# Edge beads removal in a photolithography process through a polymer mold

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Original Article

Edge beads removal in a photolithography process through a polymer mold

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Abstract

In this paper, a new approach for achieving a higher uniformity while spinning photoresist is presented. The proposed method allows to overcome the well-known problem of the edge beads formation, which shows either with circular, small or irregular samples. The method consists in the fabrication of an elastomeric mold for housing the substrate, to obtain an equivalent uniformly planar and round surface. After the spin-coating, it is possible to pull out the coated sample from the mold and use it in a standard optical lithography process as well in any technological process. Moreover, the mold can be reused if the sample requires different lithographic processes.

Keywords: photolithography, soft lithography, edge bead remover, photoresist
1. Introduction

Optical lithography consists in the transfer of a specific pattern from an optical mask to a lightsensitive polymer, usually named as photoresist, deposited on a substrate (Mack, 2007; Levinson, 2005; Xiao, 2012). Therefore, the first main step is the deposition of a uniform thin film. This is achieved through a spin-coating process (Luurtsema, 1997). A small amount of material is poured at the center of the substrate. The substrate is then rotated at high speed to spread the coating material by centrifugal force. A schematic of the process is represented in Fig. 1. Then, after a thermal bake process, the substrate is exposed trough an optical mask to a UV light source to transfer the pattern from the mask to the photoresist. The exposure causes a chemical transformation in the resist that allows, when the sample is deep in a solution, called developer, to remove the exposed photoresist, positive lithography, or the unexposed photoresist, negative lithography. The maximum resolution is achieved by controlling the distance between the mask and the photoresist during the exposure. The best result is obtained when the photomask is pressed against the sample and therefore any non-uniformity of the photoresist film may hinder the contact condition (Levinson, 2005). The advantage of the spin coating is the ability to reproduce very uniform films from a few nanometers to a few microns in thickness (Lawrance, 1988). The thickness of the film is a function of (Nguyen & Wereley, 2006):

\[ h = k C \left( \frac{\mu}{\omega^2} \right)^{\frac{1}{3}} \]

where C is the initial concentration of polymers in solution, k is a constant (depending on the characteristics of the polymer), \( \omega \) is the angular rotation velocity, and is the viscosity. The main problem that occurs during a spin coating process is the formation of a no uniformity in the photoresist film, due to a thickening at the edges of the sample. This can cause a no proper contact between the sample and mask during the exposure, thus affecting the resolution of
the lithography process. The problem is widely diffuse, so that recently a work the definition of
a model that predicts the reflow planarization (surface levelling) of ‘edge bead’ features resulting
from the spin coating process has been presented (Arscott, 2020). This effect is more evident for
noncircular samples (Jekauc, Watt, Hornsmith, & Tiffany, 2004), but it appears also on circular
ones. Moreover, during a spinning process any irregularity can cause an air flow which disturbs
the regular air flow on the surface (Suzuki, 1991). The main effect is an increasing of the friction
between the air and the photoresist at the periphery, that leads to a faster drying respect the center
(Atthi et al., 2009). This is a problem both for research centers, where it is useful to work on small
irregular samples, as well as for microelectronics industries, which aim to achieve a level of
accuracy as high as possible. So far, several methods have been applied to obtain a better thickness
uniformity of the photoresist layer deposited by a spin coating process (He, Han, Zhao, & Cao,
2009; Yang & Chang, 2006). These are based on different approaches for the deposition of the
photoresist. Meniscus or capillary coating consists in a process where the resist is dispensed by a
porous tube, with pores of 10 mm, on the substrate that moves face down over the tube, closed
enough to allow the contact between the resist and the sample surface (Schurig, Muehlfriedel, &
Kuebelbeck, 1994). Another different technique, called extrusion coating, uses a small
rectangular opening to deposit a thin photoresist layer on the moving substrate. One of the most
used technique is a chemical edge bead remover (EBR) that employs a chemical solvent dispensed
on the edge of the wafer through a nozzle (Tran & Phan, 2000). The advantage of this method is
that it can remove every coating material, both photoresist and AntiReflective Coating (ARC).
However, a wrong position of the wafer on the spin chuck, and every imperfection on the wafer
can introduce several defects in the photoresist layer, mainly due to the transport of droplets of
solvent in undesirable areas. An alternative method is to use the flow of a positive inert gas in the
radial direction with respect to the wafer, to avoid the migration of particles and solvent droplets
from the edge to the center during the removal process. The main disadvantage of this method is
that it is necessary to use complex and expensive equipment to dispense the solvent (Cuthbert &
Soos, 1985). A different approach is the use of a broadband exposure only on the outer ring of the
photoresist layer to obtain an exposed external circular area, that is possible to remove with a
conventional developing process.
The main disadvantage is that it is necessary to use a different optical system and that it cannot remove an ARC layer. More recently, a method using tape to avoid edge beads formation have been proposed (Park, Kim, Roh, Choi, & Cha, 2018). The approach is simple and low-cost since it consists in covering the edge of a chip-level substrate with heat-resistant tape during patterning. The solution has been tested using SU-8.

