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Hybrid surface-relief/volume one dimensional holographic gratings

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ABSTRACT

Many one dimensional optically patterned photopolymers exist as surface relief or volume phase gratings. However, as far as we know, holographically recorded acrylate-based gratings in which both configurations are present are not described in literature. In this work we report a two steps fabrication process in which a large-area high-resolution hybrid volume/surface relief grating phase gratings is created in a thin film of multiacrylate material spinned on a proper designed substrate. Optical and morphological investigations, made on the optically patterned area, confirm the presence of a one dimensional double (surface relief and Bragg volume phase) periodic structure.

1. Introduction

High resolution thin periodic structures known also as surface relief gratings (SRGs) are currently used in many research fields including nanophotonics [1], biophotonics [2], integrated optics [3] and plasmonics [4]. Some of those applications [5] require large-area, high resolution structures made in thin layers (a few micrometers) of material. Optical interferometry in principle, gives the possibility of writing such structures in photo-polymers in a cheap and fast way. One of the most used materials for optical patterning and nano-imprinting is the photopolymer SU-8 [6], an epoxy-based and viscous negative photo-resist. SU-8 is usually spinned on flat surfaces with thickness ranging from below 1 μm up to above 300 μm and an aspect ratio of 1:10 when periodically patterned. However, thin layers of patterned photopolymers can be obtained also in different ways. In Ref. [7] for example, it has been shown how the fabrication of such gratings is possible in materials characterized by linear chains doped with azo-benzene structures. It is worth noting how in some situations these periodically patterned structures derive from self-assembling processes and how, once settled, are sensitive to the polarization state of an impinging light [8]. Following this well established technological path, in this work we show the possibility of recording double structured large area thin and stable polymeric gratings in a simple mixture mainly based on a pure multiacrylate monomer. The recording process is fast and simple and requires only a two step procedure to be accomplished. The so recorded gratings are characterized by high resolution, high optical contrast and thickness in the range 0.05–2.0 μm. More in general, depending on the ratio between grating pitch and grating depth, from an optical point of view, these structure can be distinguished into SRG or volume phase gratings. In particular, Klein and Cook [9] introduced a parameter Q, defined as $Q = 2\pi\lambda_0 L/\Lambda^2 n_0$ (where L is the grating thickness, λ_0 is the vacuum wavelength of light, Λ is the grating pitch, and n_0 is the mean refractive index of the structure) to discriminate the two situations. Values of $Q < 1$, i.e., thin gratings, were believed to give Raman–Nath operation whereas large values of Q ($Q > 10$), i.e., thick gratings, were believed to give Bragg regime operation.

2. Experimental details

2.1. Materials

Di-pentaerythritol-penta/hexa acrylate (DPPHA), N-Vinyl-Pirrolidone (NVP), (1R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione (Camphorequinone, CQ) from SIGMA–Aldrich, Bis-(trimethyl-phenyl) phosphine oxide (Irgacure 819) from CIBA Specialty Chemicals are used in this work.

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2.2. Methods

A first mixture (mixture A) made by 84% w/w of di-pentaerythritol-penta/hexa acrylate (DPPHA), 14% w/w of the cross-linker monomer N-Vinyl-Pirrolidone (NVP), 2% w/w Bis-(tri-methyl-phenyl) phosphine oxide, Irgacure 819, a free radical photo-initiator with maximum absorption at $\lambda = 360$ nm, is dissolved in ethanol (mixture A:Ethanol = 1:1). The mixture is spinned on a glass substrate at 3000 rpm for 60 s; residual traces of ethanol possibly present in the solution after spinning are completely removed by baking the sample for a few minutes at 70 °C. After this procedure, the sample is polymerized using a standard large area UV lamp (180 UL; Mercury Exposure Unit NuArc mod. 26-1 K-11LC). The final result is a flat polymeric film ready to be used as substrate for the mixture B.

Mixture B is made by 99% w/w of DPPHA and 1% w/w of CQ as photo-initiator (active in the visible range, having a maximum absorption at $\sim\lambda = 470$ nm). The mixture B is dissolved in ethanol (ratio mixture B:Ethanol = 1:10). After spinning at 3000 rpm for 60 s the film is baked for 30 s at 70 °C in order to remove any eventual trace of ethanol. The resulting geometry is sketched in Fig. 1.

After the recording process, the sample is washed in ethanol until an iridescence, due to the grating presence, is evident at a visual inspection. After that, ethanol is evaporated at 70 °C for a few minutes. Lastly, the sample is furthermore polymerized under UV lamp (180 UL), to finally fix the grating to the first substrate.

