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Synthetic holograms based on photochromic diarylethenes

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ABSTRACT

Diarylethenes are P-type photochromic systems showing reversible light-induced modulation of optical properties, e.g., transmittance and refractive index, in the visible and near infrared regions. Transmittance can be progressively tuned according to the illumination dose, and the pattern written and erased several times with light. We demonstrated binary Computer Generated Holograms based on photochromic materials, to be used as adaptable reference surfaces in interferometric tests. We encoded by Direct Laser Writing binary amplitude Fresnel Zone Plates into photochromic substrates and successfully tested them into an interferometric setup. More recently, we exploited the non-threshold behavior of photochromic materials to encode grayscale CGHs, which give a better wavefront reconstruction than binary holograms. We propose to use a device based on a Digital Micro-mirror Device as a real-time reconfigurable mask. We recorded for the first time amplitude grayscale CGHs and reconstructed them with high fidelity in shape, intensity and size.

Keywords: Computer Generated Hologram, grayscale CGH, photochromic material, optical testing, wavefront shaping, DMD

1. INTRODUCTION

Computer Generated Holograms (CGHs) are useful for wavefront shaping and complex optics testing, including aspherical and free-form optics. CGHs are classified as phase holograms, which are obtained by recording a phase variation in a material having a modulated refractive index or thickness, and amplitude holograms, where an intensity pattern is recorded in a material whose transparency can be locally controlled.

The ability to reversibly change color upon irradiation with light is the peculiar property of photochromic materials. In particular, organic photochromic compounds are usually uncolored in the thermodynamic stable isomer and colored upon irradiation with UV light. Accordingly, photochromic materials are convenient substrates with tunable transmittance in the visible region, which makes them attractive to realize smart optical elements, as amplitude computer generated holograms (CGHs).

Photochromic materials are non-threshold materials, i.e., the transparency of the photochromic layer depends on the light dose absorbed. This easily opens to the development of amplitude grayscale patterns, which are known to give a better image reconstruction as respect to binary amplitude holograms, at the cost of a lower diffraction efficiency. For this reason, photochromic materials do not require a development step after the light exposure, i.e., the hologram is ready to use, and the reversibility of the photoconversion makes the device rewritable. These features reduce the error propagation during the CGH production, which is desirable when producing CGHs for optical testing, but also give the devices a limited lifetime.

In this paper we report on our research activity to realize synthetic holograms for wavefront shaping and optical testing of complex surfaces with photochromic materials, in particular diarylethenes¹. We will describe the methods to obtain photochromic coatings with the desired modulation of optical properties, the two techniques to produce the CGHs and the results we obtained on binary and grayscale photochromic CGHs.

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2. PHOTOCROMIC MATERIALS

Photochromic materials change reversibly their color when exposed to light. They usually become colored when illuminated with UV light, coming back spontaneously to the uncolored state (T-type materials) or when exposed to visible light (P-type). T-type compounds found practical application for a long time as pigments for photochromatic lenses. We here refer to diarylethenes¹, belonging to P-type photochromic compounds, which show interesting photochromic properties such as large fatigue resistance (they survive after many switching cycles), good thermal stability and quantum yields.

We followed two different approaches to realize the photochromic coatings: *i*) dispersion of the chromophore into a suitable matrix or *ii*) directly polymerization of the chromophore to obtain photochromic polymers. The former approach is the most versatile, but the matrix can be doped with a small amount of active dye, which depends on the relative solubility of the dye into the matrix in order to avoid aggregation and subsequent light scattering. To obtain a large modulation of the optical properties, the starting photochromic molecule must show a large absorption coefficient. The latter approach allows to produce coatings with 50% wt. or more of active units, and large optical responses may be obtained with reasonably thin films (in the order or less than 1 μm). As a drawback, the chromophore must possess the chemical groups suitable for the polymerization reaction.

Accordingly, we obtained dispersions of photochromic 1,2-bis(2-methyl-5-dimethylamino-phenyl)perfluorocyclopentene in CAB (Cellulose Acetate Butyrate) with 20% wt. concentration by spin coating onto glass. Processing parameters were optimized to obtain a film thickness of 3-4 μm , and a very smooth and flat surface. To follow the second approach², we synthesized a photochromic polyurethane based onto the monomer 1,2-bis-(5-*p*-methoxy-*m*-hydroxymethylphenyl-3-thienyl)perfluorocyclopentene in 50% wt. content over all components. The thickness of the coatings was set to 3 μm , giving a maximum optical density in the visible of 3. Since the polymerization reaction is carried out in situ, the coatings show good surface quality, bulk homogeneity, and surface flatness, which make them suitable for application in interferometry.

