Preparation of Gold Particles in Gelatin Layer Film by the Use of Photographic Materials (11): Preparation of Hologram Made of Striped Gold Layer

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Abstract

We have refined upon the method of preparing an image with gold particles in gelatin layer by the use of photographic materials and a certain gold development. When a photographic glass plate exposed with interference fringe was immersed in the gold-thiocyanate complex solution, a gold particle deposited on a latent image speck and diffraction grating made of stripes with gold particles was obtained. After calcining the grating at max. 480 °C the gelatin layer was burned out, and the gold particles were fused and formed a gold layer. Then, we obtained the grating made of striped gold metal layers stuck on the glass plate. Clear gratings of 333 nm ~ 1 μm pitch were observed with AFM. Thickness of the gratings was several ten nm. The gratings of 1 μm pitch showed a clear diffraction at both transmitted and reflected light after calcination. The maximum diffraction efficiencies were about 9 % at transmitted light for the grating without calcination and 1.6 % at reflected light for the calcined one. It would be possible to prepare hologram images stable even in severe environments with this method.

Introduction

Hologram is widely used for 3-D displays or other optical techniques. Now, there are three main hologram recording materials, the first one is silver halide photography, the second is dichromate gelatin and the third is photopolymers[1,2]. All materials make diffraction gratings with some kind of polymers. Because the change in quality of polymer is inevitable, hologram images are not stable especially in severe environments, such as in outdoors. This is one reason to prevent holograms from being widely used.

We reported the new method to prepare a photographic image made of gold particles in a gelatin layer[3-7]. This used a certain physical development. Gold atoms deposit on a latent image speck and gold particles form on a silver halide grain, when the exposed photographic material is immersed in the gold-thiocyanate complex solution, which is similar to the solution for gold latensification[8]. After fixation only the gold particles are left behind in a gelatin layer, and a photographic image made of gold particles forms instead of silver particles.

It is also possible to record a hologram image with this method, as the image has similar resolution power to the normal photographic development process. This image is made of gold particles and so the change in quality of silver particles is avoidable. As this hologram is one kind of amplitude hologram, the image is dark as it should be observed at transmitted light. Moreover, as gold particles are kept in gelatin layer, the change in quality of gelatin is inevitable.

Accordingly we proposed a new method to remove the gelatin layer to make the image with stable gold metal only[7]. We found that calcination of the above image burnt off the gelatin and gold metal layer were left behind on a glass plate as the gold particles fused each other.

We applied this method to prepare a stable hologram images and got diffraction gratings made of striped gold metal layers on a glass plate. This hologram would be stable and possible to store for a long period in outdoors or under any other severe environments, as the gratings were made of stable gold and glass only.

Experimental

Photographic material used was the photographic plate for hologram recording (Konica-Minolta, P5600). Optical system to record interference fringe is shown in Fig. 1. The light source was an Ar laser with 488 nm light. The light beam was devided to two beams and both entered to the plate symmetrically. The light intensities of both beams were the same value of 1 mW / cm^2 and exposure time was 0.1~0.3 s. The cross angle of both beams were adjusted to make the interference fringe from 1000 nm (28°) to 333 nm (94°) pitch.

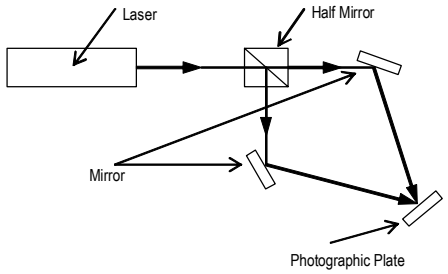

Fig. 1. Optical system to record interference fringe on photographic plate.

A schematic diagram to prepare the striped gold metal layers is shown in Fig. 2. Procedures (a) to (c) are the preparation process of gold particles in gelatin layer, which is the same one in the previous papers[3-6]. Gold ion concentrations were changed from 1 x 10^{-3} to 1 x 10^{-4} mol/L. Procedure (d) is the calcination process to prepare gold metal layers in the previous paper[7]. Glass plate with gold particles of the sample (c) was heated in an electric furnace at max. 480°C for 5 to 10 hours.

