Journal of Imaging Science and Technology® 55(2): 020510-1–020510-6, 2011.

Hologram Recording Using Photothermographic Materials

Ken'ichi Kuge▲
Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho Inage-ku, Chiba 263-8522, Japan
E-mail: kuge@faculty.chiba-u.jp

Hironobu Mori and Tomoko Sakai
Faculty of Engineering, Chiba University, 1-33 Yayoi-cho Inage-ku, Chiba 263-8522, Japan

Abstract. *Holograms were formed on a silver halide photothermographic material without carrying out wet treatment. Amplitude holograms whose gratings consist of rows of developed silver grains were formed, and the maximum diffraction efficiency of the gratings was almost 1.5%. When the amplitude holograms were bleached using bromine gas, they were converted to phase holograms, and the diffraction efficiency increased to a maximum of 6%. All areas turned yellow in color because of the formation of silver bromide. The mechanism of formation of gratings after bleaching has not yet been established. The authors propose that stripes of silver bromide, developer, toner, or other components may be formed by thermal development and subsequent bleaching. These stripes are transparent but have different diffraction indices, and this leads to the formation of gratings. © 2011 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.2011.55.2.020510]

INTRODUCTION

Exposure of a photosensitive material to an optical interference pattern during hologram recording results in the formation of diffraction gratings. As the interval between the gratings is almost equal to the wavelength of visible light, the materials used for hologram recording must have high resolution. There are several kinds of materials that have a high resolution, such as silver halide photographic materials, photopolymers, photoresists, and dichromated gelatin.[1] Among these materials, silver halide photographic materials have a far higher sensitivity than other materials, especially to light of longer wavelengths. However, these materials have some disadvantages; for example, wet treatment is necessary in the development process, and a significant amount of the developer is wasted after the development.

There is a kind of silver halide photographic material in which these disadvantages are overcome, however. Photothermography is a process in which development is carried out by heating.[2] This process is a dry process that does not involve the use of water, and no waste developer remains. Hereafter, we refer to photographic materials which use developer solutions as wet-type materials.

▲IS&T Member.

Received Sep. 7, 2010; accepted for publication Jan. 3, 2011; published online Mar. 10, 2011.
1062-3701/2011/55(2)/020510/6/$20.00.

The size of silver halide grains used for photothermographic materials is several tens of nanometers; this size is similar to the size of grains in a wet-type photographic material used for hologram recording.[3] Therefore, photothermographic materials might be expected to have sufficiently high resolution for recording holograms. Thus, we tried to prepare holograms in photothermographic materials.

Holograms that are recorded on silver halide photographic materials are generally thick holograms because the gratings are formed in a thick emulsion layer. There are two types of thick holograms: amplitude and phase holograms.[4] In the former type of hologram, light is diffracted because of the difference in the absorption by the diffraction gratings, and in the latter type of hologram, light is diffracted because of the difference in the refractive indices of the gratings. Amplitude holograms suffer from a limitation on the diffraction efficiency because the gratings absorb a part of the incident light. On the other hand, theoretical results have shown that phase holograms should have much higher diffraction efficiency than amplitude holograms.

In general, when a hologram is recorded on a silver halide photographic material, an amplitude hologram in which diffraction gratings are formed by parallel rows of developed silver grains is obtained. In order to obtain higher diffraction efficiency, these amplitude holograms are often treated so that they are converted into phase holograms. There are some reports on bleaching treatments in which silver grains are converted to silver halide grains, and additional fixing treatments are sometimes carried out after bleaching.[5] After bleaching treatments, diffraction gratings are formed because of the difference in the refractive indices of the clear gelatin layer with ultrafine transparent silver halide grains and that without the grains, and, after additional fixation, the gratings are formed because of a variation in the refractive index within the gelatin layer.

Since holograms have not generally been recorded on photothermographic materials, there are no reports on the conversion of amplitude holograms to phase holograms in these media. Therefore, we tried to convert an amplitude hologram formed on the photothermographic material into a phase hologram by bleaching treatments. Because in many photothermographic materials, hydrophobic polymers are

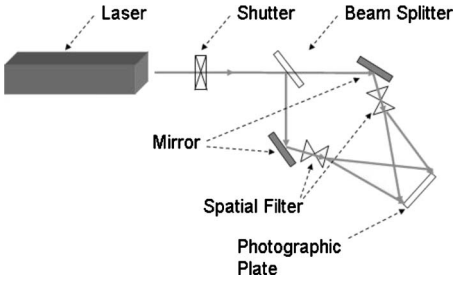

Figure 1. Optical system used to record diffraction gratings.

used as a binder rather than gelatin, bleaching treatment is difficult insofar as aqueous solutions cannot penetrate the layer.