Considering amplitude diffraction elements, their diffraction efficiency is directly linked to the film contrast CT, defined as

$$CT(\lambda) = \frac{T_A}{T_B} \approx 10^{Abs_B} \quad (1)$$

where T_A and T_B are the transmittance of the film in the transparent and opaque forms, respectively³. As shown in Figure 1 for binary amplitude holograms, a good diffraction efficiency is obtained only for CT larger than 100, that was reached in the red region of the spectrum by both the photochromic coatings previously described.

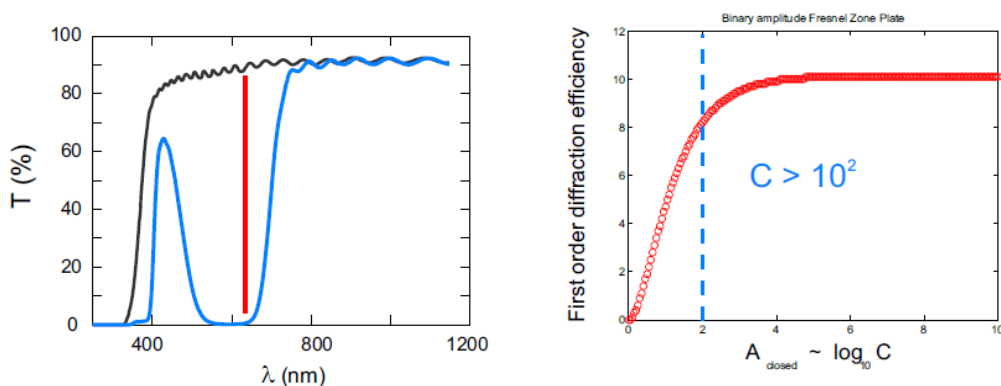


Figure 1: Transmittance of a photochromic polyurethane in the A (gray line) and B (blue line) states (left) and first order diffraction efficiency of a photochromic binary hologram as function of the absorption of the opaque form.

3. STRATEGIES FOR CGH PRODUCTION

In a typical route for the production of amplitude patterns, the photochromic coating is converted in the whole volume to the colored form by irradiation with UV light. Then, the layer is patterned upon exposure to visible light, which induces a selective decoloration of the film. We considered two different strategies for the substrate patterning: *i*) a scanning system, by direct laser writing (maskless lithography) and *ii*) a raster system, by mask projection based onto a spatial light modulator.

3.1 Maskless lithography

In the first approach, the pattern is transferred to the photosensitive layer using a light beam focalized in a diffraction limited spot onto the substrate. The laser power is continuously adjusted while the substrate is scanned in the plane and exposed where necessary. Usually, an autofocus system keeps the substrate in the correct axial position to guarantee the best spot resolution.

Our first CGHs were produced with a simple He-Ne laser plotter, developed in house to transfer rotationally symmetric patterns on the photochromic layer. The laser beam was focalized onto the sample with an aspheric lens, giving a spot size of 4 μm , and the substrate was scanned under the beam with a r -theta moving system. The light wavelength of 632.8 nm was chosen to match the sensitivity region of the photochromic material. We hence obtained patterns with good contrast and definition, by carefully adjusting the writing speed (1-10 mm/s) and light power (0.5-1 mW)⁴.

In order to verify and push at the limit the production of photochromic CGHs, we performed tests with a commercial direct laser machine, in collaboration with the Institut für Technische Optik of the Universität Stuttgart⁵. A maskless lithography machine in polar coordinates (CLWS300) based on a 514 nm laser (which is at the limit of sensitivity of the photochromic polymer) has been used. The determination of the correct speed rate and light power turned out to be the main issue, since the facility is characterized by high speed rates (hundreds of mm/s) and very high light powers (tens of mW/ μm^2). Low powers were not able to completely convert the volume of the material, giving a low definition of the pattern, and high powers caused the formation of surface reliefs on the coating. Nevertheless, we produced different patterns (variable gratings with 4.0 to 1.8 μm periods and Fresnel Zone Plates), verifying a very high resolution of the photochromic coating, which was limited only by the writing beam size to 1 μm (see Figure 2).

