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Fabrication of Nanoscale Features on Surfaces

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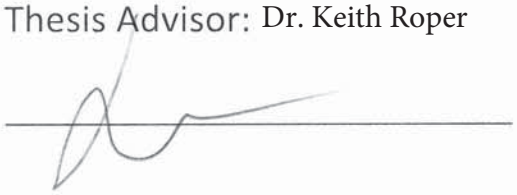

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Fabrication of Nanoscale Features on Surfaces

An Undergraduate Honors College Thesis

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by

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Introduction

Nanoscale fabrication is an important topic due to the fact that a growing number of research areas have discovered structures on the nanoscale of interest to their field. Nanotechnology has already demonstrated a major impact in the fields of medicine, material science, and microelectronics and is quickly moving into applications. In order to fuel this movement from theoretical to applied science it is necessary to be able to fabricate nanoparticles and nanostructures of interest. This ability to fabricate nanostructures is known as nanolithography when the structures are to be formed on a surface. The formation of simple nanoparticles is well understood and applied. The new frontier is one in which more complex shapes or organizations of these particles be achieved on an industrial scale.

Established Techniques

Surface patterning for nanofabrication has been accomplished through several methods such as optical, electron beam, extreme ultraviolet (E-UV), X-ray, and nanoimprint lithographies. Each of these methods, however, presents its own advantages and limitations. If patterned surfaces on the nanoscale is to develop as fully as it has in microelectronics on the microscale, one method must achieve a large versatility in the materials which it can be used for and demonstrate economically viable fabrication in both volume and cost.

Optical lithography is an attractive technique because it has been widely used in industry. As a well-established lithography technique, optical lithography is the cheapest and highest throughput technique. Optical lithography is not readily adaptable to the nanoscale because it is limited by diffraction.[1] Some enhancement techniques have been used to push past the

theoretical limit; however, even enhanced optical lithography doesn't exhibit sufficient resolution to be considered a nanolithography technique.

Electron beam lithography (EBL), although it has exhibited the ability to create sub 20 nm features, cannot be implemented in manufacturing of nanostructures due to the fact that it is inherently a low throughput technique.[2] EBL requires high vacuum and a stable electron beam, both of which are expensive to maintain. It is therefore an accurate but expensive technique which has found significant utilization in research. Without scale-up capability, however, EBL does not present a viable option for economic nanolithography. A similar technology, E-UV lithography, has been in development since 1988 and yet still faces issues in beam source, power, defect free masks, and throughput.[3]

X-ray lithography has the potential for sub 5 nm features but in practice is an extremely impractical lithography method. The source for the high energy beam is expensive to produce and the high energy beam itself causes issues with the mask, stepper, resist, and exposure spreading.[4], [5]

Nanoimprint lithography (NIL) has been considered one of the most promising lithography methods due to its high resolution, low cost, and high throughput. NIL has been shown to have many issues with adhesion and friction of the stamp with the mask and substrate during liftoff that can results in pattern defects. [6]

Dip-pen nanolithography techniques have demonstrated the greatest success in bio-related fields where a significant number of "inks" have been developed that allow for direct writing of self-assembled monolayers on the surface.[7] Unfortunately, the most successful approach to scale-up with this technique has been to use multiple tip AFM devices which

presents a new set of issues due to the increasing complexity and potential for problems with each additional tip.

Fabrication of Structures Using Prefabricated Polymer Nanostructures

The use of polymeric structures to fabricate nanostructures in other materials could present a potential alternative to high input lithographic techniques. For some structures, novel methods of fabrication can be developed in order to allow growth of nanostructures in arrays. This and other additive techniques, such as dip-pen nanolithography, are attractive because they reduce the amount of waste generated in a process as well as the cost of the materials used to fabricate the process. For other more complex structures and patterns roll-to-roll NIL (R2RNIL) presents a potential high throughput lithography method utilizing polymer nanostructure rollers to fabricate patterns continuously. Both of these techniques require arrays of nanostructures to be fabricated in polymeric surfaces. Polymers are an ideal material to use for this purpose because the ability to customize the material properties through additives and blends, the relatively low cost compared to other materials, and the feature dimensions that can be achieved stably.

