Characterization of t-Butoxycarbonyloxy-containing Polymer (II) : Development and Evaluation of the Binary Hologram Master

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The binary hologram master for hologram color filter was developed and evaluated in their characteristics. The chirped diffraction grating was fabricating by electron-beam lithography. This manufacturing process is consist from a volume hologram master and contact copy process. Hologram Color Filter (HCF) is a hologram optical element (HOE) of RGB colors for a Liquid Crystal (LC) projection TV. The mass production of such HOEs is possible by the development of a precise replication technology from EB lithographed elements.

Keywords: electron beam lithography, binary holographic master, grating, diffraction efficiency, hologram color filter,

1. Introduction

Electron-beam (EB) lithography has proved to be excellent for manufacturing diffractive optics surface [1]. The holographic grating based on both the surface relief structure and refractive index modulation has potential applicability for optical elements and devices [2]. In particular, surface relief structures have many interesting applications in the area of nanotechnology and furthermore the fabrication of diffractive elements such as zero-order grating [3], slanted surface relief grating for planar optical interconnects [4], and subwavelength infrared optics [5] represents one aspect of their uses.

Recently, LC projection TV has been become popular in the market. Most of the projection TV is equipped with 3 LC panels. Such a 3 panel system has the problem, for it uses as many as 3 costly panels and optical system for color separation

and composition. Then it needs many optical devices and large volume [6]. Then single-panel system is desirable. But absorption type color filter, which is used in a conventional single-panel system, has two problems. First, it reduces light efficiency by absorption and cut-off. Second, it has become difficult to produce because the pixel pitch has been getting finer. The hologram color filter (HCF) has been presented for resolving this problem [7]. HCF is a HOE that separates white light into primary colors. This HCF can realize as a single-panel system with the high brightness that is equivalent to the 3 panel system.

In this paper we reported on fabrication techniques and experimental study of highly efficient holographic transmission grating recoated in t-butoxycarbonyloxy-containing polymer resist. EB direct-writing has excellent lateral accuracy and uses only one exposure step. Disadvantage is

lower vertical accuracy because of electron scattering during exposure. This effect leads to undesired exposure of the resist in regions adjacent to those actually addressed by electron beams. We have produced grating that have 1st-order diffraction efficiencies greater than 87%. These efficiencies are very near the theoretical limits reported [8].

2. Experimental

2.1 Materials and Measurements.

2-(4'-Metoxynaphthyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (TAZ-106), used as an ionic photoacid generator (PAG), was purchased from Aldrich. Commercially available monomer, methacrylic acid (MAA), was purified by distillation before use. 4-t-Butoxycarbonyloxystyrene, t-butyl methacrylate and p-hydroxystyrene, were purchased from TOSOH Co. The methylated β -cyclodextrin (Me- β -CD) was obtained from Aldrich, with an average degree of methylation of about 2% glucose unit.

Figure 1 shows the synthetic route to prepare terpolymer. The initiator 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. 2,2'-Azobis(amidinopropane)dihydrochloride (AAP) and benzyl triethylammonium chloride (BTEAC) was obtained from Wako chemicals. All the organic solvents used in this investigation were distilled and dried with molecular sieves before use.

Fig.1 Synthesis of t-butoxycarbonyloxy-containing terpolymer

The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with polystyrene standers using a model

CCPP-D GPC (TOSOH Co.) system equipped with a G4000H (108 mm $\times$ ID 600 mm) and AS-8070 column at 40°C in THF. A 70 KeV EB exposure system (Hitachi) was used in the evaluation of the resist performance such as sensitivity and resolution capability. The resist patterns were observed with a scanning electron microscope (SEM).

Figure 2 shows the schematic diagram of the experimental setup for the holographic grating and observing the intensity of the diffracted beam. A nonpolarized He-Cd laser beam was used a probing beam. A He-Cd laser beam is split using the beam splitter (BS).

Fig.2 Schematic diagram of the experimental setup for the formation of a holographic grating and observation of diffraction efficiency

The two beams, after reflection from the mirror (M1, M2) are allowed to interfere with each other at the holographic grating. Two polarizes are used to control the polarization state of the measuring beams. The power density of the beams was 2.7mW/cm² and incident angle θ was selected. The diffraction efficiency of the +1st order diffracted beam from the gratings in transmission mode was monitored as a function of time using an optical powermeter (Newport, 1815-C).