The results convinced us on the necessity of a custom direct laser machine for the production of photochromic CGHs, which is now in the construction phase at Brera Observatory.

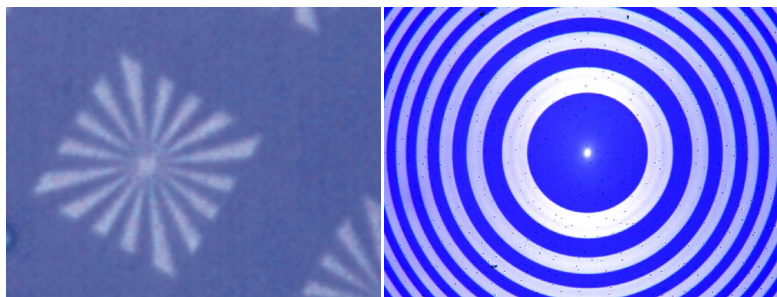


Figure 2: Resolution test (left) and an $f/1.5$ Fresnel Zone Plate (right).

3.2 Mask projection

The second approach consists in the projection of a mask onto the photochromic substrate. This approach is currently employed at the Laboratoire d'Astrophysique de Marseille, where a mask projection setup was constructed within the OPTICON Project (EU, FP7). The concept, derived from the BATMAN project⁶, is based onto the image projection by an Offner relay; the sample plane is conjugated with an intermediate focal plane, where a Digital Micromirror Device (DMD) is placed. The DMD is the largest device produced by Texas Instruments and is composed of 2048x1080 micromirrors with a pitch of 13,64 μm . It is illuminated homogeneously by a collimated beam from a filtered light source and the light is then redirected toward the plate with a magnification of 1:1 in an almost aberration free projection. The set-up resolution is 2-3 μm , therefore the CGH resolution is not limited by the optics but by the DMD itself. Finally, a post-

CGH imaging system is located right after the CGH plate and equipped with a filter centered around 600 nm and a CCD camera. This system in an afocal assembly allows the CGH imaging during writing, both in situ and in real time. Magnification is tuned by changing properly the pair of lenses, from a value of 1 up to 4. DMD, CGH and camera planes are hence conjugated. Note that the DMD plane is a tilted focal plane due to the nature of micro-mirror array: each micro-mirror tilts out of the array plane by 12° , leading to a global 24° tilted focal plane. This effect is reproduced as well at the post-CGH imaging camera level (the camera plane is tilted by 24°). The set-up dedicated to the CGH recording is reported in Figure 3.

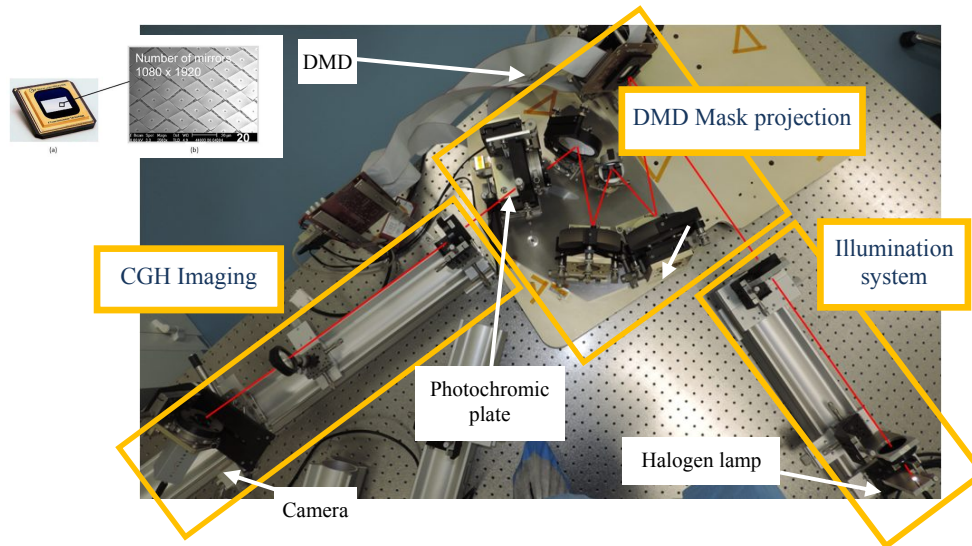


Figure 3: the DMD based set-up developed for writing the photochromic CGHs. The three main subsystems, namely illuminating system, DMD mask projection and CGH imaging are highlighted. In the inset, a picture of the DMD used is reported.

