequent transfer of the surface relief into another material by means of ion machining, epoxy replication, or embossing.

The major limitation of photoresist as a holographic medium is low exposure sensitivity and spectral sensitivity limited to the UV-violet portions of the spectrum. In addition photoresist has a delicate surface vulnerable to damage by abrasion or chemical attack.¹⁵⁴ In the case of transmission holograms, residual absorption by the photoresist can limit the efficiency somewhat, although the absorption is less at longer wavelengths.

Applications of Photoresist. A major application of photoresist holograms has been to make classical diffraction gratings for spectroscopic instruments. Compared to ruled gratings, diffraction gratings made by holographic techniques, usually referred to as holographic gratings, interference gratings, or interferometrically ruled gratings, have lower noise but comparable efficiency.¹⁴⁷ Furthermore, ghosts caused by periodic and random ruling errors in mechanically ruled gratings are not present in diffraction by holographic gratings and scattering noise is less. Schmahl and Rudolph¹⁴⁷ measured scattered light levels comparable to scattering by an aluminized mirror. Dunning and Minden¹⁵⁵ measured scatter noise levels from holographic gratings at 10.6 μm that were better than 2 orders of magnitude lower than scattering by ruled gratings, and in the visible region, noise levels are typically 1 order of magnitude less than from ruled gratings.¹⁵⁶ Gratings made by holographic techniques are readily formed on substrates of arbitrary shape or curvature, often on concave substrates for aberration correction.¹⁵⁷ Another advantage of holographic gratings is the construction wavefronts can be modified from plane waves to reduce aberrations in the optical system employing the grat-

ing.^{158,159} Diffraction gratings fabricated in photoresist are typically overcoated with a reflective metallic film, usually of aluminum or gold. As with ruled gratings, holographic gratings can be replicated in epoxy resins.¹⁶⁰ Large diffraction gratings with high groove densities are available only as holographic gratings^{153,161} because of the problem of diamond wear in ruling such gratings.

In their simplest form, holographic gratings have groove profiles roughly sinusoidal in correspondence to the sinusoidal profile of the fringe pattern formed by interference between the exposing wavefronts. Despite a nonlinear material response, Schmahl and Rudolph¹⁴⁷ achieved this result without any apparent special care, whereas Austin and Stone^{143,144} obtained sinusoidal groove profiles by optimizing exposure and development to establish a more linear response of groove depth with exposure.

The diffraction efficiency of surface gratings is a complicated subject that has generated a considerable body of research (see, for example, Refs. 162 through 166). The efficiency depends on the groove profile, depth, and spacing relative to the wavelength of the incident wavefront and, for reflection gratings, on the conductivity of the metallic coating. In addition, the grating efficiency is usually polarization sensitive. Under conditions in which only two orders propagate, gratings with sinusoidal profiles can have high diffraction efficiencies. For configurations in which the ratio of the wavelength λ to the grating period d is in the range $0.7 \leq \lambda/d \leq 1.5$, the efficiency of a grating with a sinusoidal groove profile can be comparable to that of a ruled grating with a sawtooth profile,¹⁴⁷ but is strongly polarization dependent. Kramer¹⁵¹ reported transmission gratings in photoresist with diffraction efficiencies at more than 90%. Furthermore, under similar conditions and with only two orders propagating, nonsinusoidal groove profiles also provide high diffraction efficiencies, as reported by Breidne and Maystre¹⁶³ for reflection gratings, and by Enger and Case¹⁵² for transmission gratings.