3. Results and Discussion

3.1 Synthesis of Polymer.

A three-necked flask, fitted with stirrer and nitrogen inlet, was evacuated and filled with nitrogen. The following monomers were complexed [9]: To carry out the copolymerization of the complexed monomers in a molar ratio of 1:1.5 (monomer: Me- β -CD), 18.88g (14.40 mmol) of Me- β -CD was dissolved in 70ml of water. Then 0.68g (4.80 mmol) of t-butyl methacrylate and 0.32g

(0.48 mmol) of methacrylic acid (MAA) were added. The mixture was stirred under a nitrogen atmosphere for 30 min, yielding a colorless solution of the complexed monomers. The solution was heated to 60 °C for 3hr. To start the copolymerization, freshly prepared solution of the initiators 100mg of $K_2S_2O_8$ (or 50mg of AAP) were added with stirring. The polymerization was terminated by cooling the reaction mixture in the ice bath. The precipitated polymer was filtered off and washes with 50 ml water. The obtained colorless polymeric product still contained a small amount of Me- β -CD. The copolymer was soluble in dichloromethane and dimethylformamide.

The copolymer (3.99g, 1.92mmol) and 4-*t*-Butoxycarbonyloxystyrene (2.46g, 11.2mmol) dissolved in dichloromethane were added dropwise to cooled mixture (0°C) of triethylamine (4.08g, 40 mmol) in 50 ml ice water. The mixture was stirred for 30 min with 100mg of BTEAC and after heated with 50mg of AIBN at 60°C for 2hr.

The reaction mixture was poured into 300ml water mixture of dichloromethane and water. The organic phase was dried over $MgSO_4$. Finally, the organic phase was evaporated, and terpolymer was obtained as colorless polymeric product. Typical polymerization yields above 32% (2.06 g). Less than 2mol% of Me- β -CD remained in the in the products [10].

3.2 Principle of the HCF

Figure 3 shows the principle of the HCF, which we are supplying with [11-12]]. Hologram lens elements are located in front of reflecting electrode at a distance of just focal length of the hologram lens.

Fig.3 Structure of HCF system

White light from a light source is converted to S polarization by a polarizing device, and impinges on HCF at a slant angle. This beam is focused and dispersed through the diffraction of the HCF, so that a color spectrum pattern is generated on the plane of liquid crystal.

The light beam is converted by reflecting electrode. The reflected beam impinges on the HCF again. The beam doesn't diffract and pass through the HCF because of next reason. First, the HCF has polarization selective effect and diffracts S polarization light more efficiently than P polarization light. Second, re-entrant light impinges on a different point from a first pass point in the HCF plane, and consequently doesn't match Bragg's condition. After passing a polarizer, the image is enlarged and projected to a screen by projection lens. Principal specification of the HCF is shown in Table 1.

Table 1 Principal specification of the HCF

Display area size	1.22 inch
Number of lens elements	1280
Width of lens elements	22.8 μ m
Hologram type	Volume phase hologram
Focusing Pattern	Cylindrical
Thickness of hologram	2.5 - 4.5 μ m
Diffraction efficiency	75 - 85 %
Index modulation (Δn)	0.040 - 0.045

The production process is composed of 4 steps that is design of a grating pattern, making of a binary hologram master, making of a volume hologram master and contract copy to a final hologram [13].

3.3 Development of the binary hologram master (EB lithography)

Grating pattern of HCF is designed to satisfy the specification. The binary hologram master is made from the grating pattern data. The grating pattern data is generated by computer, like ordinary computer generated hologram (CGH). Figure 4 shows the grating pattern. This grating is composed of linear line and space and has gradation pitch for the cylindrical focusing function. The center pitch is as fine as 0.410 μ m.

The resist was prepared by dissolving *t*-butoxycarbonyl-containing polymer and photoacid

generator in DMSO. A photoresist solution was made by dissolving 1.5 g of polymer and 0.15 g of a PAG in 30ml of dichloromethane. The solution was filtered through a $0.3 \mu\text{m}$ filter, spin-coated onto a clean substrate surface at 2500 rpm for 15 s, and prebaked at 80°C for 2 min. A 3000 – 3500 Å thick film was obtained.

Binary grating of this master is formed of chrome pattern on a glass substrate. Making process is composed of 5 steps that is coating chrome on a glass substrate, coating resist material on the chrome layer, patterning the resist by electron beam, patterning the chrome by dry etching and removing the resist from the chrome pattern.

Fig.4 Grating pattern

The EB resist was spin coated on a glass substrate, and was also coated with a conductive polymer film, which is necessary to avoid electrical charge buildup during EB writing. For precise measurement of the diffraction efficiency, antireflection coating was provided at the backside of the substrate to remove multiple reflections within the substrate.