The advantage of the mask projection system is the possibility to easily write grayscale CGHs^{7,8}. Since the DMD is a programmable mask, the mask can be changed during recording, in order to expose each pixel the desired time and provide the photochromic layer with the required light dose. The photochromic material becomes progressively transparent when illuminated by visible light, and a given level of transparency, i.e. a given level of gray, is obtained with a well-defined exposure time. The material response, which is not linear with time, can be easily characterized by using the post-CGH camera. Figure 4 illustrates an example of a grayscale CGH, with four different masks and the corresponding exposure time. The darker areas are illuminated with the first masks only, while the most transparent areas are illuminated through almost all masks. In general, a CGH is exposed in 30 to 60 minutes.

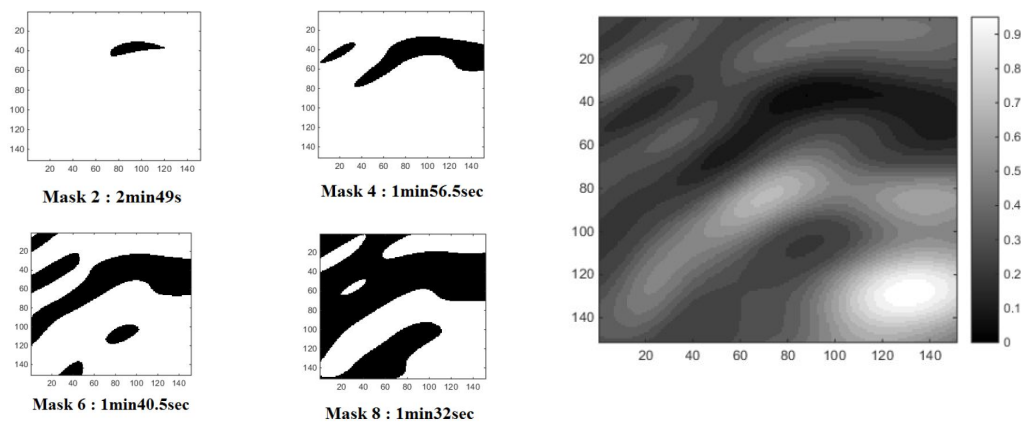


Figure 4: Detail of four masks applied to the DMD and the resulting grayscale CGH and.

4. RESULTS

4.1 Binary CGHs

Binary CGHs may be realized by both direct laser writing and mask projection techniques. The first technique is usually preferred, giving better resolution at the cost of a slower process. In order to prove the applicability of photochromic materials to produce amplitude CGHs for the optical metrology, we designed and produced binary amplitude FZPs, as prototypes of more complex CGHs. We produced the FZPs by direct laser writing onto photochromic polyurethane coatings. In the interferometric test, the photochromic FZP was the optical element under test, compared to the reference spherical surface in a double pass setup. The interference fringes obtained with a 200 mm focal length FZP were well visible (see Figure 5), thus indicating that the CGH satisfied the contrast requirement described above.

The overall transmission of the CGH was 36.3% and the contrast 200 at 632.8 nm. The diffraction efficiencies of the zero order and of the first converging order were 30.1% and 9.0% respectively, approaching the theoretical values of 25% and 10.1% for amplitude patterns with infinite contrast⁴. Actually, surface flatness errors (not accounted for during the hologram design phase) and pattern distortion errors were introduced in the CGH production, giving an overall accuracy of the element of 3 waves PV and 0.5 waves RMS.