Vapor bleaching may also be carried out as the bleaching treatment,[6] and it is appropriate for materials in which hydrophobic polymers are used as binders. As halogen vapors are hydrophobic, they can penetrate hydrophobic polymers and bleach silver grains to silver halide grains. We therefore tried to convert amplitude holograms recorded in photothermographic materials to phase holograms using bromine or iodine vapors, and we investigated the improvement in the diffraction efficiency of the hologram thereby.

EXPERIMENTAL

We used a photothermographic film, Dry-Pro™ SD-P (Konica-Minolta), as the photographic material; in this film, a hydrophobic polymer is used as the binder. For comparison, we used a photographic glass plate (Konica-Minolta, P5600) for hologram recording. The P5600 plate is of the wet type and is developed in an aqueous developer solution.

Interference fringes were generated using the optical system shown in Figure 1, with a 633 nm He-Ne laser. The laser beam was divided into two beams, each of which entered from the same side of the film at the same angle. The cross angle of the light beams was 36°, and gratings with 1000 lines/mm perpendicular to the film surface were recorded. The total light intensity was 600–840 $\mu W/cm^2$, and the intensities of both light beams were set such that they were equal. The exposure times were 0.2–3.0 s, and hence the exposure value was altered from 136 to 2010 $\mu J/cm^2$.

Sensitometry was carried out using a JIS III type photographic sensitometer. The material was exposed to white light or monochromatic light (wavelength: 633 nm) generated by an interference filter in the sensitometer. When the material was exposed to 633 nm light, the intensity was measured using a power meter in order to calculate the exposure value. The spectral sensitivity was measured using a spectrophotometer (Narumi, GR-II).

A hot plate was used for the thermal development. The exposed films were placed on the hot plate and covered immediately with a glass plate that had been heated to the same temperature on the hot plate. The development time ranged from 5 to 80 s. The standard development temperature for this photothermographic material is 120°C. However, since the development proceeded very fast at this temperature and it was difficult to heat the film uniformly in operating by hand, we developed the films at 110°C in order to reduce the development speed. Because we used such a simple method, uneven heating was unavoidable. We developed the P5600 photographic plate in diluted D72 developer solution at 20°C for 5 min. Optical density was measured using a photographic densitometer. We observed the diffraction gratings recorded on the film using an optical microscope.

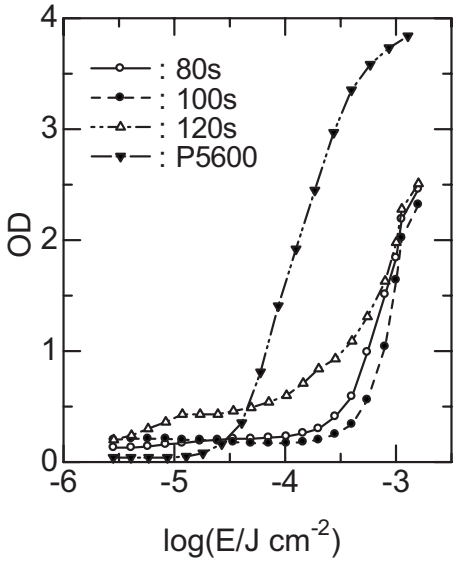

Figure 2. Photographic characteristic curves obtained for the photothermographic film at different development times and those obtained for the wet-type hologram-recording plate (P5600). The film and the plate were exposed to monochromatic light with wavelengths of 633 and 488 nm, respectively. The exposure value is represented as the energy of the monochromatic light. Development time for photothermographic film: open circles with solid line, 80 s; closed circles with dashed line, 100 s; and open triangles with dashed-dotted line, 120 s. Closed inverted triangles with double-dotted-dashed line: P5600.

