

Photochromic materials for holography and astronomy

Andrea Bianco, Giorgio Pariani, Rossella Castagna, and Chiara Bertarelli

Photochromic materials are a versatile medium for creating rewritable computer-generated holographic optical elements that can be used in a wide range of optical testing and astronomical applications.

Many of the optical functions of astronomical instrumentation and other disciplines can be performed by holographic optical elements (HOEs). These objects transmit and manipulate light analogously to more conventional lenses, mirrors, and diffraction gratings. Of particular interest are computer-generated holograms (CGHs), which can be designed and constructed purely from knowledge of their optical layout and intended function, and without requiring any physical reference object.

In general, holograms fall into two classes: amplitude elements and phase elements. Amplitude elements are created by modulating the transparency of the active substrate, while phase elements are created by modulating the substrate's refractive index and/or thickness. Although many materials are suited to holography, our research has mainly centered on photochromic materials, which undergo a reversible color change when illuminated by specific wavelengths of light: typically, they become colored when illuminated by UV light, while visible light renders them colorless again.¹ As shown in Figure 1, this color change is basically a change in transparency in the visible light range. At near-IR wavelengths (typically 800–2000nm), both forms are transparent, and the transition is instead associated with a change in refractive index. These differences of transparency and refractive index can be exploited to create amplitude elements in the visible light range and phase elements in the near-IR.²

Among the different classes of photochromic materials, we have focused our attention on diarylethenes, whose thermal stability and fatigue resistance make them especially attractive candidates.³ Like all photochromic materials, they have the advantages of rewritability and self-development. Rewritability means that a hologram can be erased from the substrate, and a new one written over it, as often as desired. Self-development

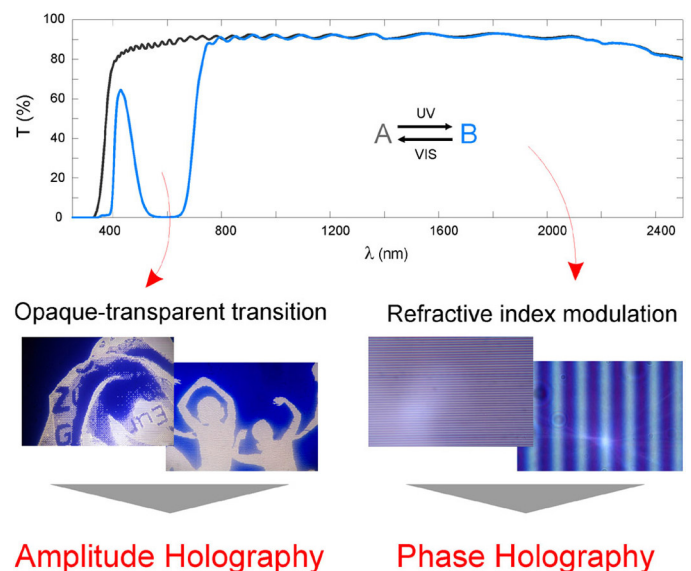


Figure 1. Ultraviolet-visible-near-IR spectrum of uncolored (black line) and colored (blue line) photochromic thin films. A, B: States of photochromic material. λ : Wavelength. T: Transmittance. VIS: Visible light.

implies that after exposure to the writing light, the hologram is ready for immediate use, without (for example) chemical postprocessing. The diarylethene-based polyurethanes we have developed boast good, easily tunable optical properties.⁴

One application of photochromic amplitude CGHs is as reference surfaces for interferometric optical testing of lenses and mirrors.⁵ If the optical system under test is highly aspheric or free-form, the creation of an appropriately complex reference optical surface may be difficult or even impossible. Figure 2(a) shows how the problem can be overcome using a rewritable CGH to mimic the wavefront that would be returned from the reference surface.⁶ As interferometric measurements confirm, the performance of our photochromic CGH depends mainly on

