Optimization of Step and Flash Imprint Lithography: Imprinting a Substrate for One Step Release of Drug Delivery Nanocarriers

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Abstract:

Step and flash imprint lithography (S-FIL) is a nanoimprint lithography technique that can be used to fabricate nanoparticles of specific shape, size, and aspect ratio. The Imprio 100 (Molecular Imprints, Austin, TX) is a commercially available S-FIL tool that uses silicon (Si) wafers as the imprinting substrate. To create a suitable imprinting surface that will initially act as an adhesion layer during the imprinting process and then as a release layer to mildly remove the nanoparticles from the surface; the Si wafer is pre-treated with a bottom anti-reflective coating (BARC) and then a water soluble polymer layer: polyvinyl alcohol (PVA). Defects on the imprinting substrate will result in imperfections in the imprints as shown in Figure 3. The objective of this project was to determine the optimal spin coating speed and percent polymer solution of the PVA that yielded a uniform, reproducible pre-coated substrate. Success in the spin coating process allows for a greater area to be imprinted upon and therefore, contributes to the success of the S-FIL process in creating a maximum number of nanoparticles per wafer. Optimization of the imprinting substrate coating process is required to fabricate uniform imprints and therefore more uniform, reproducible nanoparticles.

Introduction:

Nanoscale drug delivery carriers have become more applicable due to their improvements over current small molecule drugs. Nanoscale drug delivery carriers allow for interaction on the cellular level and real time response and release. With precise control of size and shape, nanoscale drug carriers also can allow for better targeting and response meaning smaller doses of dangerous drugs administered to healthy cells. Limitations in current nanocarrier methodology include bottom up synthesis producing poly-disperse particle size, difficulty of *in vitro* / *in vivo* correlation of kinetics and the use of passive targeting through the enhanced permeability and retention (EPR) effect.

Top down manufacturing, using the S-FIL method as shown in Figure 1, allows for incorporation of multiple properties directly into the nanocarriers. Highly mono-disperse nanocarriers of precise sizes and shapes have been developed using this method [1].

Methods/Materials:

The imprinting substrate consisted of two layers: a bottom anti-reflective coating (BARC), which acts as an adhesion layer and prevents backscattering during the imprinting process, and a water-soluble polyvinyl alcohol (PVA) layer that allows for one step release of the particles upon exposure to aqueous solution, as shown in Figure 2. This PVA layer also allows for simple removal of the particles without using mechanical force, therefore preventing damage and loss of the particles. Imperfections in the substrate cause inconsistency in the imprint and difficulty in creating reproducible, uniform imprints (Figure 3).

The objective of this project was to create a more uniform, reproducible pre-coated substrate by determining the optimal spin-coating speed and percent polymer solution of polyvinyl alcohol to create the substrate.

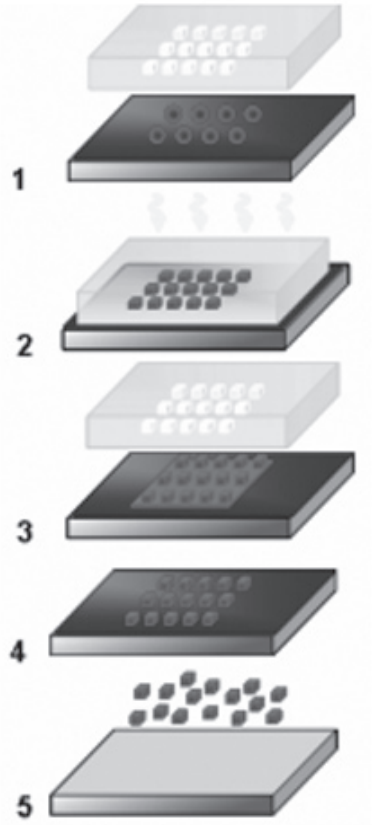

Figure 1: Step and flash imprint lithography method.

1%, 2% and 5% (w/v) polymer solutions of PVA were made by heating distilled (DI) water to 85°C and adding PVA one gram at a time until all was dissolved. The solution was brought up to its correct volume, sealed and left to stir overnight. The next day, the solution was vacuum filtered. To test viscosity, 5 mL of the solution was pipetted into a Canon-Fenske Routine glass viscometer. The solution was timed moving from marks A to B giving the viscosity. Prior to spin-coating, 4 inch silicon wafers were cleaned in a 30 minute piranha solution, a 10 minute buffered oxide etch (BOE) and spun dry for 3.5 minutes. Approximately 650 μL of BARC was spun on a wafer at 2500 RPM for 25 seconds and post baked at 180°C for 1 minute. The wafer was then allowed to sit for ~ 20-30 minutes to allow the BARC coating to dry and the wafer to cool.

Approximately 5,000 μL polyvinyl alcohol solution (PVA) was dispensed onto the center of the wafer. The wafer was allowed to sit for one minute and was then spun for 60 seconds on variable speeds. 1%, 2% and 5% (w/v) polymer solutions were used at speeds of 1000 RPM, 2000 RPM, 3000 RPM and 4000 RPM. Afterwards, BARC and PVA film thicknesses were measured using a Cauchy model with a J. A. Woollam M-3000 ellipsometer.