Bleaching treatment for converting a developed silver grain into a silver halide grain was carried out using bromine or iodine gas. For this bleaching, we used a desiccator in which bromine water saturated with bromine was placed at the bottom. A thermally developed film was placed in the upper part of the desiccator and left for 10–24 h at room temperature. In the case of iodine bleaching, iodine powder was placed at the bottom of the desiccator.

For measuring the diffraction efficiency, the prepared gratings were irradiated with a 633 nm laser beam at an incident angle of 18°. Both the intensity of the incident light I_0 and that of the transmitted diffraction light I_{DT} were measured using a power meter, and the diffraction efficiency was calculated as the ratio, I_{DT}/I_0.

EXPERIMENTAL RESULTS

Hologram Recorded on a Photothermographic Material

Photographic characteristic curves obtained when the photothermographic film was exposed to 633 nm light are shown in Figure 2. The exposure value is represented as the energy of the 633 nm light. For comparison, the characteristic curve for the P5600 silver halide photographic plate (used for hologram recording) that was exposed to 488 nm

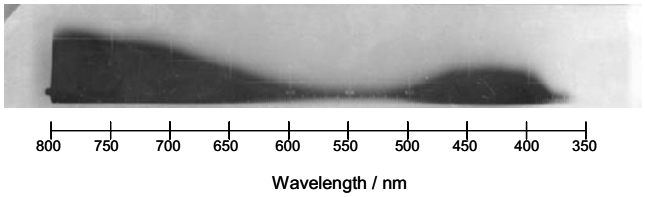

Figure 3. Spectrogram of the photothermographic film.

light and developed using a wet developer is also shown. Although the wavelength of light to which the photothermographic film was exposed differs from that of light to which the photographic plate was exposed, it appears that the sensitivity of the film is lower than that of P5600 by approximately one order of magnitude.

A spectrogram of the photothermographic film is shown in Figure 3. The film is sensitive to blue light with wavelengths of 380–550 nm and to red light with wavelengths greater than 600 nm. It is therefore also sensitive to the 633 nm He-Ne laser light, although sensitivity is not very high for this wavelength. Because this photographic material is usually exposed to laser light in the infrared region, it is designed such that it is most sensitive to light whose wavelength is around 800 nm. By appropriate spectral sensitization, the sensitivity of the film to 633 nm light could be increased. Nevertheless, this material has higher sensitivity than other photosensitive materials used for hologram recording. Moreover, since this film is not sensitive to green light with wavelengths of around 550–600 nm, it is possible to use green light as a safe light, which makes easy handling of the films in the darkroom.

The optical density increased with increasing development time. However, the prolonged development results in the formation of a significant amount of fog rather than in increased sensitivity. The relationships between diffraction efficiency and exposure value for each development time are shown in Figure 4 for both light intensities, namely, 680 and 840 $\mu W/cm^2$. The exposure value was adjusted by adjusting the exposure time. The change in the development time led to a change not only in the optical density but also in the diffraction efficiency. At the optimum exposure value, a maximum efficiency of a little under 1% was obtained.

The relationships between the diffraction efficiency of the amplitude hologram and the optical density are shown in Figure 5 for each exposure value. The optical density was altered by altering the development time. A maximum diffraction efficiency of 1.5% was obtained; maximum diffraction efficiencies were attained for optical densities of 0.5–1, in spite of the difference between the exposure values.

Optical micrographs of diffraction gratings prepared at different exposure times and development times are shown in Figure 6. The diffraction efficiency corresponding to each figure is different. The efficiencies vary as follows: [Fig. 6(a)] 0.84%; [Fig. 6(b)] 0.18%; and [Fig. 6(c)] 0.60%. The figures show that the gratings consist of rows of silver grains, and the grains in a row are not continuous. As shown in Fig. 6(a), which corresponds to a high diffraction efficiency,