Continued on next page

the accuracy of the written pattern and not on the properties of the material. The red line in Figure 2(b) shows the contrast at the laser wavelength (633nm) used in the interferometer, and Figure 2(c) shows a sample CGH exploiting this effect.⁵

Phase holograms are generated by modulating the material's refractive index. Figure 3(a) shows the results of this behavior in a thin film of diarylethene-based polyurethane. In the near-IR region ($\lambda > 800\text{nm}$), where the photochromic film is essentially transparent (see Figure 1), the change in refractive index (Δn) is on the order of 0.01–0.04. This difference may be exploited to create a volume phase holographic grating, by writing a pattern that modulates the refractive index periodically (typically sinusoidally), such as the one in Figure 3(d).⁷ The diffraction efficiencies of a typical grating at various incidences and wavelengths are shown in Figure 3(b). It is well known that achieving good efficiencies for such a grating requires a large Δn (> 0.02) and a film thickness between 3 and $50\mu\text{m}$. From a materials point of view, this implies that the concentration of the photochromic moiety in the film must be as large as possible. But if it is desired to convert all of the photochromic material, then there is an upper limit to the film thickness, since the substrate's absorptivity in the UV-visible is very large. Another important consequence of this strong absorptivity, shown in Figure 3(c), is that the conversion proceeds highly nonlinearly through the thickness of the material. As a result, the exact refractive index profile produced is complex and depends on the exposure time and on the light power.

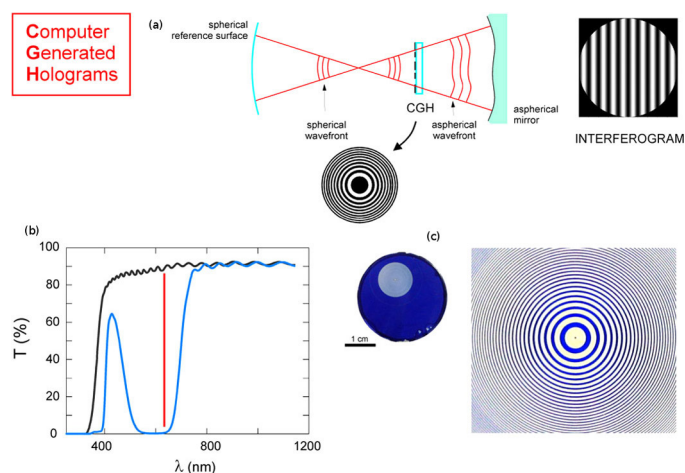


Figure 2. (a) Interferometric test using a CGH (computer-generated hologram) as a reference optical surface. (b) Contrast between the colored and uncolored forms of the photochromic polyurethane film at the interferometer laser wavelength (633nm). (c) The amplitude photochromic CGH.

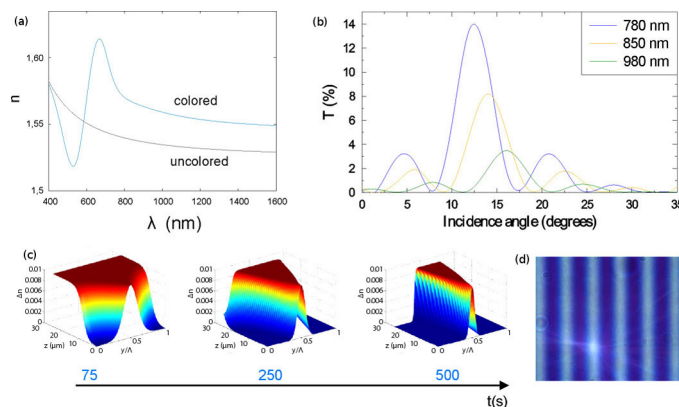


Figure 3. (a) Refractive index modulation in a photochromic polyurethane thin film. (b) Diffraction efficiencies of a photochromic volume phase holographic grating (VPHG) at different wavelengths. (c) Concentration/refractive index profile of the uncolored form through the film during holographic exposure with a sinusoidal illumination profile. (d) Micrograph of a photochromic VPHG. n : Refractive index. Δn : Change in refractive index. t : Time. y/Λ : Distance along film (normalized period). z : Depth below film surface.