Results/Conclusion:

As the weight/volume percent (w/v%) of the polymer, PVA 31,000, in the solution increased, the viscosity and refractive index increased proportionally. Higher percent polymer solutions yielded higher average thicknesses at all speeds. An exponential trend was found when examining increasing spin speeds and thicknesses as shown in Figure 4. The 5% PVA polymer had the thickest layers; however, the high viscosity of the solution caused a large amount of air bubbles to form causing multiple imperfections in the substrate. The 1% polymer had such a low viscosity that its average thickness always ranged from 250 to 300 Å regardless of spin speed. Although the substrate was consistently the most uniform and had the least imperfections, the PVA layer was too thin so that particles, when imprinted on the wafer, may still adhere to the BARC. The 2% solution had more imperfections in the substrate than the 1% solution, but its thickness was high enough at speeds of 1000 to 2000 RPM to create a uniform, reproducible substrate. Thus, the 2% polymer was found to be the most ideal concentration to use, while 2000 RPM was found to be the best spin speed to create the least number of imperfections.

Future Work/ Acknowledgments:

In the future, this imprinting substrate will help produce uniform, reproducible imprints, maximizing the number of particles created. I would like to acknowledge the National Nanotechnology Infrastructure Network Research Experience for Research Program and National Science Foundation for funding, and UT Austin, Microelectronics Center, Mary Caldorera-Moore, and my PI, Dr. Krishnendu Roy, for their assistance in completing this project.

References:

[1] Glangchai, L.C., Caldorera-Moore, M., Shi, L. and Roy, K. Journal of Controlled Release 125, 263-272 (2008).

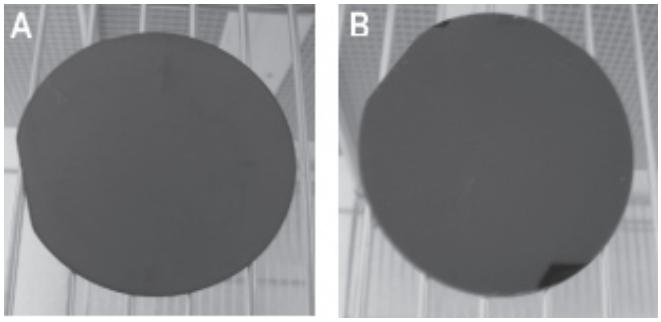

Figure 2: A. BARC coated wafer; B. PVA coated wafer.

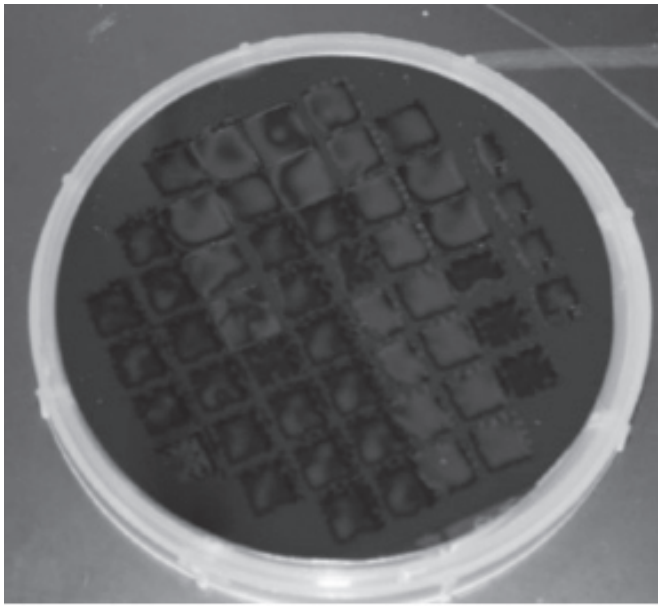

Figure 3: A wafer that has been fully imprinted on. Areas with various coloring show imperfections in the substrate.

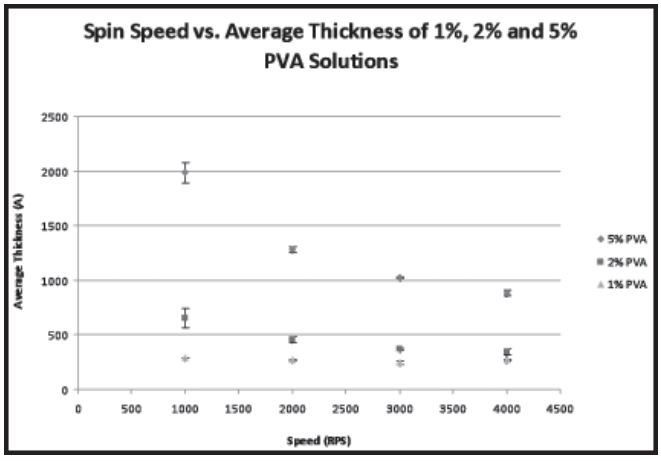

Figure 4: Graph of spin speed vs. average thickness of various percentages of PVA solutions: 5% showed an exponential trend while 2% and 1% polymer solutions had nearly linear trends in thickness.