Referring to the high-frequency condition discussed above as sinusoidal blazing, Breidne and colleagues¹⁶⁷ point out that when $\lambda/d < 0.7$, several orders propagate and scalar theory can be used to show that the maximum diffraction efficiency of a grating with sinusoidal grooves is limited to 34%. Under those conditions several techniques have therefore been developed to form holographic gratings with grooves that have a triangular, or sawtooth, profile. Sheridan's technique¹³⁵ for making blazed holograms in photoresist with highly slanted fringes in a reflection hologram exposure configuration was further investigated by Nagata and Kishi¹⁶⁸ and by Hutley.¹⁵⁰ Obermayer¹⁶⁹ and Mashev and Tonchev¹⁷⁰ discussed recording slightly tilted fringes in a transmission hologram exposure configuration to produce a sawtooth profile in the developed photoresist layer. Aoyagi, Sano, and Namba¹⁷¹ directed an ion beam obliquely at a photoresist grating to etch a sawtooth grating of high quality into a polymethyl methacrylate substrate. Flamand and colleagues¹⁵⁶ more recently used a similar technique to produce blazed gratings on flat and concave glass substrates.

Another method for approximating a sawtooth groove profile is a Fourier synthesis technique¹⁴⁷ that adds a second photoresist exposure at twice the spatial frequency of the desired grating and phase matched as the second harmonic of a Fourier series expansion of a triangular or sawtooth waveform. This is a challenging task, but one for which several approaches have succeeded in producing the desired result. Schmahl and Rudolph¹⁴⁷ combined the first- and second-order diffracted wavefronts from a

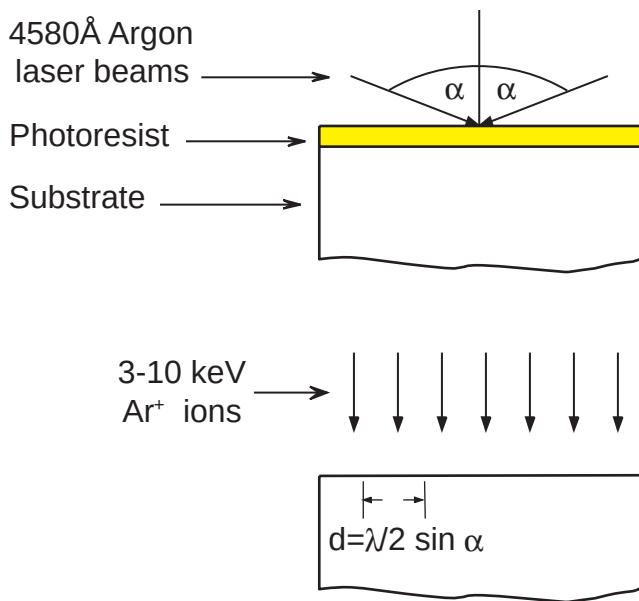


Figure 8. Simplified sketch of process to transfer grating formed in photoresist to the substrate material by means of ion etching (after Garvin et al.).¹⁷³

large grating, using phase plates and apertures as needed in the wavefronts to control the phase relationships of the fringe patterns. Breidne and colleagues¹⁶⁷ used a reference grating on the periphery of the grating substrate to aid in adjusting the tilt angles of the exposure wavefronts between the fundamental and second-harmonic exposures to provide accurate phase matching of the interference patterns.

Photoresist gratings can be transferred into a substrate by an etch process. Hanak and Russell¹⁷² used RF sputtering to etch a photoresist grating pattern into glass and other hard materials. Garvin and colleagues¹⁷³ used a holographic grating formed in photoresist as a mask pattern for an ion beam sputtering process to form surface gratings in GaAs and silicon substrates. Figure 8 is a sketch illustrating their process of forming a holographic grating in a layer of photoresist and, after developing the photoresist, transferring the grating to the substrate by ion etching, or machining. Johnson, Kammlott, and Ingersoll¹⁷⁴ discussed the formation of gratings in photoresist coated on GaAs substrates. They considered the effects of the reflection from the photoresist–GaAs interface in optimizing the photoresist grating for subsequent ion beam or chemical transfer to the GaAs substrate. Referring to the process as holographic photolithography, Heflinger and colleagues¹⁷⁵ exposed gratings in thin (0.12-μm) photoresist films, and transferred them to GaAs substrates by ion beam etching, adjusting the etch procedures to form either a sinusoidal or a sawtooth groove profile in the GaAs surface.