In this work, we propose a method for avoiding the edge beads formation using an elastomeric holder for the sample. The solution allows to simulate the behavior of a larger substrate, to minimize the edge beads formation during the spin coating process.

2. Materials and Methods

The conceived method leads to a high improvement in the maximum resolution of a lithography process, by increasing the planarity of the photoresist film. The process consists in the fabrication of a holder made in a polymer material that can perfectly adapt to any sample, with regular and irregular shape. A schematic of the method is represented in Fig.2.

The first step for the realization of the polymer mold consists in the preparation of the sample. During this step it is necessary to fix the sample on a larger circular support, such as a glass slide or a silicon wafer. It is important to consider that the sample should be fixed to the support in a no permanent way, since at the end of this first step it need to be removed. Before starting the process, it is necessary to clean the sample and the circular substrate that will act as support. The cleaning procedure is necessary to remove any impurity and to prepare the substrate surface for the following processes. Then, in the second step the polymer is poured on the sample, previously fixed on the support.

After that, it is necessary to induce the polymerization process to harden the polymer. This phase will be different per the type of the polymer, i.e. it could be a thermal or a chemical treatment. Once the polymerization process is completed, the polymer stamp and the sample
should be removed from the support. The last step consists to relocate the sample in the polymer mold, and then spin the photoresist. The procedure requires the fabrication of a mold using a polymer material. Different polymers (Lipomi, Martinez, Cademartiri, & Whitesides, 2012) can be used for this purpose, if the material in the first stage is in a gel form and it can be hardened after a curing treatment. Therefore, the polymerization process is started once the monomeric units are exposed to an initiator. The obtained bulk will have a physical and mechanical structure that will vary according to the length of the polymer chains. To the great length of the polymer chain, polymers are bulk materials. Often, an important parameter to take into account while choosing the material for a molding application is the glass-transition temperature $T_g$. When the material is at a temperature below the $T_g$, it is hard and its mechanical resistance is high. When the material is brought to a temperature above the $T_g$, it becomes viscous and it can be molded (Shivaprakash et al., 2019; Whiteside et al., 2003). Polymers that can be softness and hardness by thermal shifts are used for example for device fabrication by injection molding, hot-embossing or imprinted lithography. Considering the fabrication, for most of the materials the resistance to pressure load need to be in the range used for the referred process. A wide diffuse class of materials is the one referred as elastomeric polymers. These are very weakly cross-linked polymer chains, and if an external force is applied, the molecular chains can be stretched, but relax and return to their original state once the external force is removed. Elastomers also do not melt before reaching their decomposition temperature (Becker & Gärtner, 2000). For all the polymers used for any micro-molding or micro-machining applications, it is important that they are chemically resistant to soft solvent.