Polymer Nanostructure Fabrication

Although many methods of fabricating nanostructures in polymers exist, the simplest approach is to cure a polymer when it is in contact with a mold containing the inverse of the desired features. Because the desired features are on the nanoscale, the issue of defects is extremely important to consider. Some factors that can contribute to defects are non-homogenous mixing of the polymer, gas trapped at the interface, and tearing or inelastic stretching during separation of the polymer and mold. As with any nanolithography technique, it is important to address each of these potential sources of defects.

Non-homogenous mixing in polymers is important to consider because it can lead to variations in the properties of the polymer that could cause defects when the nanofeatured polymer stamp is used. It can occur due to settling caused gravity over long periods of time, differences in curing conditions, and poor initial mixing. Poor initial mixing can be easily addressed by using machinery specifically designed to rigorously mix the solution. In the scope of this work, all polymers were mixed using a FlackTek Inc SpeedMixer which mixes the polymers in containers spun at high revolution rates in order to achieve mixing non-invasively. Settling can be addressed by reducing production time because most polymer bases are quite viscous and therefore separation occurs very slowly. In general, the most significant processing time is the curing of the polymer. This can be reduced by using a polymer which can be cured thermally or by UV exposure. In most cases, variation in curing conditions is not an issue. However, it can be an important consideration when presented with two options such as the benefits of curing in an oven over curing on a hotplate. The oven is capable of delivering heat more uniformly than a hotplate for the duration of the thermal cure and is therefore the better choice. However, the differences should ultimately be insignificant without a difference in the heating methods as would be the case if a convection oven were used instead.

Gas trapped at the interface of the polymer and the mold can directly cause defects by physically preventing the polymer from conforming to the mold. For this reason it is important to ensure that gas is only present in the smallest amounts possible. The easiest method of ensuring this is to deposit the polymer onto the mold surface under a vacuum. This is unfortunately difficult to achieve without an apparatus or machinery specifically designed to do so, therefore, degassing the sample under vacuum after the polymer has been applied is the best course of action for applications smaller than industrial scale production.

Due to the very good contact that is achieved when a polymer mixture is properly degassed and cured, the force required to separate the two surfaces can sometimes be greater than the force required to inelastically stretch or tear the polymer. This can be addressed a number of ways. A portion of development in NIL has been to optimize the temperature at which the stamps separate. In this there is a balance between retaining the shape of the features and separating when the stamp is less rigid. When good separation cannot be achieved by modifying temperature or other clever means the only other option is to use an antisticking layer which decreases the force required to separate the surfaces by coating one of them. The negative effect of this, however, is that in coating the sample the features change on a very small scale thus raising the minimum size of features and lowering the quality of the replicate. Another concern is the retention of the coating molecules by the polymer. This can introduce contaminants that can affect the properties of the polymer, allow for unintended reactions, and modify the surface interactions by again acting as a coating.

Fabricating the Polymer Stamp

In the work that has led to this topic, it became important that the polymer nanofeatured stamp's surface parallel to the featured surface be flat. The simple method of curing a polymer in a mold often introduces a meniscus which made optical methods of analysis and some fabrication methods difficult. In order to create a flat surface, it was necessary to confine the polymer during curing. Although it would be ideal to introduce this confinement after the degassing has been completed it ultimately proved more difficult to accomplish in practice. Thus a method for degassing confined fluids was developed so that the polymer could be degassed with the confinement already in place.

The specific scenario in which it was introduced was for the purposes of replicating a small stamp containing an array of nanofeatures. The stamp being approximately 0.7mm in height allowed for glass slides of approximately 1mm in height to be used as spacers or supports for a second glass slide which was used for the flat secondary surface. Glass slides were ideal for these purposes because they are readily available and very cheap when compared to other surfaces of similar smoothness.