Development of the resist was achieved by the desired binary structure. In this process, the control of the electron-dose distributions was most important. In our case, the diffraction efficiency was improved by repeating the experiments. We optimized the electron-dose distributions and EB exposure parameter in accordance with the grating period. The optimum distributions depended on the grating period because of the proximity of the EB exposure.

For the EB writing system, we used Hitachi HL-700. We selected a high accelerating voltage of 70 KeV and a small beam current of 0.5 - 1.0 nA

to improve of patterning was 50 nm in the field of $60 \mu\text{m} \times 60 \mu\text{m}$. From our experiment, we found that the subfield boundaries could almost be removed by adjusting the subfield size including the proximity of the EB.

Figure 5(a) shows a cross section of the resist pattern, and Figure 5(b) shows the chrome pattern by Scanning Electron Beam Microscope (SEM). Both pictures are taken on the finest area. We found that the fabricated grating structure has a smooth surface and a sharp edge with an almost right 90° angle, qualities that are necessary to achieve high efficiency.

Fig.5 (a) Cross section of resist pattern

Fig.5 (b) Chrome pattern

The existence of t-butoxycarbonyloxy groups increased the dry-etching resistance of the resist. A $0.13 \mu\text{m}$ line and space pattern were achieved by 70 KeV EB lithography. The terpolymers as a single-component resist showed high resolution in positive-tone images by using a standard aqueous base developer.

3.4 Evaluation of the HCF

Generally hologram can be made by two methods. The one is relief phase hologram and another is amplitude hologram. The amplitude hologram is adopted into this HCF because index-matching fluid must be used at the contact copy process. If relief type is used, the index matching fluid fills up the groove of the relief, and eliminates the diffraction effect. In the resist patterning and chrome patterning process, precise

quality control was needed. There are several reasons because grating pitch has a gentle gradation, zero defect and complete uniformity are required, and grating pitch is as fine as $0.410\ \mu\text{m}$ on the center.

The binary hologram master has low light efficiency, which is sum of 0th order and 1st order efficiency, as an ordinary amplitude hologram does. If this is used for a contract copy process, long exposure time is needed and the production yield gets low. Then we make the volume hologram master for mass-production process, which has higher light efficiency. The volume hologram master is made by contact copy method from the binary hologram master. To get a final hologram with high diffraction efficiency, 0th order beam and 1st order beam of the volume hologram master must have approximately same diffraction efficiency. To satisfy this condition, the hologram materials were controlled thickness of hologram layer and mass-production conditions.

Photopolymer is used for hologram recording material like final hologram. Because photopolymer is not hard sufficiently for contact copy process, a protection glass sheet covers the contacting surface.

Figure 6 shows the structure of contact copy from the volume hologram master to the final hologram. A recording plate for a final hologram is brought into contact with the volume hologram master. The volume hologram master is illuminated by copying beam through a coupling prism. Apart of copying beam go through hologram layer as 0th order beam, and other part is diffracted as 1st order beam. Interference fringe by these two beams is recording material as a final hologram.

Fig.6 Structure of contact copy to final hologram

By this method, the final hologram can have a

designed focal distance and simultaneously doesn't have gap nor overlap between neighboring lens elements in the hologram plane. Index matching fluid and an absorption layer are used to prevent the unwanted reflection at each surface.

The diffraction efficiency (DE) of the volume hologram is 100% theoretically and the optical efficiency in each color has been improved.

Table 2 shown samples of diffraction efficiency of the binary hologram master, the volume hologram master and the final hologram. The following equation is applied to calculate the DE [14].

$$DE(\%) = \frac{\text{The intensity of diffraction light}}{\text{The intensity of diffracted and undiffracted}} \times 100$$

In the volume hologram master, 0th order beam and 1st order beam have approximately same diffraction efficiency.

Table 2 Diffraction efficiency of masters and final hologram

	Diffraction Efficiency (%)	
	0th order	1st order
Binary hologram master	<15	<15
Volume hologram master	35 - 50	35 - 50
Final hologram	5 - 15	80 - 85

Final hologram's efficiency is 75 to 85%. As a result, the superior and optical characteristic imaging was performed.

4. Conclusion

Synthesized *t*-butoxycarbonyloxy-containing polymers were evaluated as EB resists. By optimizing EB writing parameters and electron-dose distributions, binary grating with excellent phase structures was fabricated. This manufacturing process is consist from a volume hologram master and contact copy process. The grating profiles utilized as a binary hologram master was evaluated by regarding the 1st-order and 2nd-order diffracted light. Grating depth $0.3\ \mu\text{m}$ of duty ratio 1.5 was achieved in the maximum DE of the HCF.

The mass production of such HOEs would be possible by the development of a precise replication technology from EB lithographed elements.

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