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Complex Optical Surfaces Formed by Replica Molding Against Elastomeric Masters

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Complex, optically functional surfaces in organic polymers can be fabricated by replicating relief structures present on the surface of an elastomeric master with an ultraviolet or thermally curable organic polymer, while the master is deformed by compression, bending, or stretching. The versatility of this procedure for fabricating surfaces with complex, micrometer- and submicrometer-scale patterns was demonstrated by the production of (i) diffraction gratings with periods smaller than the original grating; (ii) chirped, blazed diffraction gratings (where the period of a chirped grating changes continuously with position) on planar and curved surfaces; (iii) patterned microfeatures on the surfaces of approximately hemispherical objects (for example, an optical surface similar to a fly's eye); and (iv) arrays of rhombic microlenses. These topologically complex, micropatterned surfaces are difficult to fabricate with other techniques.

Replica molding of an organic polymer (for example, polyurethane, polymethylmethacrylate, or epoxy) against an elastomeric master [made, for example, of poly(dimethylsiloxane) (PDMS)], while that master is deformed, provides a strategy for the fabrication of complex micropatterns on surfaces. Deformation of the elastomeric master, followed by replication of the structures present on the surface of the deformed master in the rigid polymer, provides a route to structures that would be impractically difficult to generate through other procedures. Molding and embossing of organic polymers against rigid masters is used to manufacture optically functional microstructures such as diffraction gratings (1) and compact disks (2). The procedure described here differs in the use of an elastomeric master, and important features of the replica structure are generated by the mechanical deformation of this master (3, 4). Deformation of the elastomeric master occurs isotropically, and simple, regular, planar microstructures present on the original surface can be transformed into topologically and spatially complex microstructures in the replica with good preservation of optically relevant characteristics, such as grating regularities and blazing.

In the procedure for replica molding against an elastomeric master under mechanical compression (5, 6) (Fig. 1A), a liquid prepolymer reaction mixture of PDMS is cast against a rigid master whose surface has been patterned in an appropriate relief structure (a diffraction grating or a

more complex structure made by photolithography or micromachining). After curing, the cross-linked PDMS is peeled from the master; its surface replicates the surface of the rigid master. These replicated features are then reconfigured by the mechanical compression of the elastomeric master, and the deformed structure is replicated by the casting of ultraviolet-curable liquid polyurethane (PU) against it. If desired, this procedure can be repeated, with the PU replica used as the starting point, to make structures more complex than can be generated in one cycle (although with some degradation in the quality of the fabricated optical surface).

In the procedure that we used to fabricate diffraction gratings on cylindrical surfaces (Fig. 1B), a thin PDMS master (≈50 μm thick) was bent to make conformal contact with a curved surface coated with a thin film of liquid PU. After curing of the PU, the PDMS master was removed to reveal the PU replica on the surface of the cylindrical substrate. A similar procedure was used to produce an approximately hemispherical object having micropatterned relief structures on its surface (Fig. 1C). We mounted a thin PDMS master (≈1 mm thick) across the end of a hollow glass tube and deformed it by applying positive or negative pressure through the tube. The resulting surface was replicated in PU.

Cross-sectional scanning electron micrographs (SEMs) (Fig. 2, A through C) show a square-wave test pattern produced in PU over several cycles of replication in PDMS, compression, and replication in PU. Using this test structure, we found that two cycles of compression and replication reduced the size of some features (that is, the recessed areas on the master) from ~1.6 μm to ~200 nm and reduced the period of this test pat-

tern from ~3.6 to ~1.5 μm. During the cycles of compression and replication, the dimensions of the recessed areas decreased more than those of the raised areas. The reductions in dimensions that were observed were consistent with the computer-simulated results (Fig. 1A) (7). Because profiles of the relief microstructures on the elastomeric master changed in a predictable and controllable way under mechanical deformation, the master could be fabricated such that the relief microstructures have the proper profiles after deformation. Figure 2B is an expansion of the smallest features (~200 nm) that have been made; a larger field view of these features (Fig. 2C) illustrates their regularity. This procedure thus allows the formation of gratings with a range of values of the period starting from a single master.