Below, a list of some of the polymers that meets the above-mentioned requirements and that are widely used in microfabrication:
• Polydimethylsiloxane (PDMS), a commercially available, thermally curable, elastomeric polymer (Xia & Whitesides, 1998).
• Polymethylmethacrylate (PMMA), a synthetic polymer of methyl methacrylate (Goh, Coakley, & McGehee, 2005).
• acryloxyperfluoropolyether (aPFPE), a fluoropolymer, photocurable, composed only of carbon, fluorine and oxygen.
• Polystyrene (PS), a synthetic aromatic polymer made from the monomer styrene (Zhang & Low, 2008).
• Polyurethane-acrylate oligomers, a new class of polyurethane which are produced by the reaction of polyols with diisocyanate and capped by acrylate (Seo, Kim, & Lee, 2007).
• Polyvinylchloride (PVC), it is a polymer with UV transparency, mechanical hardness and formability, widely used as material for flexible UV-NIL (UV-nanoimprint lithography) templates (Hong, Hwang, Lee, Lee, & Choi 2009).
• Polylimide (PI), like PVC, it is a UV transparent polymer frequently used in UV-NIL. It is characterized by a high glass-transition temperatures, high thermal stability and high tensile modulus (Wu, Hsu, & Lo, 2010).
• Organic-Inorganic hybrid resins, materials that are attracting great attention at the moment since they possess the advantageous characteristics of both organic and inorganic materials (Lee, Hong, Lee, Kim, & Kawai, 2009; Segawa, 2008).

In this work, we used the PDMS (polydimethylsiloxane). It is a mineral-organic polymer (a structure containing carbon and silicon) of the siloxane family (word derived from silicon, oxygen and alkane) and is widely used for the fabrication of microfluidic chips (Whitesides, 2006; McDonald et al., 2000; Mata, Fleischman, & Roy, 2005). For the manufacture of microfluidic devices an amount of PDMS...
liquid mixed with a crosslinking agent is poured onto a micro-structured mold and heated to obtain a replica of the elastomeric mold (PDMS crosslinked) (Xia & Whitesides, 1998). The material is transparent, biocompatible and gas permeable, properties that make it suitable for several applications (Hongbin, Guangya, Siong, Shouhua, & Feiwen, 2009). Moreover, PDMS samples can be permanently bonded to glass substrates, through an oxygen plasma treatment. Another key feature, that makes it suitable for our method, is the easiness in molding even structures of a few nanometers (Hua et al., 2004; Fujii, 2002).

2.1 PDMS mold fabrication

A whole silicon wafer (4 inches) was used as support, and a square-shaped (about 1 cm x 1 cm) silicon piece as sample. The following steps were performed. First, the sample and the circular support were cleaned with a standard RCA procedure (Kern, 1990), that involves three steps chemical processes performed in sequence. The first, aimed to removal the organic contaminants. The second, for the removal of the thin oxide layer. And the last to clean the sample from any ionic contamination.

To ensure the perfect adhesion of the sample to the substrate, while pouring PDMS on it, a thin film of photoresist (OIR 90612i) was spin-coated on the substrate. The sample should be placed on the substrate immediately after the spin coating process, while the photoresist was still viscous and the sample could adhere perfectly to the surface. Then a thermal treatment on a hotplate was performed to improve the adhesion between the sample and the photoresist. Parameters like temperature and time, depend on the characteristics of the photoresist used for the process.
Then, the actual sample and the substrate were placed inside a desiccator together with a beaker containing TMCS (trimethylchlorosilane). The silicon sample and the silicon substrate are in this way exposed to fluorinate silane vapor which deposits a "non-stick" film on the surface. This chemical film is particularly important, since it avoids the formation of a covalent bonds between the PDMS and the silicon surfaces. This process, known as silanization, is necessary to prepare the surface in order to prevent the irreversible bonding of the polymer to the sample.