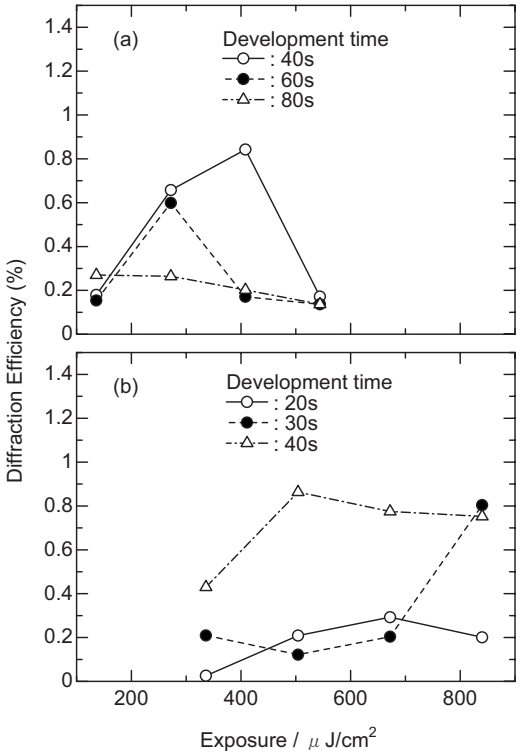

Figure 4. Relationship between diffraction efficiency and exposure value at different development times. Light intensity: (a) 680 $\mu W/cm^2$ and (b) 840 $\mu W/cm^2$.

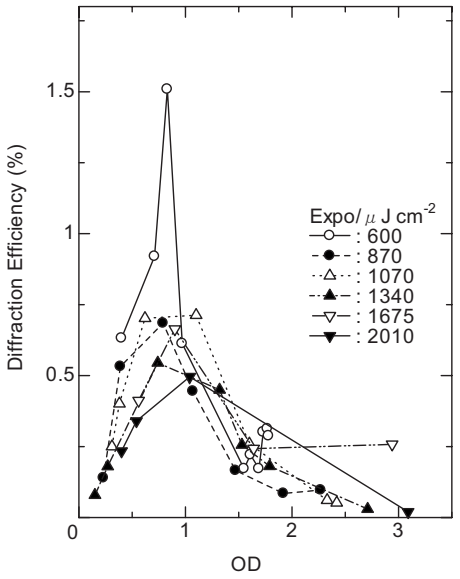

Figure 5. Relationship between diffraction efficiency of the amplitude hologram and the optical density at each exposure value. The optical density was altered by altering the development time.

silver grains are located close to each other and the gratings are well defined. When the exposure value is small, the grains are separated by larger intervals, and the gratings had many open spaces, as shown in Fig. 6(b), which causes decreases both in the optical density and in the diffraction efficiency. On the other hand, when the development time was prolonged, the optical density increased. This is partly

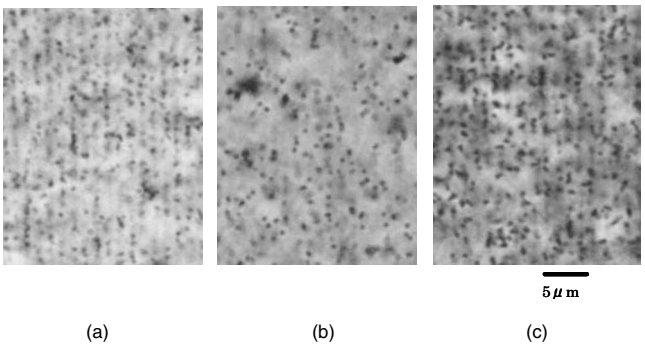

Figure 6. Optical micrograph of the diffraction gratings formed on the amplitude hologram, as obtained at different exposure times and development times. Exposure value and development time: (a) 408 $\mu J/cm^2$ and 40 s, (b) 136 $\mu J/cm^2$ and 40 s, and (c) 272 $\mu J/cm^2$ and 60 s. Diffraction efficiencies: (a) 0.84%, (b) 0.18%, and (c) 0.60%.

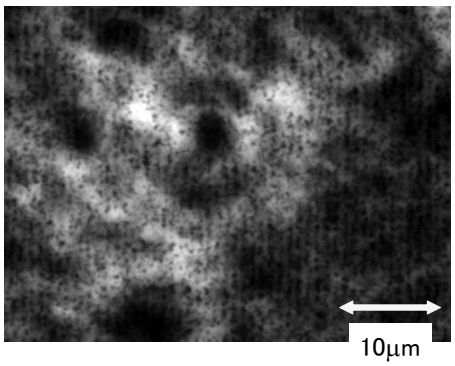

Figure 7. Example of optical microphotograph of the diffraction gratings formed on the amplitude hologram with high optical density.

due to an increase in the size of silver grains, as shown in Fig. 6(c). However, at the same time, the amount of fog in the unexposed area increased, which may be due to the uniform generation of silver atoms by overheating. This formation is the main reason for the increase in optical density, and it also results in a decrease in the diffraction efficiency.