By compressing one end of the elastomeric

![Fig. 1. Schematic procedures for molding-replication against an elastomeric master under (A) mechanical compression, (B) bending, and (C) stretching. In the finite element analysis of the material response of the PDMS master to mechanical compression, it was assumed that the top surface of the PDMS master was stress-free and that the Poisson's ratio of PDMS was 0.4 [see (7)].](image-url)
master more than the other, we were able to fabricate a chipped diffraction grating—a grating whose period changes continuously with position (8). More interestingly, the shape of the diffracting elements was largely preserved in this process: if we used a blazed grating as the starting master, the resulting chipped PU replica was also a blazed grating (Fig. 3, A and B). The period (A) of this chipped, blazed grating changed continuously from a value of \(1.55 \text{ to } 1.41 \mu m\) over a distance of \(0.9 \text{ cm}\): the rate of chirping (\(dA/dz\)) was \(1.6 \times 10^{-5}\). This grating was characterized in transmission at normal incidence. Figure 3C shows the diffraction patterns (the zero-order and the two first-order peaks) of the PDMS master, its PU replica, and the chipped PU grating. The PDMS grating and its PU replica were not operated in the blazing condition. The two first-order diffraction peaks had similar intensities (9).

The relief pattern on the surface of a planar, chirped, blazed grating could be easily transferred onto a curved surface by replication against a thin PDMS master cast from this planar grating (Fig. 1B). Figure 4A is an optical photograph of a chipped, blazed grating that was fabricated on a negative cylindrical lens (a concave grating (11)). The shape of the diffracting elements was preserved in the process of bending and replication (Fig. 4B).

Figure 4, C and D, shows SEM images of a hemispherical PU object with a pattern of relief microfeatures on its surface (a fly’s eye; Fig. 1C) (10). The shape of this polymeric object can be easily tuned by changing the thickness of the PDMS master, the applied pressure, or both. A range of different relief patterns could be made; the smallest feature had a size of \(1.5 \mu m\).

In addition to reducing the size of features, mechanical compression can also be used to change their shape while preserving size (Fig. 4, E and F) (11, 12). One-dimensional compression changed the shape of the microreliefs from square to rhombic. We could readily fabricate microlenses with different geometric shapes and therefore different focusing characteristics.

Molding-replication against a deformed elastomeric master is a strategy for making topologically complex structures with micropatterned surfaces: it allows the size and shape of features present on the surface of the master to be changed by using mechanical compression, bending, stretching, or a combination of these techniques, and generates complex structures with variable feature sizes from simple, regular structures. The highly isotropic deformation in the shape of relief patterns on the master permits micropatterned structures to be formed with gradients in size and shape.

We believe that this strategy will have broad application in applied optics: the chipped, blazed grating on a nonplanar surface is a good example of a structure that would be difficult to produce by other procedures. It may also be useful in other applications that use complex micropatterned surfaces (for example, cell culture with anchorage-dependent cells (13), studies relating interfacial structure to properties such as wetting behavior (14)).
Cytoplasmic Tail–Dependent Localization of CD1b Antigen-Presenting Molecules to MiC5s

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CD1b proteins have been implicated as antigen-presenting molecules for T cell–mediated immune responses, but their intracellular localization and trafficking remain uncharacterized. CD1b, a member of this family that presents microbial lipid antigens of exogenous origin, was found to localize to endocytic compartments that included the same specialized subset of endosomes in which major histocompatibility complex II (MHC class II) molecules are proposed to bind endocytosed antigens. Unlike MHC class II molecules, which traffic to antigen-loading endosomal compartments [MHC class II compartments (MiC5s)] primarily as a consequence of their association with the invariant chain, localization of CD1b to these compartments was dependent on a tyrosine-based motif in its own cytoplasmic tail.

Non–MHC encoded CD1 molecules have been implicated as a family of β₂-microglobulin–associated nonpolymorphic polypeptides that function in antigen presentation. Identification of a T cell line that recognizes mycolic acid, a complex fatty acid from the mycobacterial cell wall, in a CD1b-restricted fashion (1) and the subsequent derivation of two other CD1b-restricted T cell lines that recognize lipoproteinmannan from Mycobacterium leprae demonstrate the capability of CD1b to present exogenously derived microbial lipid antigens (2). These CD1b-restricted lipid and glycolipid antigens appear to require intracellular processing in acidic compartments, as do peptide antigens presented by MHC class II molecules (1, 2). Thus, it is proposed that CD1b molecules, despite their MHC class I–like protein structure (3), might traffic to endocytic compartments, including those in which MHC class II molecules encounter endocytosed antigens.

