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Polyvinyl alcohol templates for low cost, high resolution, complex printing

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Templates for imprint lithography and MxL (molecular transfer lithography) are generated by adhesion of a spin-cast film of polyvinyl alcohol (PVA) to a carrier comprised of materials selected for conformability or distortion reduction. Template formation using both polymeric carrier materials and rigid materials, including quartz and glass carrier materials, is demonstrated. The absence of a carrier material altogether to form a suspended thin film is shown to be feasible. The rigid template material is formed by bonding the PVA patterned film to a rigid carrier while still connected to the master pattern, and it is demonstrated that separation occurs at the PVA-silicon master pattern interface. Form factors for the templates include a 25 mm × 25 mm patterned film attached to a 65 mm × 65 mm glass substrate, a full 100 mm pattern bonded to a quartz substrate, and a 100 mm mask of Mylar™ bonded with a patterned PVA film for MxL applications. These carrier materials are developed in a form factor compatible with commercial nanoimprint lithography tools, and for standard contact aligners adapted to perform MxL processing. © 2004 American Vacuum Society. [DOI: 10.1116/1.1827218]

I. INTRODUCTION

High-resolution printing is an important step in fabricating microelectronics, displays, and data storage devices. Current research focuses on low-cost printing methods that are essential for emerging nanotechnology applications, including microanalytical systems, microelectromechanical systems, biological sensors, and photonic devices. These new printing methods, which achieve high resolution at a low cost, include imprint lithography schemes of nanoimprint lithography (NIL),1 step-and-flash imprint lithography (SFIL),2 soft lithography,3 and molecular transfer lithography (MxL).4–9 These methods use either rigid masks, or polymeric masks with special properties, to form patterns on substrates. The NIL and SFIL masks are generated from a high-resolution tool, forming the pattern in silicon or quartz. The soft lithography and MxL methods use polymer templates formed by replicating the surface topography using various casting processes. Soft lithography methods predominantly use polydimethylsiloxane (PDMS) as the template material, and MxL uses polyvinyl alcohol (PVA).

The PVA material has several desirable properties for printing, including a high Young’s modulus of 1.9 GPa, compared to 1.8 MPa for PDMS, which is important for minimizing distortions. The PVA material is used to replicate surface topography using a spin-casting process with film formation occurring in less time than 1 min. The formed replica is used for printing in a single-use format. This approach prevents defects from propagating since the replica or stamp is used only a single time, and not utilized repeatedly from field to field. Moreover, the PVA film is dissolvable in water, enabling new forms of transfer printing that exploit this property. The material properties are also modified to achieve greater strength, solubility, or elasticity characteristics, among other factors, by the inclusion of secondary materials within the film-forming solution prior to spin-casting.

Previous work has demonstrated the generation of PVA-formed replicas for MxL processing comprised entirely of water-dissolvable materials. In this article we extend the range of materials used in the formation of PVA-based replicas, introducing a method to obtain attachment to rigid carrier materials for imprinting applications with a form factor consistent with commercial tools. In this case, the patterned film performing the imprint or MxL process is attached to either a polymeric or rigid carrier that defines the general physical properties and handling characteristics of the template.

II. REPLICATION AND TRANSFER PROCEDURE

The general PVA-based replication procedure is depicted in Fig. 1. The procedure begins with a spin casting of the replicating liquid to form a solid thin film via an evaporation process at room temperature. The replication material is comprised of an ethenol-homopolymer, ethanol, butanol, and water formulation. After spin-casting, the formed film is lifted from the master substrate by adhesion to a preformed carrier. The carrier may be of the same material as the replicating material or, as this article demonstrates, may be of a different material. The carrier, and method of adhesion, will dictate the macro properties of the template relating to conformability, thermal expansion, and stiffness.

The typical process recipe to form a PVA stamp consists of spin-coating the solution at 6000 rpm for 45 s under ambient conditions. At the conclusion of the spinning process, the film is dry and does not require any further thermal processing or additional time. The film thickness is dependent

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upon the composition of the homopolymer, alcohols, and water solution, and can run as thick as 20 µm. The flatness of the formed film is dependent on the underlying topography, and results on the replication of films from smooth surfaces are presented in Ref. 7. For fine geometry replications, high-speed casting, above at least 1500 rpm, is preferred since slower speeds will not provide maximum film dryness, and may leave a haze over the master surface and replicated film. The connection of the carrier to the film for detachment may be accomplished with a spin-coated UV-curable material applied to the surface of the replicated film, and examples are presented in Secs. IV and V. A polymer carrier may be attached through a rolling process in the case of a film. External pressure is not normally utilized, and may be useful for the removal of air bubbles. The separation of the film and carrier can be accomplished manually by a peeling processing or a cleaving process. The challenges in this approach are associated with the initiation of the peel and with the aspect ratio of the replicated pattern. The edge of the master pattern, which can be a wafer, needs to detach cleanly, but can get held up due to an edge bead or buildup during the spin-casting process. The template is useful for printing in a variety of ways (see Ref. 9), and here we depict the MxL procedure in Fig. 2, since it will be demonstrated later in the article. One variation of the MxL method involves spin-casting an etch-resistant adhesive on the surface of the substrate. While the adhesive is still in liquid form, the template is brought into contact and bonded to the substrate via the adhesive, after curing. The cure process may be achieved through thermal, UV, or moisture mechanisms. The template is washed away in water to reveal the pattern formed in the resist. For the UV and moisture mechanisms, small applied forces are used; for example, a manual rolling operation is sufficient to achieve contact between the stamp and the resist. The conformable nature of the stamps enables low-pressure contact on hard substrates.

