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Replication of an antireflecting element in COC plastics using a hot embossing technique

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Replication of surface relief microstructures into COC (cyclic olefin copolymers) plastics using a hot embossing technique is considered. The replication accuracy has been investigated by optical characterization and scanning electron microscopy (SEM) of the replicated surface profile, which is a diffractive anti-reflection layer. Good agreement between theoretical and experimental results is shown.

1 Introduction

In the past decades a branch of optics utilizing surface relief microstructures has developed to complement conventional optics. A major advantage of surface relief microstructures is their excellent ability to be replicated by techniques such as embossing, molding and casting. Micrometre and even nanometre sized features can be reproduced with these technologies at very low cost.[1] The replication technique of surface relief elements involves three processing steps: e-beam lithography, electroplating and replication. The first two steps of the process produce a metallic (nickel) stamper that is used as a template for the replication for microstructures.

A number of plastic materials exist which are suitable for replication of surface relief microstructures *e.g.* poly(methyl methacrylates) (PMMA) and polycarbonates (PC). In this paper, a new commercial, cyclic olefin copolymer TOPAS was used due to its excellent optical properties. Cyclic olefin copolymers are amorphous or semicrystalline, transparent thermoplastics prepared by copolymerization of a cycloolefin with an olefin, preferably by means of metallocene catalysis. The cyclic monomers are usually norbornene† or derivatives of norbornene. The olefin is usually ethylene. These materials exhibit unique property combinations such as optical clarity, excellent dielectric strength, moisture barrier, high water vapour resistance and high temperature resistance compared with typical polymers.[2] Cyclic olefin copolymers are expected to compete with polycarbonates and poly(methyl methacrylates) in the optical, data storage and medical device fields.[3–6]

In this paper we describe the replication of a surface relief microstructure, by a hot embossing technique into cyclic olefin copolymers. The replicated microstructure is designed to act as an anti-reflection surface for the air–plastic interface. This type of structure was selected as the example due to the high precision that is required in replication to realize the sub-wavelength features that are present in the profile.

2 Experimental

2.1 The master element

It is well known that a periodic surface profile can act as an anti-reflection layer if the period is shorter than the optical wavelength and if the profile geometry is chosen correctly.[7] This effect can be understood by consideration of the effective media.[8] Instead of resolving the actual details of the profile, light appears to pass through a homogeneous layer of media. The refractive index as well as other optical properties such as birefringence of this layer are determined by the surface profile and can be evaluated by means of the rigorous diffraction theory.[9] Our aim was to prepare a polarization independent anti-reflection layer for a HeNe-laser with wavelength $\lambda = 633$ nm. A straightforward optimization of the profile parameters leads to a doubly periodic structure (*i.e.* periodic in both the x-and y-directions), with period $d_x = d_y = 400$ nm, consisting of cylinders of the higher refractive index, in our case TOPAS plastic with $n_s = 1.53$, surrounded by air. The radius and the height of the cylinders are 150 nm and 125 nm, respectively.

In the mastering step original microstructure is patterned into a resist by a suitable lithography technique. In this case, patterning of anti-reflection surfaces was carried out using Leica LION LV1 low voltage electron beam lithography with the acceleration voltage of 20 kV and the nominal dose of 160 μC cm^{-2}. The desired binary structure was produced in a standard PMMA e-beam resist spin-coated on a 4″ silicon wafer. During a suitable development step, performed after exposing (60 s in methyl isobutyl ketone and propan-2-ol 1 : 2), exposed dots were transferred into surface profile.

2.2 The replication procedure

For replication of the optical component, *i.e.* the anti-reflection surface, a commercial TOPAS 5013 cyclic olefin copolymer (Ticona GmbH) was used. Cyclic olefin polymers (COC) are obtained by copolymerization of cyclic olefins such as norbornene, with ethylene or α-olefins. The norbornene stiffens the main chain and prevents crystallization.[10] TOPAS 5013 contains 47 molar percent norbornene and the microstructure of the polymer was mainly alternating (isotactic) according to ^{13}C NMR resonances.[11–13] The type of distribution of the norbornene units has no significant influence on the morphology of cyclic olefin polymers.[14] The thermal properties of the plastic material were determined using a differential scanning calorimeter (Mettler Toledo DSC 821).

Cyclic olefin copolymers are transparent on account of their amorphous structure and have excellent optical properties. Because of their aliphatic structure, without double bonds, they

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†The IUPAC name for norbornene is bicyclo[2.2.1]heptene.

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are optically isotropic, *i.e.* possess no inherent birefringence.[2,15] In the visible light range, from 400 to 800 nm wavelength, COC polymers have excellent transparency. The transmission of a 2 mm disk is about 93%, which indicates that virtually all losses in the transmission result from the Fresnel reflections. Only in UV light below 300 nm wavelength, do cyclic olefin copolymers become opaque. With a refractive index of 1.53 (quartz glass 1.46) and an Abbe number of 58, cyclic olefin copolymers are ideally suited for use in optical components for the visible range.[2,15–18] Compared with their competitors poly(methyl methacrylate) and polycarbonate, cyclic olefin copolymers give higher continuous service temperature and have lower water absorption.[19] These properties are also important in optical components.

