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Obtaining relief structures in silver halide materials

Obtención de estructuras de relieve en materiales de registro de haluros de plata

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ABSTRACT:

Diffraction transmission gratings were recorded in AGFA-8E75 film, chemically treated under processes with D-19 + potassium ferrocyanide and a chemical processing technique proposed for PE-2 film to obtain embossed stripes. Holographic structures were measured topographically by the technique of atomic force microscopy in noncontact mode (NC-AFM) and we observe changes in the depths under variations in exposures and used photochemistry. We find that the best performance in terms of relief depth obtained is given by the conventional process which reached depths between 0.15 μm and 0.3 μm for spatial frequencies of the order of 400::500 lp/mm. In this study we evaluated the possibility of obtaining matrices highlighted in silver halide holograms replication processes.

Key words: Atomic Force Microscopy (AFM), Holographic Gratings, Bragg Gratings, Photochemical Silver Halides.

RESUMEN:

Se registraron rejillas de difracción de transmisión en película AGFA 8E75, tratadas químicamente bajo procesos convencionales con D-19 + ferrocianuro de potasio y una técnica de procesamiento químico desarrollada para película PE-2, para la obtención de franjas con relieve. Las estructuras holográficas fueron medidas topográficamente mediante la técnica de microscopía de fuerza atómica en modo no contacto (AFM-NC) y se observan cambios en las profundidades bajo variaciones en las exposiciones y la fotoquímica utilizada. Se encuentra que el mejor rendimiento en términos de profundidad de relieve obtenido está dado por un proceso tradicional con el cual se alcanzaron profundidades entre 0,15 y 0,3 μm para densidades ópticas y frecuencias espaciales bajas. En este trabajo evaluamos la posibilidad de obtener matrices de relieve en haluros de plata para procesos de réplica de hologramas.

Palabras clave: Microscopía de Fuerza Atómica (AFM), Rejillas Holográficas, Redes de Bragg, Fotoquímica, Haluros de Plata.

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1. Introduction

In order to massively produce holograms that can be reconstructed using white light, there is a method which allows printed or stamped holograms from a matrix which functions as a mold in which the diffraction grating is recorded as variations in height on a relief structure [1]. In this technique the holograms must be transmissive due to the fact that, in the holograms, the Bragg reflection gratings are spatially distributed on the film's thickness, which cannot be translated into variations of relief. On the other hand, for a transmission hologram to be used with white light, we must resort to rainbow holography, a technique made viable by Benton in the 70's [2], which allows the use of all wavelengths in the reconstruction of a transmission hologram, without the problem of blurred overlap of the images.

The material conventionally used for generating these arrays of embossed holographic structures is the photoresist; particularly in the case of AZ1350, the behavior of the Relief Depth vs exposure tends to saturate on 1500 mJ/cm^2, reaching a maximum depth of 1 μm [1]. Thus, the biggest disadvantage of this is the low sensitivity and the need of an Argon-ion laser or He-Cd with wavelengths in the violet and ultraviolet to generate records, which represents high cost [3,4]. Typically the photoresist is about 250,000 times less sensitive than a silver halide conventional film like AGFA-8E75 [5].

In the developing process, when the emulsion is subjected to various chemical baths that modify its molecular structure, it is possible to control some features that appear macroscopically, such as the depth of the relief obtained. This has been worked by Benton [2], Bjelkhagen and Galpern [3], Pizzaneli [4], and Necati, Alaçakir and Aydin [6], who report results oriented to obtain the necessary matrix relief to make identical replicas of holograms from a master in conventional silver halide materials. The main benefit of using these materials are low exposure times required for these films to save records of the interferometric pattern due to their sensitivity to wavelengths in the visible spectrum corresponding to the most commonly used, and lowest cost lasers such as He-Ne [3,4].

Other authors have dealt with experiments to optimize these processes seeking to maximize the relief obtained for a given exposure on the emulsion; Altman [7] for example, using 649-F film, working with optical density exhibits near 4, using HRP developer and R-10 bleach, obtained relief in the order of microns (1 to 3 microns). Later Bustov and Ioffe [3] undertook to investigate the parameters of holographic gratings in Mikrat-VRL and AGFA-8E75 with and without bleach, obtaining relief depths greater than 1.5 microns to spatial frequencies of the order of 30 mm^{-1}. On the other hand, Rigler [3] reported in 1965 that using chemical treatment on silver halide emulsion are achieved relief structures and diffraction efficiencies on aluminized matrices that depend inversely of the spatial frequency of the recorded grating. As shown in his results, to an angle of 20° between beams, the relief reached depths of 210 nm.