We observed diffraction grating on the plate with an optical microscope or an AFM. Diffraction efficiency of the grating was measured with a similar optical system. The light beam of 633 nm from He-Ne laser entered to the grating at the angels of 18.5° for the measurement at transmitted light and of 0° for the one at reflected light. The intensity of diffracted light transmitted through the grating plate or that reflected on the plate was measured with an photometer. We measured only the diffraction efficiency at transmitted light for the gratings before calcination as they did not have enough reflection.

Results

The obtained grating before calcination had purple color due to plasmon absorption of gold particles at transmitted light. After calcination it changed to dark blue color at transmitted light and a bright gold luster appeared. Those changes were clearly appeared in Fig. 3 and Fig. 4. Fig. 3 shows absorption spectra before and after calcination. The spectrum before calcination revealed a sharp peak at 560~570 nm. This is a typical plasmon absorption by nano-sized gold particles. The calcination caused a red shift and a broadening of the peak. This suggested that the particle size increased. Fig. 4 shows the reflection spectra. The spectrum after calcination shows an increase of

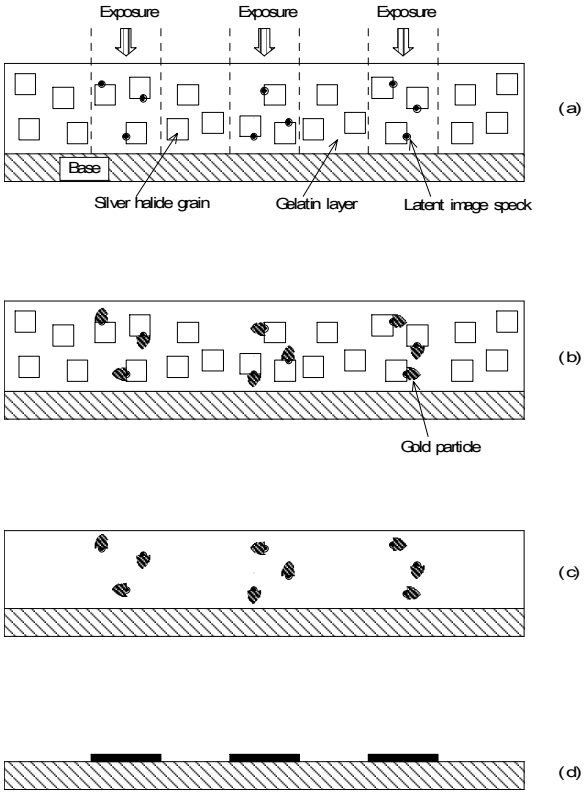

Fig. 2. Schematic diagram preparing a diffraction grating made of striped gold metal layers. (a) exposure with interference fringe, (b) gold deposition by immersing in gold-thiocyanate complex solution, (c) fixation by photographic fixer, (d) calcination at max.480°C.

reflection at longer wavelength than 500 nm. This is a typical spectrum by gold luster. Those suggested that the gold particles fused each other to make larger particles and continuous layers.

Optical micrographs of the gratings of 1 mm pitch before and after calcination are shown in Fig. 5. The gratings from 1μm to 500 nm pitch were observed but the one smaller than 500 nm was not. The grating before calcination is made of gold particles in gelatin layer and the one after calcination is made of gold metal layers without gelatin. The latter seems to have clearer fringe than the former. Both grating pitch were almost same each other and those were also same as the interference fringe used in the exposure. This suggested that the gold deposition method had a high resolution power and the calcination treatment did not disturb this resolution power.

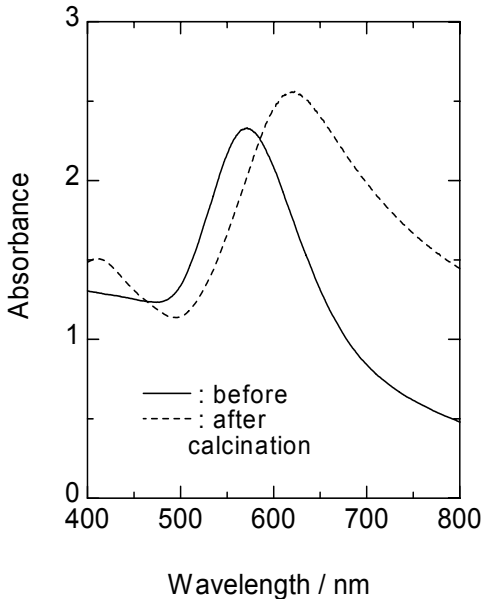

Fig.3. Change of absorption spectra of the image with gold particles to that with gold metal layer by calcination.