As consistent with this hypothesis, CD1b induced on peripheral blood monocytes by stimulation with granulocyte-macrophage colony-stimulating factor (GM-CSF) and interleukin-4 (IL-4) (1) was found by immunofluorescence microscopy not only on the cell surface, but also in peripherally distributed vesicles into which Texas Red–conjugated ovalbumin was endocytosed (Fig. 1). Double labeling of CD1b+ monocytes with antibodies against lysosome-associated membrane protein 1 (LAMP-1, a marker of late endosomes and lysosomes) showed that most CD1b+ endocytic vesicles coexpressed this protein (4). Furthermore, most CD1b+ vesicles in monocytes, as well as in a CD1b-transfected human B cell line (CIR/CD1b) (1) stained with antibodies to MHC class II molecules (4). This profile was characteristic of the recently described MHC class II compartment (MiC5) of specialized or “professional” antigen-presenting cells, which is the proposed site at which newly synthesized MHC class II molecules accumulate and acquire exogenous peptide antigens (5–7).

Previous studies using electron microscopy have identified MiC5s morphologically as electron-dense structures, characterized by extensive membrane invaginations producing either a multivesicular or multilamellar appearance (5–7). Immunogold–labeled transmission electron microscopy of ultrathin cryosections of GM-CSF– and IL-4–stimulated monocytes revealed expression of CD1b in MHC class II–positive dense multilamellar organelles (Fig. 2A), which were characteristic of MiC5s previously observed in mononuclear phagocytes (8). As was consistent with the localization of CD1b in

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**References**


6. Syagrid 194 (Dow Coming, A/B = 1:2.0) silicone elastomer was used. It was cured at room temperature for 2 hours and then at −65°C for −6 hours in a cooled, vacuum-tight container. The PDMS was removed and cured at room temperature for 2 hours.


9. This different behavior can be attributed to their difference in period. When a blazed grating is used in transmission, each groove acts as a prism, and the components of the light given by A tanhβ = −(1 − x²(β)²)/β, where β is the period of the grating, or the refractive index of the grating material, and x is the facet angle. The PDMS master replicates from the commercial grating blazed in the near-infrared region (~1000 nm): the chirped grating is expected to be at shorter wavelengths (that is, closer to the wavelength of the visible laser that was used) because the period of the chirped grating is shorter than that of the PDMS master. The relation between the diffraction angle β and x can be described by the equation: sinβ = (x² + x²)[x²β² + Aβ²], where Aβ² is the period of the grating. Therefore, in the chirped grating angles so calculated were in agreement with the measured values.

10. PDMS prepolymer reaction mixture (Sygard 184 A/B = 1:15) about 1 mm thick was poured over a rigid master that had been coated with silicon oxide. The PDMS was cured in an oven at 50°C for 2 hours and then at −65°C for ~4 hours. A glass tube (~4 cm long) was then vertically placed on the top of the cured PDMS, and PDMS prepolymer reaction mixture (A/B = 1:10) ~0.5 cm thick was added. The glass tube was pressed against the first layer of PDMS with Scotch tape, and no fresh PDMS prepolymer reaction mixture could enter the glass tube. The whole system was cured at room temperature for ~12 hours and then at −65°C for ~5 hours. Adhesion between the second layer of PDMS and the glass was good.

11. Masters were fabricated according to a three-stage procedure (5, 12): (i) the first used microcontact printing to form lines of hexadecanethiolate on a silver surface; (ii) the second used microcontact printing to print lines of hexadecanethiolate perpendicular to the lines of (i) on the same silver surface; (iii) the third assembled liquid prepolymer reaction mixture of PDMS onto the bare regions of the silver surface and cured the liquid PDMS under an ultraviolet light.


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**Abbreviations**

CD1b: Cluster of Differentiation 1b; PDMS: Polydimethylsiloxane; MiC5s: MHC class II compartments; GM-CSF: Granulocyte-macrophage colony-stimulating factor; MiC5: MHC class II compartment; IL-4: Interleukin-4; MHC: Major histocompatibility complex; T cell: T lymphocyte; PDMS: Polydimethylsiloxane; MiC5: MHC class II compartment; CD1b: Cluster of Differentiation 1b; GM-CSF: Granulocyte-macrophage colony-stimulating factor; IL-4: Interleukin-4; MHC: Major histocompatibility complex; T cell: T lymphocyte.