The elastomeric mold was obtained using a mixture of PDMS base and curing agent, in a ratio of 10:1. A vigorous mixing for about 2 minutes is necessary to ensure that the curing agent is uniformly distributed. The PDMS solution thus prepared was poured onto the sample. To remove the air bubbles that form inside the polymer mixture, the sample was placed in a glass desiccator, connected to a vacuum pump for about one hour. Once the mixture of PDMS was free of bubbles, the sample was placed on a hot plate at 100 °C for 30 minutes. After the thermal treatment, the PDMS mold can be removed from the substrate. At this point, we cut the polymeric support using a dull razor blade following the circular profile. In this way, a circular support, mimicking a circular wafer was obtained.

Last step consists in putting the mold holding the silicon sample in an acetone bath, to separate it from the mold. A flow chart of the complete fabrication process is showed in Fig. 3.

Then, before performing a photolithography process using the prepared mold, both the silicon sample and the PDMS mold must be cleaned. We performed a standard procedure that includes the following steps: 10 minutes in acetone bath, rinse in
water, 10 minutes in isopropanol and oxygen plasma treatment. The cleaning in acetone and isopropanol has been performed using a sonicator.

2.2 Edge beads thickness measurements

The thickness of edge beads was measured on the squared (1x1 cm) silicon samples, on which the spin-coating of the resist was performed with or without the polymeric holder. Measurements were performed using a stylus profilometer (KLA-Tencor Profiler). This method is widely diffused for thin film characterization (Piegari & Masetti 1985). It works well in the presence of a step, as in our case the presence of the edge beads at the corner of the spin-coated resist layer. Measurements were repeated at different and opposite position around the sample in order to ensure consistency in the collected data.

3. Results and Discussion

The novel approach that we propose was tested using PDMS among the different elastomeric materials available. A square-shaped (about 1 cm x 1 cm) silicon piece was used to test the method. As we also described in our procedure, PDMS is fabricated by inducing polymerisation of a monomer when it reacts with an initiator. After the curing, the polymer tends to shrink and the entity of the effect is a function of the curing temperature (Badsahah, Jang, Kim, & Kim, 2014; Eddington, Wendy, & Beebe, 2003; Ye, Liu, Ding, Li, & Lu, 2009; Lee & Lee, 2008). One of the most used method to avoid this is to cure PDMS at low temperature. However, this can take long and it has the effect to reduce the mechanical properties of the polymer. In our work, we didn’t observe a significant shrinkage in the PDMS mold. Indeed, we could be able to place the silicon sample several times again in place and the levelling between the sample and the top of the
PDMS mold was sufficiently satisfying, in a way that no non-uniformity during photoresist distribution was observed.

To evaluate the proper operation of our approach, several samples were fabricated, and a comparison between the edge beads effect in the case of spinning the photoresist with and without the polymer holder was performed. One of the square silicon samples in a PDMS holder before and after the spin coating process is showed in Fig. 4. Two of the realized samples are showed in Fig. 5. The differences in the results obtained from the two spin coating processes are evident. There are four colored fringes on the four corners of the sample coated without using the holder (on the left). These fringes are a clear indication of a bead edges. On the contrary on the same sample that has been coated using the PDMS holder (on the right) is evident a better uniformity of the film. Indeed, there are no fringes at the edges. It should be remarked that the effect is more evident on an irregular sample, like a square one, than on a circular or whole silicon wafer. Moreover, to get a better characterization of the film, the film thickness at the edges was measured through profilometer measurements were performed. The edge thickness was evaluated for samples coated with the photoresist by setting the spin-rate at 2000, 3000 and 4000 rpm. The process was repeated with and without the PDMS holder for the same samples. The edge thickness was measured at five different points of the samples. These data are reported in Table 1. The graph in Fig. 6 shows the average thickness achieved at the setting the spin-rate at three different values, when the film is deposited with and without the PDMS holder.