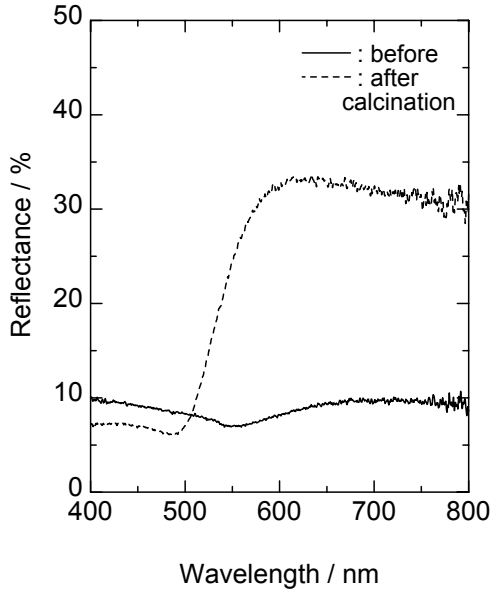

Fig.4. Change of reflection spectra of the image with gold particles to that with gold metal layer by calcination.

AFM images of the gratings of 1μm and 333 nm pitches after calcination are shown in Fig. 6. Grating was observed on every sample including even the grating of 333 nm pitch. Consequently, it was due to the lack of resolution power of the optical microscope that we could not observe the grating smaller than 500 nm pitch. The bottom figures show the cross section of grating. The AFM images of the gratings of 1μm and 333 nm pitches after calcination are shown in Fig. 6. Grating was

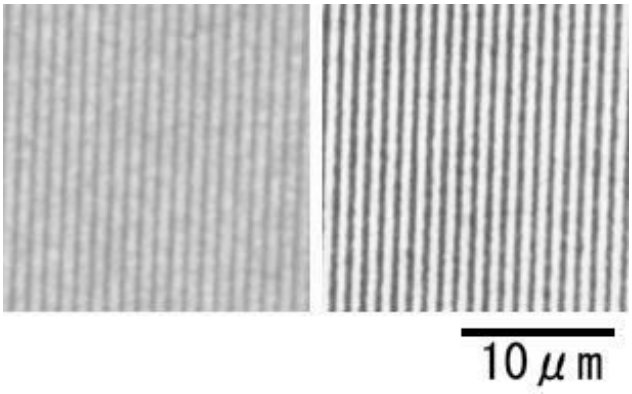

Fig.5. Optical micrographs of gratings of 1 μm pitch before (left) and after(right) calcination.

observed on every sample including even the grating of 333 nm pitch. Consequently, it was due to the lack of resolution power of the optical microscope that we could not observe the grating smaller than 500 nm pitch. The bottom figures show the cross section of grating. The height of grating is 60~80 nm for the 1 μm pitch grating and 10 ~ 30 nm for the 333 nm pitch one. Before calcination the gelatin layer with gold particles was about 5 μm thick. Therefore, the calcination decreased the layer thickness to about 1/100 and the grating of gold layer sticks on the glass base in a very thin layer form.

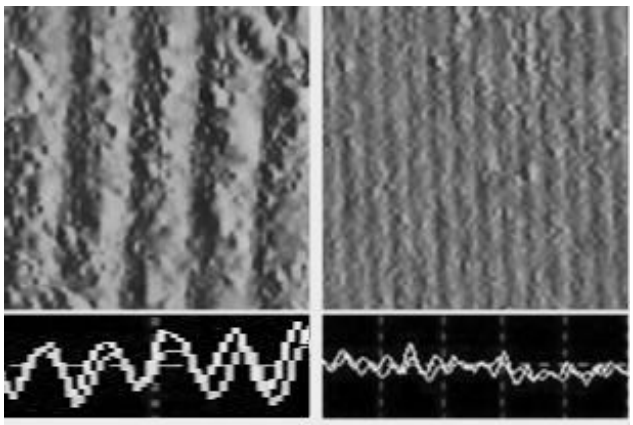

Fig.6. AFM images of gratings after calcination. Left : 1 μm pitch, right : 333 nm pitch. Top : height images, edge length of the squares = 5 μm. Bottom : cross sections, height of the rectangles = 100 nm.