Moreover, as the heating for thermal development was carried out by hand on the hot plate, a large amount of fog that was unevenly distributed appeared occasionally. An example of an optical microphotograph of the diffraction gratings with high optical density is shown in Figure 7. The development proceeded in an uneven manner and resulted in the formation of a large amount of fog. There are many black areas in which fog obscures the gratings. The presence of these black areas also decreases the diffraction efficiency.

Conversion of Amplitude Hologram into Phase Hologram

By carrying out a bleaching treatment using bromine gas, the black images of developed silver grains were made transparent. Every area turned lemon yellow in color. When iodine was used for bleaching, a dark brown coloration appeared because of the deposition of iodine. As the gratings were not well defined, bleaching by iodine was not pursued further.

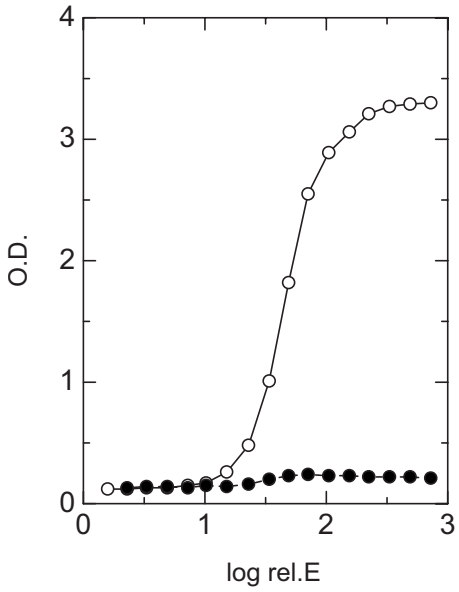

Figure 8. Photographic characteristic curves obtained for photothermographic film before and after bleaching were carried out using bromine gas. The films were exposed to white light. Open circles with solid line: before bleaching; closed circles with dashed line: after bleaching.

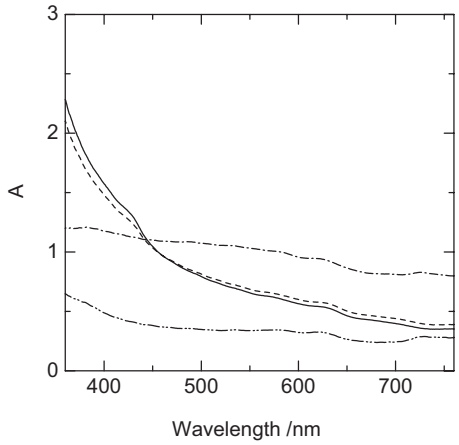

Figure 9. Absorption spectra of the images recorded on a photothermographic film before and after bleaching were carried out using bromine gas. Solid line: exposed area after bleaching; dashed line: unexposed area after bleaching; dashed-dotted line: exposed area before bleaching; and double-dotted-dashed line: unexposed area before bleaching.

Characteristic curves obtained before and after bleaching by bromine gas are shown in Figure 8. The film was exposed to white light. The optical density decreased significantly, which suggests that the developed silver grains disappeared.

The absorption spectra of the film before and after the bleaching are shown in Figure 9 for both exposed and unexposed areas. Before the bleaching was carried out, the absorption in the exposed area was higher than that in the unexposed area at all wavelengths. The absorption spectrum was flat, and this indicates that the film was black in color. On the other hand, after the bleaching was carried out, the