Knop¹⁷⁶ fabricated photoresist gratings with rectangular groove profiles for use as polarizing elements in the infrared. The gratings were copied from a chrome grating mask, also made by holographic techniques, and then coated with a thin film of gold to provide a conductive surface. Knop also electroplated nickel to the gratings to form a master for grating replication through embossing or casting methods. The use of photoresist holograms to fabricate wave plates was subsequently investigated by Enger and Case¹⁵⁴ and by Cescato, Gluch, and Streibl.¹⁷⁷

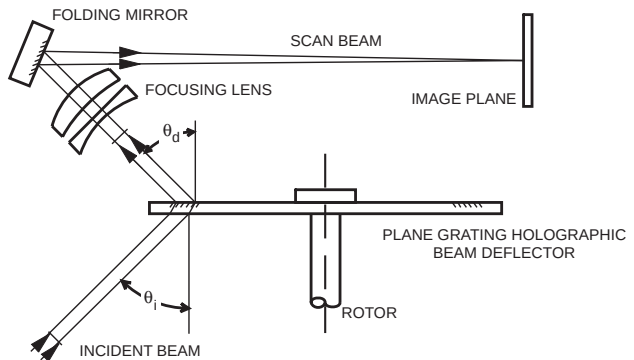


Figure 9. Scanner system using photoresist transmission grating as the scan element (after Kramer).¹⁴⁸

Kramer^{148,151} used photoresist gratings as the basis for optical scanners. The stability of the photoresist medium was attractive for the fabrication of high-precision scan disks, which require that the grating periodicity be constant to within 10^{-12} m to achieve a tracking error of less than 1 arc sec. Figure 9 is a sketch of Kramer's holographic scanner system with a transmission photoresist hologram as the scan element. Kramer also pointed out that for scan disks that rotate at very high speeds, reflection photoresist gratings can be used on metallic substrates for increased mechanical strength.

An important application of photoresist is to form master holograms for embossed products^{11,12,178,179} including credit card holograms and decorative materials. After a master hologram is formed in photoresist, a metallic layer such as nickel is electroplated over the surface of the hologram. The metallic layer is subsequently removed from the photoresist and used to emboss the holographic surface pattern into thermoplastic films. Haines¹² reported as an alternative to embossing, casting techniques employing UV curing resins, which, in some cases at least, can be cast directly from the photoresist masters.

In other research, photoresist holograms were investigated for making beam-sampling mirrors,¹⁸⁰ antireflection devices,^{154,181} and as master elements for holographic diffrusers. In a reverse of the usual exposure process, Kimura, Sugama, and Ono¹⁸² formed holographic optical elements by contact printing an electron-beam generated pattern into a layer of photoresist.

Other Materials

Other materials used to fabricate holographic optical elements include silver halide emulsions, a variety of photopolymerizable or crosslinking materials, and matrix materials. Silver halide materials are attractive because they are readily available; easy to use; and, compared to nonsilver materials discussed above, have a high exposure sensitivity. The grain structure inherent in silver halide emulsions, however, causes an unacceptable amount of scatter noise for most applications of holographic optics. Nonetheless, many investigators have used silver halide emulsions to demonstrate feasibility with the expectation that ultimately another material would be substituted for improved performance.

In 1980 Graver, Gladden, and Eastes¹⁸³ reported that a by-product of the photographic processing of bleached silver halide emulsions is gelatin crosslinking, which has spatial correspondence to the holographic fringe pattern. They noted that the latent image in hardness produced is similar to that formed by crosslinking in

dichromated gelatin, so a hologram can be produced by subsequent development in the baths used for DCG. This new process called silver halide sensitized gelatin (SHSG) has since been investigated by others.^{184,185} SHSG combines the good exposure and spectral sensitivity of silver halide emulsions with the high optical quality of dichromated gelatin holograms. The refractive index modulations reported are not as high as those achieved with DCG, however, and some scattering is expected by the silver grains during the exposure. Tai et al.¹⁸⁶ developed a holographic optical element now in production in SHSG for use in a commercial gun sight.