The first step in the replication process is to form a metal copy of the original structure. Fig. 1 shows the essential steps in the fabrication of the nickel stamper. After the surface of the original microrelief has been made conducting by evaporating a 20 nm layer of silver, a first generation nickel master (also called a shim or stamper) is obtained by electroforming. The plating was done by use of a commercial plating system (Jenoptic EFNi01). The plating bath (Barrett SNR-24 nickel sulfamate) was operated at a constant temperature of 49 °C and maintained at a pH of approximately four. The electroforming current was slowly increased up to a current density of 10 A dm^{-2}. The plating was stopped when a total nickel thickness of about 300 µm had been obtained. The first generation nickel shim was then separated from the original microrelief. In the separation procedure the resist microstructure is destroyed and some of the resist sticks to the nickel master. Remaining resist may be washed away using a suitable solvent or an oxygen plasma treatment. Additional copies of the shim can then be produced by deactivating the surface of the first generation stamper by immersing it into potassium chromate (K_2CrO_4) solution and repeating the electroforming step.

Fig. 2 shows a hot stamping press used for replication. At first, the TOPAS disks (diameter 25 mm and thickness 2 mm) used for replication were injection molded using Laboratory Injection Molding Machine (DSM Research). The following processing parameters were used: barrel temperature 240 °C and mold temperature 95 °C.

A third generation Ni shim was mounted on the both sides of the temperature controlled, polished plates. The plastic disk was then sandwiched between the nickel shims and the optically smooth plates. The hot plate was heated to a temperature that was well above the glass transition temperature, T_g, of the cyclic olefin copolymer (TOPAS 5013 $T_g = 130$ °C). A pressure of 20 bar was then applied for two minutes. When the plates had cooled down to 20 °C below T_g, the pressure was released and the high quality plastic replica was separated from the stampers.

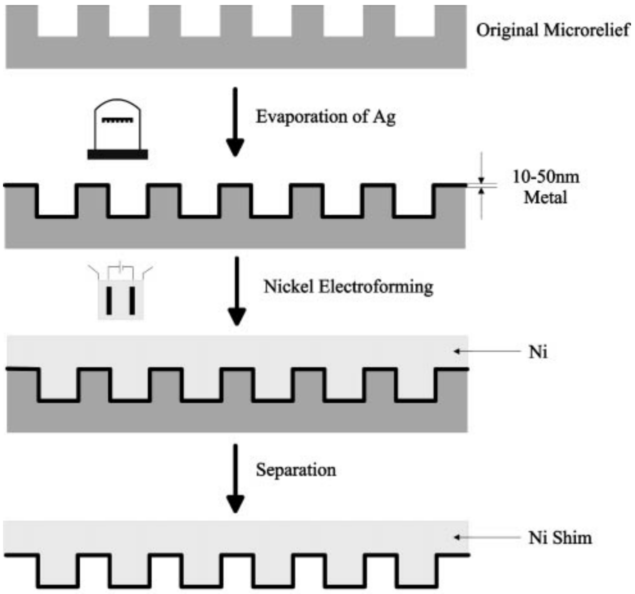

Fig. 1 The fabrication chain of the nickel stamper.

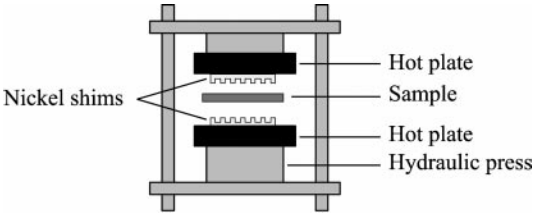

Fig. 2 Schematic view of the hot embossing system.

3 Results and discussion

Figs. 3 and 4 show SEM (Scanning Electron Microscopy) images of the nickel stamper and one replica of the antireflecting surface, respectively. The figures indicate that the shape of the diffractive structure is preserved to a high degree throughout the replication procedure. The slight asymmetry observable in both profiles, originates from the master elements and arises because of drifting of the electron-beam during the exposure. Theoretical analysis of the actual profile shows that the asymmetry makes the profile slightly polarization sensitive, but has no significance on the overall

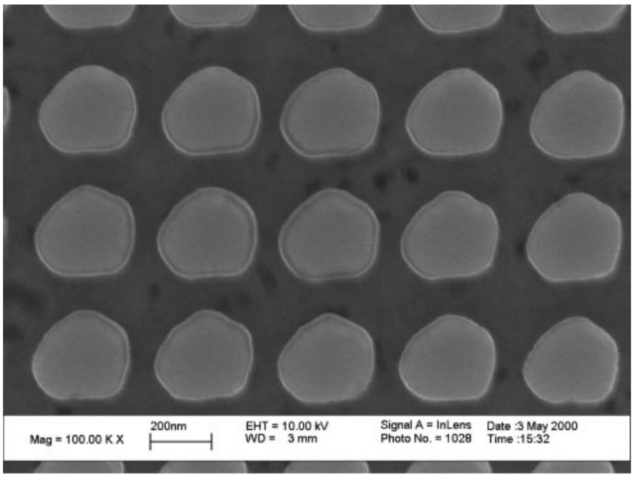

Fig. 3 SEM micrograph of a section of the nickel stamper.