During the mid 80's, Galpern [3] confirmed experimentally on Russian film PE-2, that a process with conventional developer and bleach hardener [8] which produces higher spatial frequencies reliefs and claims that processes with hardening developer are not as successful because of the resulting oxidation products extend beyond the boundaries of the lines of developed image, which leads to a leveling in the degree of hardening in exposed and unexposed areas of the emulsion. Subsequently, Koreshev Brui using a PRG developer, fixer and R-10 bleach find relief depths and also state that those profiles come into a trapezoidal shape for spatial frequencies below 300 lp/mm, and above this threshold the profiles tend to be triangular.

Other authors such as Ahlhorn and Kreye in the early 90's, proposed the biochemical treatment of the emulsion in post-process baths enzymes like trypsina or chymotrypsina [3].

The characterization of the holographic profiles relief structures were commonly obtained by electronic microscopy (SEM), and it was only until 1986, with the appearance of the atomic force microscope (AFM), that these measures started to be made without requiring a metal coating on the emulsion, presenting it as a much more versatile technique that allows topographic records without affecting the surface [9]. More recently, the work of Necati, Alaçakir and Aydin [5] reported successful results of the AFM topographic characterization of relief structures in AGFA 8E56 film obtained under different chemical treatments of the emulsion. Due to the low exposures required by the silver halide films to obtain relief depths of the order of 0.2 μm, which corresponds to typical relief depths in photoresist for copying holograms [3], enables the use of He-Ne lasers of low cost to generate matrices that satisfy these conditions.

Thus, the purpose of this study is to evaluate, using atomic force microscopy (AFM), various developing and bleaching processes in AGFA-8E75 film that allow to obtain relief structures of holographic diffraction gratings recorded by transmission to meet the expected depths for processes holograms replication.

2. Experimental setup

We have the interest to know what would be the orders of the higher values of depth obtained for sweeps between 40 μJ/cm² and 70 μJ/cm², (which correspond to a normally used range in which the diffraction efficiency of holograms recorded in AGFA-8E75 film is maximized). Gratings were recorded by the transmission of two flat wave fronts forming an angle $2\alpha = 15^{\circ}$ (less than the minimum reported by Rigler [3], in this case 15º, which corresponds to a spatial frequency of 417 lp/mm), using a He-Ne laser with wavelength $\lambda = 632.8$ nm in AGFA-8E75 film, with grain size between 35-44 nm, with a resolution power up 5000 lp/mm and emulsion thickness between 5-6 microns [3]. The experimental setup used for recording of the gratings is shown in Fig. 1.

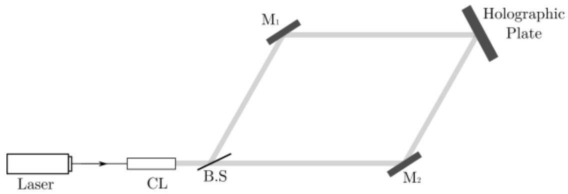

Fig. 1. Experimental setup for recording of transmission gratings. M_1 and M_2 denote mirrors, B.S a beam splitter, and CL a collimator.

Four chemical processes were analyzed, each using the same sweep exposures of 40, 54, 64 and 70 μJ/cm², handling the same ratio reference/object (1:1) and the same angle between the two beams ($2\alpha = 15^{\circ}$) on each of the gratings. This is done in order to evaluate the performance of each process and to observe the relationship between the exposure and the relief obtained for each case.

Of the various combinations of developers, fixers and bleachers for chemical processes in silver halide films, we know that each modifies the physical and chemical structure of the emulsion differently. Their choice depends on the properties that are desired as final result. Galpern [3] for example, proposes a modification of the D-19 developer, in order to maximize the relief, achieving the best reported results. The components of this modification (which we have called Galpern No 2) are detailed in Table I.

Table I
Constituents and proportions D-19 and Galpern No 2.

Constituents	D-19	Galpern No 2
Metol	2 g	4 g
Hydroquinone	8 g	8 g
Ascorbic Acid		26 g
Sodium Sulfite	90 g	
Sodium Carbonate	52.5 g	40 g
Potassium Bromide	5 g	
Potassium Thiocyanate		4 g
Ammonium Bromide		2 g
Water	To 1L	To 1L

Therefore we propose four chemical processes to assess the impact of these two developers, with several changes in the combination of fixing and rehalogenating bleach. These are:

1. D-19 developer + F-24 fixer,
2. D-19 developer + F-24 fixer + bleaching with potassium ferrocyanide,
3. Galpern developer No 2 [2] + F-24 fixer+ bleaching with potassium ferrocyanide,
4. Galpern developer No 2 [2] + bleaching with R-10 + ammonium bath dichromate 5% + sulfuric acid pH3.