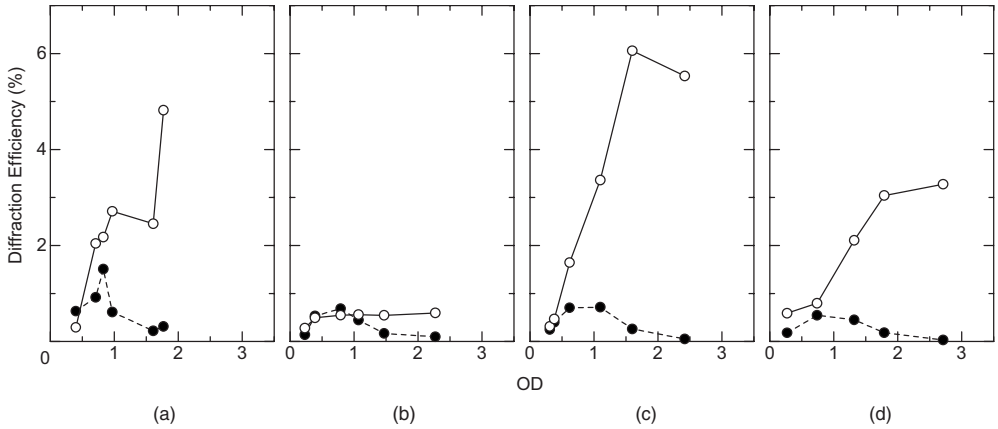

Figure 10. Relationship between diffraction efficiency and optical density of the exposed area before bleaching was carried out using bromine gas, as recorded on a photothermographic material for several exposure values. Open circles with solid line: after bleaching was carried out using bromine gas; closed circles with dashed line: immediately after thermal development and before bleaching was carried out using bromine gas.

spectra for the exposed and unexposed areas overlapped and the absorption of blue light became relatively strong. After bleaching, all areas were uniformly yellow in color and the gratings could not be recognized under an optical microscope. As these absorption spectra are identical to the spectrum of silver bromide, the formation of silver bromide was inferred.

Figure 10 shows the change in the diffraction efficiency resulting from the conversion of the amplitude holograms to phase holograms by bleaching treatment at each optical density before the bleaching and for four different exposure values. The diffraction efficiency increased significantly as a result of the bleaching treatment. We obtained a maximum diffraction efficiency of 6%. A hologram with high diffraction efficiency was obtained by converting an amplitude hologram into a phase hologram. Moreover, the efficiency increased continuously with increasing optical density. In the amplitude hologram, the diffraction efficiency in a region corresponding to higher optical density was not very high, but when the amplitude hologram was converted into a phase hologram, the efficiency in this region increased significantly.

DISCUSSION

Amplitude Holograms

Photothermographic materials had a sufficiently high resolution for recording holograms, and amplitude holograms were recorded by gratings that comprised developed silver grains. However, the diffraction efficiency was not very high, as indicated by the maximum of 1.5%. The diffraction efficiency decreased when the development time was increased, and hence, the optical density increased. This change may be mainly due to the increase in the absorption of transmitted light by silver grains that make up diffraction gratings, as shown in Fig. 6.

Furthermore, the distribution of grains was discontinuous and there were many openings between the grains in a row. This is another reason for the low diffraction efficiency. Prolonged development resulted in a continuous row of silver grains. However, this decreased the diffraction efficiency, as developed silver grains also appeared in the unexposed area and blurred the gratings.

In this study, we simply carried out the thermal development on a hot plate. Although this is a simple and easy method, it does not facilitate accurate temperature control and inevitably results in uneven heating which resulted in formation of a large amount of fog that was distributed unevenly, as shown in Fig. 7. This may contribute to a decrease in the diffraction efficiency. The diffraction efficiency could therefore be increased by precisely controlling the development and carrying out uniform heating. A decrease in the amount of fog and a decrease in the open spaces between the gratings should lead to an increase in the diffraction efficiency.

Conversion to the Phase Hologram

The diffraction efficiency increased drastically when the amplitude hologram was converted into the phase hologram. After the bromine bleaching, by which silver atoms are converted to transparent silver bromide, more light will be transmitted and gratings with different refractive indices would be formed. In an area that has high optical density but low diffraction efficiency in the amplitude hologram, the efficiency becomes larger after the conversion to a phase hologram. The gratings in the area having higher optical density may become more definite after the conversion, and this leads to an increase in the diffraction efficiency.

As there is no process of fixation in the photothermographic materials, silver halide grains still remain in the unexposed area. As silver was converted to silver bromide by the bromine bleaching, silver bromide exists in both the exposed and unexposed areas. After the bleaching, no visible grating could be observed in an optical microscope. We expect, however, that the structure of the gratings in the phase hologram after bleaching should be different from that of the gratings formed in wet-type materials by bleaching.