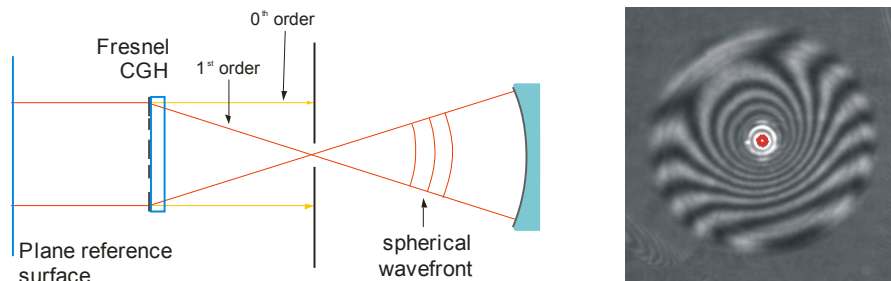


Figure 5: Scheme of the optical test (left) and recorded fringes (right).

4.2 Grayscale CGHs

While for binary CGHs direct laser writing is preferred, grayscale CGHs can be more easily obtained with the mask projection technique. In the mask projection technique, recording a binary CGH requires the projection of a single mask to the photochromic plate, while grayscale holograms can be obtained by sequentially displaying a series of defined binary masks to create with each mask a new degree of transparency. It is worth noting that the production of grayscale CGHs does not require longer time than recording binary CGHs.

We calculated with the light propagation equation a series of Fresnel holograms, in particular a 200x200 pixels “Z” and a Fresnel-type lens imaging a disk. The size of the CGH was limited to 10x10 mm², which leads to a CGH resolution of 720x720 pixels. In order to be sure that all the fringes in the CGHs are resolved the image physical size and the focus were fixed at 2x2mm² and 2m, respectively. Once obtained the continuous complex pattern, its magnitude was discretized to twenty gray levels with thresholds ranging from 0 to 1 in steps of 0.05.

Figure 6 shows the calculated and the actual grayscale CGH of the letter Z, written onto the photochromic polyurethane coating, along with the theoretical and experimental reconstructed image. The image dimension on the camera is 2x2mm as expected. Very faithful reconstruction has been obtained with respect to the simulated reconstructed image as well as the original “Z” image. This confirms the better reconstruction fidelity from the grayscale CGH as respect to the binary case.

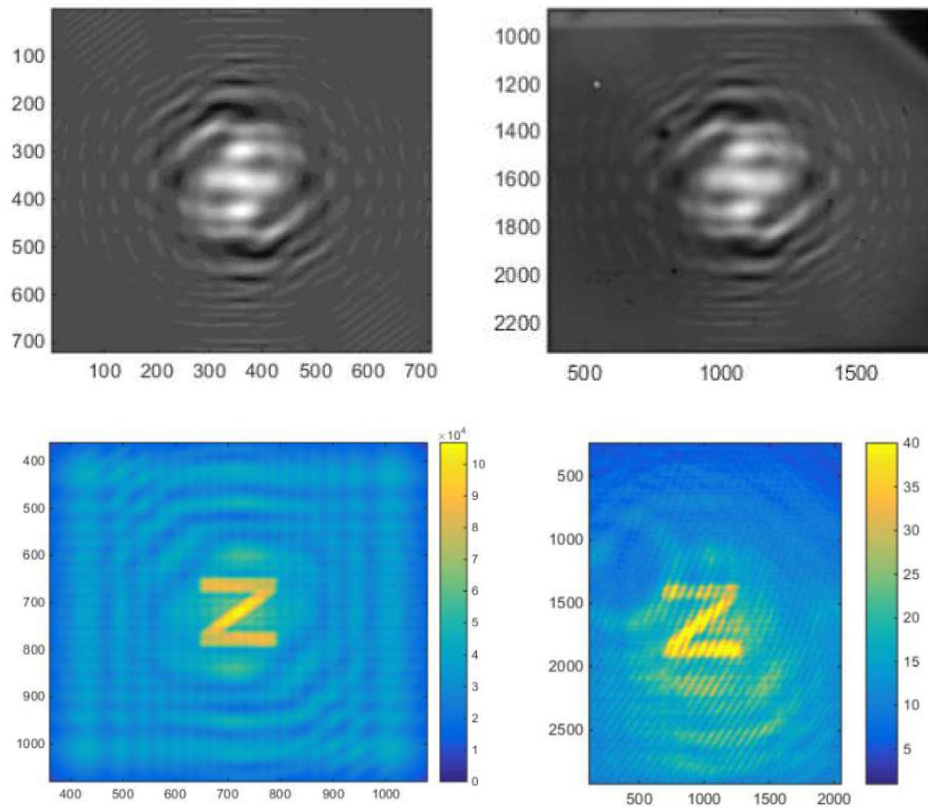


Figure 6: grayscale CGH of the letter Z (2x2mm size at a focus of 2m). Calculated (top left) and recorded CGH on the photochromic polymer (top right); calculated (bottom left) and experimentally reconstructed image (bottom right).