Photochromic materials also have non-holographic applications in astronomical instrumentation, where they can be used as the basis of rewritable focal plane masks (FPMs) for multi-object spectroscopy. The slits of the FPM select the stars and objects of interest by removing all sky contamination. Unlike traditional metal masks, photochromic masks allow the astronomer to write a slit pattern, make observations, then erase the pattern and write a new one as needed.⁸

The versatility of photochromic polymeric materials makes them an excellent choice for creating rewritable HOEs. As either amplitude elements or phase elements, they can find application in many different technological fields, from photonics to spectroscopy. Our future research will focus on methods for improving film quality and for increasing the precision of the writing process.

Author Information

Andrea Bianco and Giorgio Pariani

INAF-Osservatorio Astronomico di Brera
Merate, Italy

Andrea Bianco is a researcher. He received his master's and PhD in materials engineering from Politecnico di Milano (2000). His

Continued on next page

research activity focuses on the study of organic functional materials for optical elements.

Giorgio Pariani received his master's in materials engineering at Politecnico di Milano (2008), where he is now a PhD student in materials engineering. He is studying the development of photochromic optical devices.

Rossella Castagna and Chiara Bertarelli

Politecnico di Milano
Milano, Italy

Rossella Castagna received her master's in materials engineering at Politecnico di Milano (2009). In January 2010 she joined the Center for Nanoscience and Technology, pursuing a PhD in materials engineering at Politecnico di Milano. Her PhD research activity concerns the design, synthesis, and characterization of photochromic materials.

Chiara Bertarelli received her master's in industrial chemistry from the State University of Milan and her PhD from Politecnico di Milano (2002), where she has been an assistant professor since 2002. Her research interests focus on organic functional materials, mainly photochromic materials and conducting polymers for applications in smart optics, optoelectronics, and molecular electronics, and polymer nanofibers.

References

1. H. Bouas-Laurent and H. Durr, *Organic photochromism*, **Pure Appl. Chem.** **73** (4), pp. 639–665, 2001.
2. C. Bertarelli, A. Bianco, R. Castagna, and G. Pariani, *Photochromism into optics: opportunities to develop light-triggered optical elements*, **J. Photochem. Photobiol. C: Photochem. Rev.** **12** (2), pp. 106–125, 2011.
3. M. Irie, *Diarylethenes for memories and switches*, **Chem. Rev.** **100** (5), pp. 1685–1716, 2000.
4. G. Pariani, R. Castagna, G. Dassa, S. Hermes, C. Vailati, A. Bianco, and C. Bertarelli, *Diarylethene-based photochromic polyurethanes for multistate optical memories*, **J. Mater. Chem.** **21** (35), pp. 13223–13231, 2011.
5. G. Pariani, C. Bertarelli, G. Dassa, A. Bianco, and G. Zerbi, *Photochromic polyurethanes for rewritable CGHs in optical testing*, **Opt. Express** **19** (5), pp. 4536–4541, 2011.
6. A. J. MacGovern and J. C. Wyant, *Computer generated holograms for testing optical elements*, **Appl. Opt.** **10** (3), pp. 619–624, 1971.
7. A. Bianco, G. Pariani, C. Bertarelli, and F. M. Zerbi, *Photochromic polymers for making volume phase holographic gratings: between theory and practice*, **Proc. SPIE** **7739**, p. 77394P, 2010.
8. A. Bianco, C. Bertarelli, M. C. Gallazzi, G. Zerbi, E. Giro, and E. Molinari, *Smart focal plane masks: rewritable photochromic films for astronomical multi-object spectroscopy*, **Astronomische Nachrichten** **326**, pp. 370–374, 2005.