The diffraction was observed at both transmitted light and reflected light for the calcined samples, while only at the transmitted light for the ones before calcination. The highest efficiency was obtained at the grating of 1 μm pitch. The efficiency decreased with the pitch and the diffraction was not observed on the grating of 333 nm pitch. As the grating was formed clearly, this should be due to the structural limitation of optical system. Diffraction efficiency of the gratings of 1 μm pitch is listed in Table 1. The maximum value of efficiency was observed on the sample without calcination at transmitted

light, although it was less than 10 % and not so high value.

Table 1	Diffraction efficiency(%) of gratings of 1μm pitch with gold particles or gold layer			
	period of gold deposition / hour			
	3	4	5	6
before calcination				
transmitted light	4.9	8.8	5.8	1.9
after calcination				
transmitted light	1.4	0.22	0.85	0.11
reflected light	0.09	0.44	0.73	1.6

The diffraction efficiency at reflected light for calcined samples increased with the gold deposition period, but it was not a high value. Prolonged deposition period would promoted the growth of gold particles and so more continuous gold metal layer formed after calcination. This reflected the light strongly to increase the efficency.

Discussion

We prepared the gratings made of striped gold metal layers on a glass plate and formation of gratings of 1 μm to 333 nm pitch was confirmed with AFM. As the grating pitch was same as the exposed interference fringes, the grating was not disturbed on the calcination treatment, which altered gold particles to gold metal layers. Clear diffractions were observed for calcined samples at both transmitted and reflected light, although diffraction efficiencies were not so high. Investigation of calcination condition should be necessary to increase the diffraction efficiency.

The grating after calcination is made of metal gold layer on a glass plate. As both are very stable materials, the grating would be very stable and have good preservative ability. Gratings from 1 μm to 333 nm pitch would be enough to record hologram images. Therefore, it is expected that the hologram images made of this grating have long lifetime even in severe environments, such as outdoors.

Conclusion

We developed a new method to record interference fringes by the use of photographic materials. The final form of diffraction grating was made of striped gold metal layers whose grating pitch was same as the interval of interference fringe. The minimum pitch of grating was 333 nm. As the materials making gratings are very stable ones, this method would be applicable to prepare stable hologram images.

References

1. P.Hariharan, “Cambridge studies in modern optics 2 ; Optical holography”, Cambridge University press, Cambridge, (1984), Ch.7.
2. T.Kubota, J. Photogr. Sci. Tech. Japan, **65**, 15 (2002).
3. K.Kuge, M.Arisawa, N.Aoki, A.Hasegawa, Japanese J.Appl.Phys.,**39**(12A),6550 (2000).
4. K.Kuge, K.Kimijima, M.Arisawa, N.Aoki, A.Hasegawa, J. Photogr. Sci. Tech. Japan, **64**, 242 (2001).
5. K.Kuge, I.Suzuki, N.Aoki, A.Hasegawa, J. Photogr. Sci. Tech. Japan, **65**, 536 (2002) .
6. K.Kuge, M.Arisawa, N.Aoki, A.Hasegawa, Imaging Sci.J., in press.
7. K.Kuge, Y.Goto, T.Nakao, Y.Hikosaka, A.Hasegawa, J. Photogr. Sci. Tech. Japan, submitted.
8. H.E.Spencer, C.A.DeCann, R.T.McCleary, J. Imaging Sci., **31**, 8 (1987).

Biography

Ken’ichi KUGE received his B.S. degree in Engineering from Kyoto University in 1975 and D. degree in Engineering from Kyoto University in 1984. Since 1979 he has worked in the Department of Imaging Science (the present name ; Department of Information and Imaging Sciences) at Chiba University in Chiba. His work has primarily focused on the silver halide photographic science, including photosensitivity and sensitization. Recently his focus has been expanded to novel imaging systems based on silver halide technology. He is a member of the IS&T and the JSPST.