Following the identical process, we designed and wrote a CGH of a Fresnel-type lens imaging a disk. The CGH has been designed with a circular shape and approximated to twenty gray levels; the simulated CGH is shown in Figure 7. Using our DMD-based set-up, the CGH has been exposed onto photochromic samples formed by dispersion of molecules in polymer matrix. A picture of the actual CGH is reported in the same figure. The recorded CGH is identical to the calculated pattern, and reproduces perfectly all intensity steps. The accuracy of this recording method in terms of definition of the grey levels and edges between them may be noticed. As in the direct laser writing method, the recording resolution is not limited by the material itself, but by the single DMD micromirror.

The simulated and experimental reconstructed object is also shown in Figure 7. The reconstructed image of the recorded CGH is obtained by illuminating the CGH with a collimated 632.8 nm He-Ne laser beam. The disk appears at the right focus (2m) with a physical size of 2mm, as expected. We notice the high quality of the reconstructed pattern. The interference fringes in the reconstructed image are due to multiple reflections in the plate itself.

It is important to stress that such high quality CGHs are ready to use and they have been obtained just after the writing step, without any additional chemical or optical process. Moreover, they can be erased with UV light and written again with a completely new holographic pattern. These strong and clear evidences confirmed the potentiality of this photochromic platform combined with the DMD writing machine to write grayscale holograms on demand.

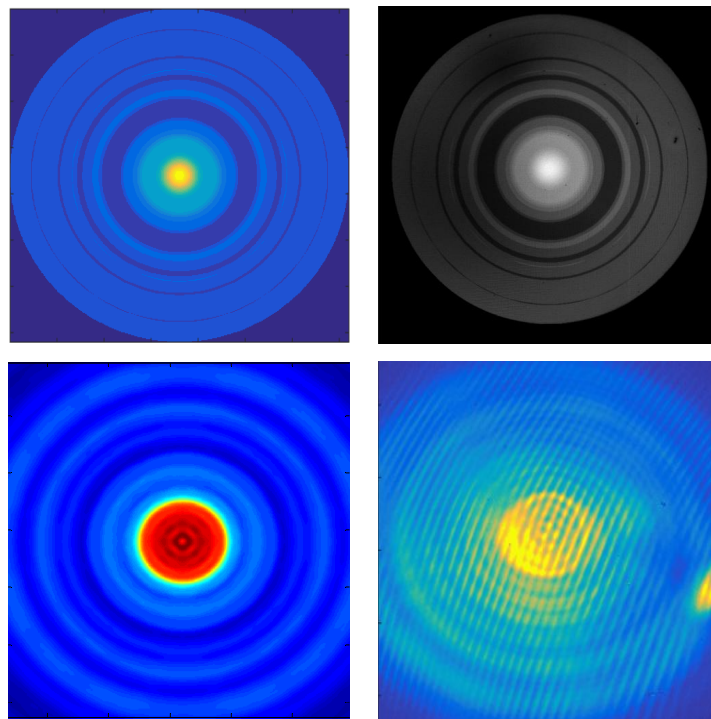


Figure 7: grayscale CGH of a 2mm disk at a focus of 2m. Calculated (top left) and recorded CGH on the photochromic coating (top right); calculated (bottom left) and experimentally reconstructed image (bottom right).

5. CONCLUSIONS AND PERSPECTIVES

We described the application of photochromic materials to realize synthetic holograms for beam shaping and optical testing. Binary CGHs realized by direct laser writing and grayscale CGH obtained by mask projection have been demonstrated. We successfully recorded several Fresnel CGHs, with binary and grayscale coding. The hologram were obtained with high fidelity in shape and local transmittance, giving a good image reconstruction. In both writing methods, the resolution is limited by the optical setup and not by the photochromic material. Next steps will be the encoding of Fourier holograms and the production of optical equalizers or apodizers, using the same protocol as for grayscale CGHs.

6. ACKNOWLEDGEMENTS

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