2.3. Optical set-up

An expanded laser light (Argon Ion laser at $\lambda = 476.5$ nm) is split into two s-polarized beams having the same intensity $I = 150$ mW/cm^2. The two beams interfere on the upper surface of the sample covering a large area of about 28 mm^2 originating a high contrast one dimensional periodic pattern. The geometry of the experimental set-up is synthetically sketched in Ref. [10]. After two minutes of irradiation the periodic pattern is transferred to the polymerizing material. It consists of subsequent stripes of polymerized and unpolymerized material. The sample morphology is analyzed, once recorded and washed with ethanol, which removes the unpolymerized parts, and furthermore exposed to UV irradiation (see Section 2.2 mixtures and sample preparation of this section).

2.4. Morphological grating characterization

A Scanning Electron Microscope (SEM) Philips X120 (30KV) is used to characterize the cross section and the surface of the recorded grating while an Atomic Force Microscope (AFM) NT-MDT Solver Pro P47 AFM, equipped with head for conductive, contact, semicontact and tapping measurements is used to topographically characterize the gratings. The AFM image is acquired in semi-contact mode with etalon tip.

2.5. Optical characterization

A low power laser beam (~5 mW, He–Ne at $\lambda = 632.8$ nm) is used as probe to optically characterize the holographic gratings. The sample is placed on a micrometric-goniometer to fast check for the co-presence of the two (Bragg/SRG) diffraction regimes. A real time spectrometer is used to acquire the transmission spectra of the samples.

3. Results

Fig. 2 reports a cross section of the recorded area in which the junction between the two layers is clearly shown.

A close view shows a thin surface pattern on the upper part of the irradiated spot area and a volume phase grating which extends inside the sample over a length of about 1 μm. A complex network interconnects the polymeric walls. This double structure has been optically investigated by using a He–Ne laser impinging perpendicularly on the sample. Two different orders of diffraction are clearly seen on both sides of a screen placed behind the sample. By rotating the sample until the Bragg condition is satisfied, a Bragg spot also appears on the screen. In order to investigate better the

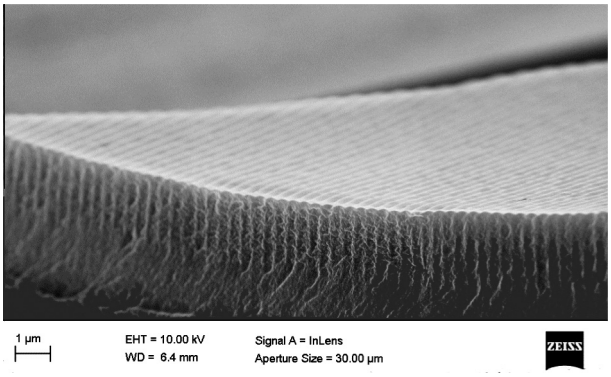

Fig. 2. SEM Cross section of the sample in which the junction between the two substrates is clearly visible.

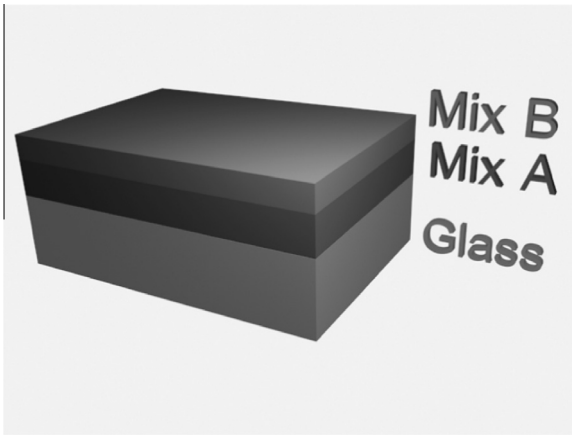

Fig. 1. Schematic view of the sample after the two polymeric layers deposition.

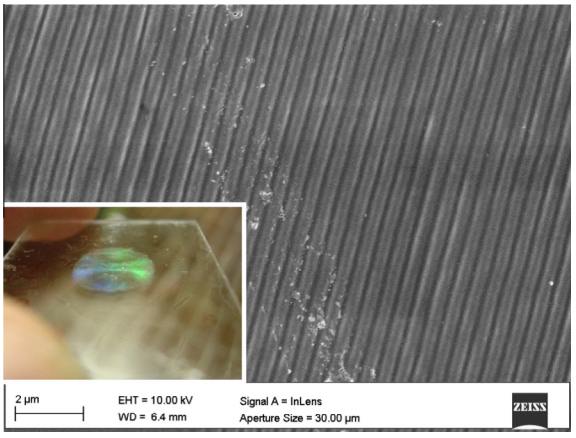

Fig. 3. SEM upper view of the grating structure. The inset shows the sample iridescence (see Experimental Section 2.2).