What is the main factor responsible for the formation of

diffraction gratings? One factor may be the formation of silver bromide. In photothermographic materials, there is a large amount of silver carboxylate that serves as a source of silver ions, and this silver carboxylate is consumed as the development proceeds. It has been reported that there is an area in which there is no silver carboxylate; this area lies in the vicinity of the developed silver grains and is called the "sphere of influence."[7] In the case of photothermographic materials, the gratings in areas with and without silver carboxylate will be formed after development. After bleaching, the entire film becomes yellow in color with no difference between the absorption spectra of the exposed and unexposed areas, as shown in Fig. 8. This indicates that silver carboxylate was converted into silver bromide. Since the silver carboxylate near the exposed silver halide grains is consumed in the course of development, silver bromide is not formed within the sphere of influence. However, the developed silver grains at the center of this area will be converted to silver bromide grains. Therefore, silver bromide exists in both the exposed and unexposed areas. As a result, the entire film shows the same color, even though it is probable that the refractive index of silver bromide converted from silver grain may be different from that converted from silver carboxylate.

Photothermographic materials also contain other reagents such as developers, toners, or silver-ion complexing agents. These reagents migrate to the exposed silver halide grains and are consumed on thermal development; on the other hand, in the unexposed area, the reagents are left behind. The presence or absence of these reagents would not result in a difference in the optical density since these reagents are almost transparent. However, the presence or absence of them might be responsible for formation of the gratings because these reagents may cause a difference in the refractive index.

Relationships between diffraction efficiency and exposure shown in Fig. 4 show a peak, and in the case of the amplitude hologram, the efficiency decreased with increasing exposure. This decrease may be due to the decrease in the amount of transmitted light. After bleaching, the samples with low initial diffraction efficiency exhibit significantly higher diffraction efficiency. In such samples, the gratings would become more definite as the gratings change from those comprising rows of silver grains with large open spaces to those comprising stripes of a combination of the aforementioned components.

Although the main factors responsible for the formation of diffraction gratings have not yet been fully established, some transparent materials form gratings because of difference in refractive indices. In future work it may be possible to increase the diffraction efficiency using reagents that help to create a greater difference in the refractive index. Also, in these experiments we used bromine gas for the bleaching. However, bromine gas is harmful and difficult to handle. One possible solution to this problem is to use a reagent that releases halogen atoms during thermal development. The released halogen atoms/molecules will diffuse into the melting layer and react with the silver grains or with the residual silver carboxylate to convert the amplitude hologram to a phase hologram.

CONCLUSIONS

1. The use of photothermographic materials enables us to record holograms in a silver halide photographic material without carrying out the wet-treatment process.
2. Amplitude holograms whose gratings consist of rows of developed silver grains are formed in photothermographic materials, although the diffraction efficiency is not very high (about 1.5%).
3. Bleaching can be carried out using bromine gas in order to convert amplitude holograms to phase holograms. By this process, the diffraction efficiency increases to about 6%.
4. Both the exposed and unexposed areas turn yellow in color on bleaching because of the formation of silver bromide. Both silver grains in the exposed area and silver carboxylate molecules in the unexposed area are converted to silver bromide.
5. The main factor responsible for the formation of gratings after bleaching has not yet been established. One possible factor is the formation of stripes of silver bromide, developer, toner, or other components during thermal development and following bleaching. These stripes have different diffraction indices, which lead to the formation of gratings.

REFERENCES

[1] P. Hariharan, *Cambridge Studies in Modern Optics 2: Optical Holography* (Cambridge University Press, Cambridge, 1984), pp. 89–90.
[2] P. J. Cowdery-Corvan and D. R. Whitcomb, in *Handbook of Imaging Materials*, edited by A. S. Diamond and D. S. Weiss (Dekker, New York, 2002), pp. 473–529.
[3] S. M. H. Kimura, T. Suzuki, T. Mitsuhashi, K. Kuge, and A. Hasegawa, J. Imaging Sci. Technol. **51**, 540 (2007).
[4] Ref. 1, p. 56.
[5] Ref. 1, pp. 96–99.
[6] A. Graube, Appl. Opt. **13**, 2942 (1974).
[7] D. H. Klosterboer, in *Neblette's 8th Edition; Imaging Processes and Materials*, edited by J. M. Sturge, V. Walworth, and A. Shepp (Van Nostrand Reinhold, New York, 1989), pp. 282–284.