The nanofeatured stamp is fixed to a support piece of glass to allow easy handling with a very small volume of uncured polydimethylsiloxane (PDMS). This small volume is spread into a thin film by the stamp and degassed to ensure good contact. Once the PDMS is cured, it acts as an adhesive keeping the stamp fixed to the glass support.

In order to replicate the stamp, uncured PDMS is poured onto the surface of the stamp so that it covers the stamp but does not run off. An approximately equal volume of PDMS is poured onto the glass that will be used as the backing in the location where it will cover the stamp. This additional volume is to ensure that the PDMS overflows the confined space between the stamp and the backing glass. It is important to have this overflow so that after the PDMS is cured it can be removed without damaging the stamps surface. In this capacity it will serve as a handle by which to pull the 300 micron thick film off the surface.

Two pieces of slide glass are then used as spacers and the two PDMS coated surfaces are brought together. When necessary, the PDMS overflow was redistributed by tilting the containment to allow gravity to flow the liquid around the stamp. The containment is then placed in a desiccation vessel and placed under vacuum.

Rapid Intermittent Repressurization for Degassing of Confined Fluids

Because glass is transparent, it is possible to observe the formation and growth of air bubbles as the vacuum decreases the pressure in the vessel. If no modification of degassing procedures were performed, the growing bubbles would spread the PDMS until they reached an edge and popped. This eliminates the handles and can lead to large portions of the surface not being coated on the macroscopic level. It was not determined if on the nanoscale residual volumes of polymer were left deposited. Although, it could be useful for some purposes, in this case deposited polymer could permanently deform the stamp features if cured. To avoid this, a method of collapsing or popping the bubbles was developed to successfully degas the polymer in the confined space.

The method, rapid intermittent repressurization, involves short bursts of pressure during the degassing process to cause the pockets of air to collapse. This is accomplished by the pressure difference on the wall of the bubble nearest the exposed edge of the fluid causing it to deform and collapse rather than simply resume its former shape, containing a smaller bubble. This process of building vacuum and then rapidly releasing a portion of it is repeated until the sample is completely degassed within the capabilities of the vacuum. Some waiting periods are necessary to allow the confined liquid to contract back after being deformed by a successfully collapsed pocket of air. Due to the surface tension of the liquid, it will always reform an approximate circle if given time. Allowing for this circle to be reformed by the fluid prevents portions from being separated which would otherwise eliminate the overflow that functions as a handle. Initially there are many bubbles that originate from pockets of air deposited at the edge of the stamp when the PDMS flows over it. After these have been released, a higher vacuum can

be achieved that releases the gas contained on the surface of the stamp. This process allows for degassing to be achieved without the PDMS being spread significantly.

Following this degassing step, the container can be removed from the desiccator and cured thermally on a hotplate or in an oven. The cured PDMS stamp can then be removed from the surface by physically deforming it in the overflow portions. This allows air to be introduced to the interface between the PDMS and glass which will then readily separate. The PDMS stamp can then be removed from the nanofeatured master stamp by a simple peal while gripping the overflow portion with tweezers. The result is a nanofeatured PDMS stamp that is relatively thin yet has a built in support in the overflow region. These nanofeatured PDMS stamps can then be used for a number of applications including NIL, physically masking substrates, and methods aimed at selective growth or deposition of particles.

Conclusions

Fabrication using prefabricated nanopatterned polymer stamps has the potential to greatly reduce the cost of nanolithography methods. Although already heavily implemented in NIL techniques, nanopatterned polymer stamps have great potential to be applied for purely additive methods of nanolithography. Although no techniques utilizing them in this capacity are well established, a number are under development. It is important to continue developing them because in most cases, scale-up can be accomplished very simply by increasing the size of the stamp. Additionally the cost using these methods is typically significantly smaller than what it would be when utilizing other more well established methods. With reduced cost and increased throughput being already demonstrated, further development should aim at application to a variety of materials. If successful, fabrication techniques using prefabricated polymer nanostructures could be considered viable next generation lithography techniques.

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