III. SUSPENDED REPLICATED FILMS

For pattern formation and materials transfer printing on nonplanar substrates, such as hemispheres, the use of a thin flexible template is advantageous for conforming to the surface. In addition, the removal of the thin film without the need for a carrier is useful for minimizing defects, and to avoid risks in damaging the master surface pattern. The procedure to generate a thin film using a PVA film-forming solution starts with a spin casting of the replicating liquid to form a solid thin film via an evaporation process at room temperature. The formed film is lifted from the master substrate by adhesion to a carrier with an annular opening. The adhesion process takes place at the perimeter of the carrier and is then removed from the master pattern by a peeling procedure. The PVA film is of suitable cohesiveness to permit this detachment process. The removal of the suspended film when performed manually can result in significant distortions, most noticeably at the edge of the annular opening. This peripheral region would be important since imperfections in the bonding process can induce damage or even tearing when the film is removed over the opening. In a production situation, distortion would seem to be repeatable and controlled, and should be taken into account during the design and calibration phase.
In Fig. 3(A), a photograph of the suspended film is depicted. The film was spun at 6300 rpm for 60 s using the ethenol-homopolymer formulation. A diameter of about 80 mm was cut in a preformed solid PVA tape, and adhered to the perimeter of the master pattern. The microstructure of the film was maintained, and is seen in Fig. 3(B) for a 0.25 μm contact hole patterning template, with a density of contact holes over a several millimeter area in a 1:1 pitch density. The suspended film is of suitable strength to support a weight, including a 1.3 g steel ball. The suspended film distorts initially, but on a microscopic scale the pattern returns to its initial position when the weight is removed. We have tried this procedure on master patterns up to 100 mm.

Surface tension is the main force available to bring the stamp into contact with the resist to form a pattern. Alternatively, the use of the suspended film to form a pattern may be accomplished using a transfer method involving the spin coating of the resist material directly onto the suspended thin film. The resist film is then bonded to the substrate, followed by dissolution of the stamp.

**IV. POLYMERIC CARRIERS**

The advantage of using a polymeric carrier relates to material or chemical properties that can be engineered to achieve specifications including distortion, handling, or conformability. The use of a pre-formed PVA film as a carrier material has been demonstrated as well as polymer materials with sufficient attractive force to the formed film to achieve detachment.\(^3\) Here we demonstrate the coordination and formation of a polymer carrier with the formed film by use of an intermediate adhesive layer. The procedure involves spin-cast replication of the master pattern to form a solid film, and a liquid adhesive, epoxy, or acrylate material, is then spun onto the solid film. A solid polymer sheet is placed on the liquid film and allowed to cure, using a photo-initiated mechanism for example. The solid structure is then detached from the master pattern.

A template with a nondissolvable polymer carrier is depicted in Fig. 4(A). The structure is comprised of a Mylar™ backing and a UV-curable material (Norland 60) bonded to the patterned PVA structure. The overall structure is 120 μm thick, and the figure demonstrates the conformable nature of the polymer carrier. A pattern on the surface of the film is shown in Fig. 4(B), demonstrating multilayer replication capability. This structure is used for patterning by following the MxL procedure of the PVA patterned side to the substrate via an intervening polymer resist film. The carrier is then peeled off, achieving detachment at one of several interfaces: resist-PVA, PVA-adhesive, or adhesive-carrier. Combinations are possible as the polymeric carrier is removed over the entire substrate. In any event, the structure is placed in a water
V. RIGID TEMPLATES

The ability to remove the formed film from the master pattern using a rigid carrier material of quartz and glass was tested. This result is important because it enables the PVA replication process to be used in forming a template that is of a form factor consistent with commercial nanoimprinting tools. (It is noted that in Ref. 6, the use of the PVA-formed film for repeated imprinting was demonstrated.) It is demonstrated here that the PVA layer has an attractive force sufficiently low to allow for a detachment process of cleaving as opposed to peeling, thereby enabling the implementation of rigid templates. This method of detachment will minimize distortions, and will provide a method to generate polymer-based template patterns for nanoimprinting at low costs.

The procedure begins with a spin-casting replication, followed by an adhesion bonding of the replication film to the rigid carrier. The solid structure is then removed from the master pattern by tilting the carrier and lifting, or cleaving, across the surface. Oil films spun prior to the replication act as release layers and assist with reducing the force required to remove the rigid carrier. In Fig. 5(A), a 25 mm x 25 mm patterned structure is located on a 65 mm x 65 mm glass plate. This structure is of the appropriate form factor for integration in a commercial imprinting tool performing UV curing. In Fig. 5(B), this process was demonstrated across an entire 100 mm master wafer pattern. The structure can also be used in a commercial imprinting tool that performs full wafer to master template contact. The microstructure of this pattern is presented in Fig. 5(C).

VI. CONCLUSIONS

Templates of various formats have been depicted, and generated from a PVA film-forming solution, for use in imprinting applications including the MxL (molecular transfer lithography) procedure where the transfer mold is dissolved away after pattern formation. The templates demonstrated include a thin suspended film which has properties useful for printing over non-planar surfaces. The use of polymeric carriers has been depicted wherein a standard polymer preformed thick film (for example, Mylar™) is connected to the PVA film, using an intermediate adhesion layer, and peeled. This approach involved the disassociation of a nondissolvable material as part of the overall method. It has also been demonstrated that the material is useful for the formation of an imprinting template of the appropriate form factor for integration in standard commercial tools. This approach demonstrated that cleaving is a feasible means of replica detachment for PVA-based replications, and one that would offer promise to reduce distortion between the replica and master pattern. Polymer submaster masks will be useful in providing an economically viable approach to imprint lithography, as the possible slow degradation of the expensive master due to repeated contact will be eliminated.

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