A number of authors have synthesized photopolymer compositions for recording holographic elements.¹⁸⁷⁻¹⁹⁶ These afford the advantage to the user of optimizing the specific composition for a particular application, but often require materials, skills, and facilities beyond those required to work with dichromated gelatin or photoresist. In some cases, however, it may be sufficient for research purposes to work with a material that has limited performance but is easy to use or has special attributes. Hill and Brady,¹⁹⁷ for example, recorded 1-cm-thick holograms in Epo-Tek Epoxy 301 (Epoxy Technology, Inc., Billerica, MA) doped with the dye methyl red. Although the authors reported diffraction efficiencies of less than 1%, they were able to fabricate very thick holograms in near real-time with the epoxy.

Polyvinylcarbazole (PVCz) is a crosslinking photopolymer used by Canon as a holographic optical element in the view finder of a commercialized camera.¹⁰⁴ A notable advantage of holograms formed in PVCz is a high degree of environmental stability, and, in particular, relative insensitivity to moisture or humidity. More recently, Kuwayama and colleagues¹⁹⁸ reported reflection holograms in PVCz comparable to DCG holograms. Relatively little work has been reported on this material, however, perhaps as a result of existing patents on PVCz as a holographic recording material.

In his discussion on dichromated colloids, Kosar¹³ refers to the substitution of a synthetic resin, polyvinyl alcohol (PVA) for gelatin. Because of its synthetic nature, PVA offers the prospect of being better controlled than gelatin, which is obtained from animal products. Bloom and Burke¹⁹⁹ added dyes to sensitize dichromated PVA to visible wavelengths and used the material as a photoresist to form surface relief patterns. Todorov, Nikolova, and Tomova²⁰⁰ formed near-real-time, reversible polarization gratings in PVA sensitized with the dye methyl orange. Others have recorded volume transmission holograms in dichromated PVA with an emphasis on the real-time nature of hologram formation.^{201,202}

Recent materials investigations have evaluated thick holograms made on recording materials embedded in a matrix of a supporting material such as porous glass. Andreyeva and colleagues²⁰³ reported holograms made by infusing a silver halide material into a 1-mm-thick porous glass substrate. The pores were connected so that processing fluids could circulate throughout the matrix to develop the hologram. Ludman and colleagues²⁰⁴ made transmission gratings in 0.7-mm-thick porous glass filled with a photopolymer. The 30-nm pore size was small enough to prevent scattering of visible light. The authors reported that to achieve optimum diffraction efficiency, they had to fill the remaining pore space with an index matching liquid. The matrix structure of these materials forces dimensional stability, and the pore structure allows the photosensitive material to be processed throughout the hologram depth. The concept thus permits the formation

of very thick holograms with recording materials that could not otherwise be used in such thicknesses because of dimensional changes and processing requirements.

Conclusions

Three decades of research into materials for holographic optical elements has produced three materials in wide use: dichromated gelatin, photopolymer, and photoresist. Dichromated gelatin has been the material of choice for applications requiring volume phase holograms and is in production for head-up display combiners, notch filters, and diffraction gratings. But strong competition is now coming from photopolymers, which are considerably easier to use and do not have high sensitivity to moisture. For those willing to endure the processing challenge of dichromated gelatin, however, the material should continue to provide high performance over a wide range of conditions. Perhaps if production volume in a future application warrants a high degree of automation, dichromated gelatin production will achieve higher yields and lower costs.

Photopolymers are the newest of the three recording materials discussed. Current forms are under investigation for various applications. Automated printing machines offer the potential for economical production of large quantities of photopolymer copies from master holograms. In addition, the material's ease of use and high optical qualities may make it the choice for a number of smaller volume but high-precision applications, such as the mask aligner mentioned above. Higher index modulations would be beneficial, and, given the complex nature of the organic compounds involved, it is not yet clear how consistent the materials will be from batch to batch.

Photoresist has been a reliable mainstay because of its ease of use and high quality diffraction gratings, ion-machined optical elements, and large-volume hologram production. Although increased exposure sensitivity and broadened spectral sensitivity would improve its utility in holography, photoresist materials developments are driven by the needs of the photolithography industry and holography must benefit as best it can. ▲

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