The data clearly shows a considerable planarization of the resist when the PDMS holder is used. Fig. 7 and Fig. 8 show one of the measurements performed on the
samples spin-coated at 3000 and 4000 rpm, with and without the PDMS holder. When the rotation speed was set to 3000 rpm, the maximum thickness obtained at the edge was 5.6 µm, in the case of a standard spin coating process. On the other hand, by using the PDMS holder during the spin-coating, the film reaches a thickness of 1.01 µm at the edge. Therefore, there is a decrement of about 80% in the edge thickness. In this case of a rotation speed set at 4000 rpm, the maximum edge thickness was 4.3 µm without using the PDMS holder, whilst the thickness decreases to about 1.6 µm when the PDMS holder is used. So, in this case there is a decrement of about 63% in the edge thickness. Hence, we could demonstrate the proper operation of the method.

4. Conclusions

The deposition of a uniform film of photoresist is the first important step in an optical lithography process. This film is usually obtained through a spin coating process. Although it is a standardized technology, there is still a problem related to the formation of a thickening of the film at the edges of the sample. This could affect the resolution of the lithography, since it introduces a no proper contact between the sample and mask during the exposure. The effect is more evident when small and no circular samples are used. So far, different methods have been proposed for reducing the problem and improving the planarization of the photoresist film. Most of these methods requires the integration of additional elements on the spin-coater increasing the complexity and the cost of the instrumentation. In this work, a novel approach for avoiding this edge beads formation have been developed. The method is based on the fabrication of a round polymer holder. In this way, we want to simulate the behavior of a larger substrate to minimize the bead edge formation on the sample. The idea was successfully tested with several silicon square samples. For each one
of these samples, first the polymer mold was realized, then it was used during the
spin coating of the photoresist. The photoresist film was characterized by optical
microscopy and profilometer. The results have showed a significant reduction of the
thickening of the film at the edge. The main advantages of our method are:

- It allows to overcome the edge beads formation in a spin coating process.
- It is not necessary any hardware upgrade to the spinner apparatus.
- It is an inexpensive technique, since it needs only a little quantity of PDMS
  (or other elastomeric polymer) and a glass desiccator without any expensive
  upgrade of the spin coater system.
- It is suitable for the research laboratories.
- It is possible to perform many lithography experiments on any little and
  irregular sample.
- It is useful for deposition of uniform thin film of multiple small samples in
  one step of spin-coating (i.e. X e-beam lithography).

Despite the promising results that we have obtained, there are still some work need
to be done to improve the process. First, a standard method for the preparation of the
sample before the salanization step should be developed. Then there is the needing
to improve the cutting step, after the thermal treatment, to obtain a more regular
PDMS holder. Moreover, we are working on the development of a standard method
for the removal and repositioning of the sample inside the housing in the polymer
holder.

Acknowledgments

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References


Figure 1 Edge beads formation during spin-coating

Figure 2 The schematic shows the main steps for the fabrication of the polymer mold.
Figure 3 Flow chart of the process for the fabrication of the polymer mold.

Figure 4 A silicon sample on the PDMS holder before and after the spin coating process
Figure 5 A film of photoresist on a silicon sample after the standard spin coating process (on the left) and a spin coating process performed with a PDMS holder (on the right).

Figure 6 Average edge thickness [µm] of the resist film at different spin-rate, when the process is performed with and without the PDMS holder.
Figure 7 Profilometer measurements of the photoresist film on a square silicon sample spin-coated at 3000 rpm with and without the PDMS holder.

Figure 8 Profilometer measurements of the photoresist film on a square silicon sample spin-coated at 4000 rpm with and without the PDMS holder.
Table 1 Edge thickness obtained from the profilometer measurements performed at five different points of the samples spin-coated at 2000, 3000 and 4000 rpm, with or without the PDMS holder.

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<tr>
<td></td>
<td>2000 rpm</td>
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<tr>
<td>3.25</td>
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