For each process we performed several records of holographic gratings with the setup described in Fig. 1, and after being developed they were taken to the AFM for topographical measurements in every one of them. Later, we bleached the emulsion in order to do further measurement so that we could make comparisons in the reliefs before and after the bleaching wherever possible.

The first process allows to obtain amplitude transmission gratings in a conventional way, i.e, it corresponds to the generally used photochemical to develop transmission holograms on film AGFA 8E75, which allows to obtain reference values for assessing the impact of other processes in the relief. The second allows to obtain phase gratings under the same developing conditions.

On the other hand, the third proposal evaluates the effect of a less alkaline developer (no sodium sulfite) which stops hydroquinone from having a tanning effect on the entire emulsion and from tending to balance the hardening levels on both the exposed areas and those not receiving the light, with the bleaching stage remaining. Finally, in the fourth process we used Galpern No 2 developer, a tanning bleach like R-10, followed by a bath in ammonium dichromate at 5% for 5 minutes, in order to increase the hardening effect of the material, and finally a bath in sulfuric acid solution with pH 3 to decrease drastically the pH of the emulsion. Bleach constituents of R-10 bleach are presented in Table II.

Table II
Constituents and proportions Part A and Part B for R-10 bleach.

Constituents	R-10 Part A	R-10 Part B
Ammonium dichromate	20 g	
Sufuric acid	14 ml	
Potassium bromide		92 g
Water	To 1L	To 1L

3. Results

We have obtained diffraction gratings in film AGFA-8E75 for the four proposed chemical processes and under the conditions listed before. The diffraction gratings were scanned in the AFM in noncontact mode, processed with SPIP 5.8 software to extract relevant information of the micrograph, and for each of the processes proposed the depth was contrasted vs the exposure in order to evaluate the response of the emulsion to each of the chemical processes in terms of the relief. The ordered pairs for each case are shown in Fig. 2.

In all cases we can observe a greater relief depth for high exposure values, achieving the best performance for the process with D-19 and bleaching with potassium ferrocyanide, with which we achieved depths between 0,15 μm and 0,3 μm. In Figs. 3, 4, 5 and 6, we present the results obtained in terms of topography, the micrographs obtained by AFM for the gratings exposed to 70 μJ/cm^2 and processed under each of the described photochemical processes.

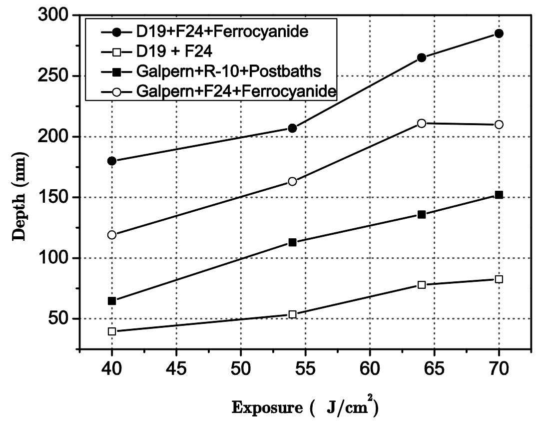

Fig. 2. Depth vs. Exposure for each of the photochemical processes implemented.

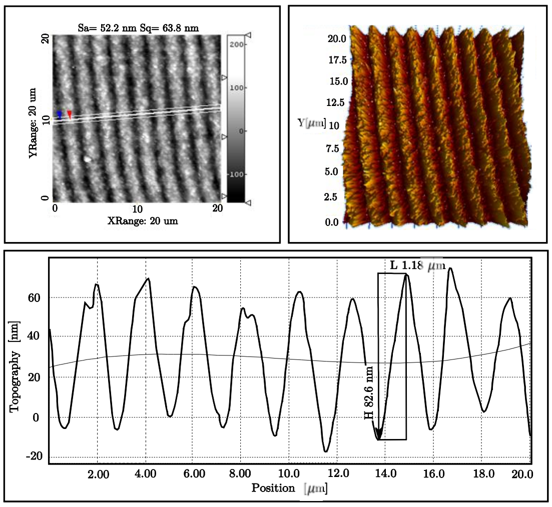

Fig. 3. Grating exposed with 70 µJ/cm² using photochemical process with D-19 + F-24. Maximum relief obtained of 82.6 nm. (Micrography and relief profile).