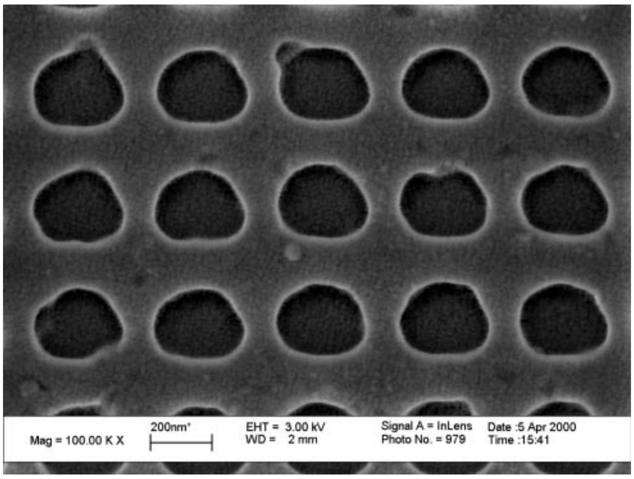

Fig. 4 SEM micrograph of a section of the replicated profile.

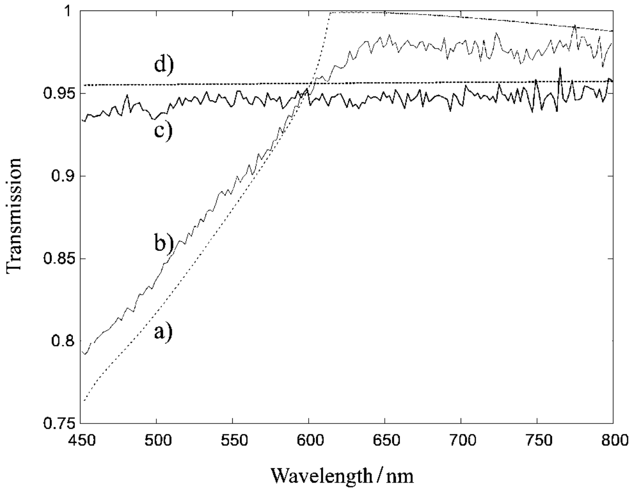

Fig. 5 Transmittance of replicated elements over the visible range of the spectrum. (a) Theoretical transmittance of the element with the anti-reflection surface replicated on both sides, (b) measured transmittance of the corresponding element, (c) measured transmittance of COC plastic and (d) theoretical transmittance of COC plastic.

transmittance as long as the ratio between different refractive indices within one period does not change considerably from period to period. In the fabricated elements, this ratio remains virtually constant.

The optical performance of the replicated elements was evaluated by measuring the transmittance and comparing it with the theoretical results obtained using rigorous diffraction theory. The measured transmittance at the design wavelength $\lambda = 633$ nm was 98.0%, whereas a transmittance of 99.5% was predicted by the theory. The difference in the experimental and theoretical results can be explained by the small amount of scattering that was observed in all fabricated elements. The sources of this scattering include the small surface roughness of the plastic pieces used and any stitching error in the patterning. Although the element was designed to operate only with wavelength $\lambda = 633$ nm, the transmittance of fabricated elements was also measured over the whole visible region of light using a spectrophotometer (Perkin Elmer Lambda 18). Fig. 5 illustrates theoretical and measured transmission curves. For comparison, transmission of a unmodulated TOPAS sample is also presented. Both curves closely agree with the theoretical results. In examining the figure, it can be seen that when the wavelength is longer than 600 nm, the transmittance of the element is clearly higher than that of the sample. However, when the wavelength becomes shorter, the situation is reversed. With $\lambda = 400$ nm the transmittance of the element drops down to 75%. This is due to that fact that the element diffracts light into higher grating orders within the substrate when the wavelength is shorter than 600 nm. Although these orders do not appear as additional transmitted beams, a considerable amount of energy is lost through them. The appearance of higher orders can be avoided by simply refining the design so that the period is shorter than the shortest wavelength used.

4 Conclusion

We have demonstrated that high precision surface relief profiles can be replicated into a commercial TOPAS plastic by a hot embossing technique. Optical characterization and scanning electron microscopy both indicate that the geometry of the replicated profile is well preserved during the replication procedure. The TOPAS plastic showed excellent suitability for the replication of diffractive optical elements. Compared with poly(methyl methacrylate), the TOPAS plastic has higher temperature resistance and very low water absorption. Because of this low water absorption, optical components replicated in TOPAS retain very good dimensional accuracy.

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