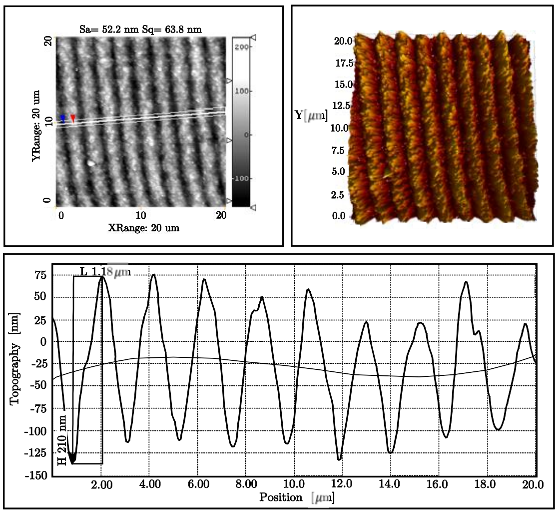

Fig. 5. Grating exposed with 70 µJ/cm² using photochemical process with Galpern No 2 + F-24 + Potassium Ferrocyanide. Maximum relief obtained of 210 nm.

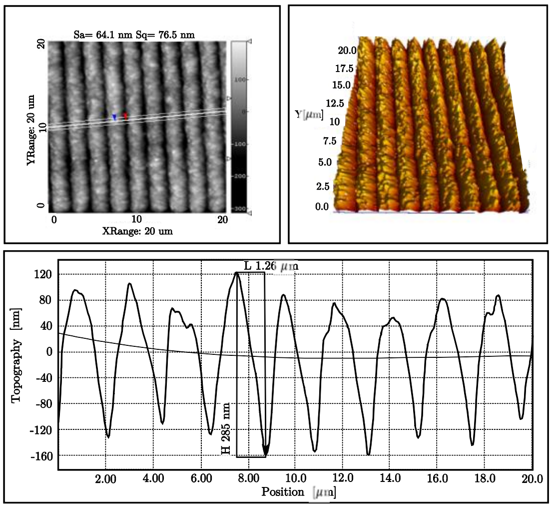

Fig. 4. Grating exposed with 70 µJ/cm² using photochemical process with D-19 + F-24 + potassium ferrocyanide. Maximum relief obtained of 285 nm.

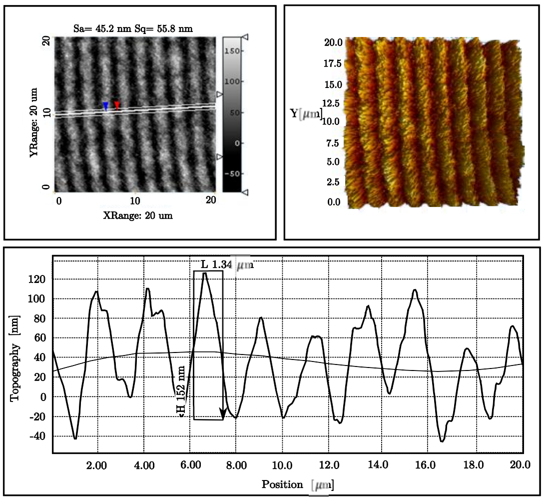

Fig. 6. Grating exposed with 70 µJ/cm² using photochemical process with Galpern No 2 + R-10 + Post Baths. Maximum relief obtained of 152 nm.

As shown, the relief profile measured with AFM shows irregularities. This roughness is due to the granularity of the silver halide in the emulsion and their order do not affect the replication process of the hologram due to the orders of magnitude (grain size: 40-50 nm, separation between stripes 2.18 µm) and variations in the depth of the relief structures are due to the spatial frequency of the interference fringes and exposure. The uncertainty of the experimental measurements according to the characterization of the atomic force microscope, is 10%.

4. Conclusions

The reliefs obtained by the process that includes the rehalogenating bleach based on potassium ferrocyanide, encompass an interesting result since there were no reports in the literature of relief structures under conventional processes such as this, and experimentally we observe that it maximizes the relief way above the bleaching processes above like the R-10 under the same exposures.

The results obtained with AGFA-8E75, aim at a maximum of 285 nm in relief, without knowing yet the saturation depending on the exposure process, which suggests an agreement with written reports aiming at obtaining low relief holographic matrices under processes on silver halide emulsions, and it is confirmed that for smaller angles (15° in this case), were achieved depths in the relief structures around 285 nm.

Although AGFA-8E75 films are not commercial yet, this work confirms that the silver halide materials can be a suitable material for embossed holograms, to get good results in AGFA-8E75 leaves an open possibility that in Russian films as PFG-01 is justifiable to work with the photochemistry to achieve similar results (as they are films with similar characteristics in grain size and resolution and even in the orders of exposure in which they respond).

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