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Resist Homogeneity

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1. Introduction

A key element in all lithography processes is resist material; unfortunately its inhomogeneity is the main source of most lithography problems. Resist inhomogeneity can be any kind of variation in its thickness, arrangement of its molecules, chemical composition, and concentration of materials in it. Homogeneity of the resist layer before exposure and also after development is required to achieve low product variation, high production yield, high resolution and small patterns. If the resist layer does not have enough homogeneity and so its thickness, chemical composition or the molecular structure changes on a wafer or from a wafer to another wafer; dimensions of the patterns will change from one device to the other. This change will cause increased variation of the product's specifications. Dramatic variations may even mar some of the products and will reduce production yield. Resist inhomogeneity in relatively small dimensions increases the so called line edge roughness. This is generally defined as the root mean square of the line width variation along a patterned line. In the other words, if the resist properties randomly changing from place to place; dimensions of the final pattern will randomly change from place to place. For example, if one tries to pattern a line with a constant width, while the resist properties are changing in distances smaller than the length of the line, the line width will fluctuate along its length. If one tries to pattern a line thinner than these fluctuations; at some parts the width of the fabricated line will be zero. So, such a variation in the resist properties can limit both the ultimate patterning resolution and the smallest achievable pattern. Even if the resist inhomogeneity does not considerably alter the pattern geometry, it can cause variation in the etch resistance of the resist. Consequently, device dimensions and properties may vary randomly.

This chapter will cover different types of inhomogeneities in different resists and lithography processes, their origins, effects; and methods to increase the resist homogeneity. At first the basic issues in wafer level homogeneity in different step of lithography will be discussed; and effect of each lithography parameter in each step will be describe. Then, last section will focus

on the most important problems in nano lithography. These problems include, resist's molecular agglomeration and line edge roughness, which are the main limiting factors of nano lithography's ultimate resolution and yield. Latest developments in solving these problems and improving the resist homogeneity to nanometer scale will be described. Here by an industrial lithography process capable of making patterns smaller than 5nm will be described in detail. These are one of the smallest patterns ever made in an industrial lithography and an important key factor in successful fabrication of these patterns is making a homogeneous layer of resist.

2. Resist material

First criteria for choosing an appropriate resist material is dictated by the exposure technology. Exposure technology determines the wavelength of the photon or electron beam the resist should be sensitive to. Resist's tune to be negative or positive, is generally chosen to minimize the exposed area. The reason is, exposing a large area and keeping small dimensions unexposed, usually increases inhomogeneity and so called proximity effects. To transfer the resist's pattern to other layer(s) two different types of processes can be used, etching and lift-off. Etching transfers the resist's pattern to the underlying layer; while lift-off transfers the negative of the resist's pattern to the layers which are deposited after lithography on top of the resist. Thus, etching processes are transferring the positive of the resist's image while lift-off processes are transferring its negative (reversed) image. So, choosing resist's tune to be negative or positive, also depend on the pattern transfer process to be etching or lift-off. For instance, if it is desired to pattern a hole by electron beam lithography in a wide blank film of aluminum, and it is designed to transfer the pattern by reactive ion etching (RIE). Then, a positive tune resist is needed. Because, if a negative tune resist be used, it will be necessary to expose a very large area, and such an exposure will introduce proximity problems, will take a very long time and will increase the exposure noise. So, the edge roughness and other inhomogeneities and deformities will increase. On the other hand if the pattern will be transferred by lift-off, a negative tune resist should be used. If one needs to make a pillar, the choice of negative or positive tune resist will be the opposite.

Next constrain for choosing a resist is its underlying layer and/or layer that may be coated on top of it. Because some resists do not adhere to some materials at all, may degrade near them, or react with them. So, the resist should be compatible with the other materials and processes used in device fabrication. For example it is not possible to use PMMA resists on copper.

An other common constrain to choose a resist is its etch resistance. In the other words, the resist should be able to hold up during the etching process. Most of the resist materials are designed to hold up in a specific etching process and using them with other pattern transfer process will introduce process complications or loss of patterning quality. For instance, SU-8 resists pill off in KOH wet etching solutions and cannot be used together with KOH wet etching. PMMA resists cannot hold up in oxygen plasma. So, they cannot be used with reactive ion etching processes which are incorporating oxygen plasma.

With modern exposure tools and established resists, generally the contrast is not a major issue and desired contrast can be easily achieved by tuning the exposure dose and development parameters. Thus, after considering the mentioned constraints, usually there are plenty of different resists applicable to the process. In order to minimize the product variation, maximize the yield and improve the resolution, it is necessary to choose a resist which can give the highest homogeneity.

Most of the commercially available and widely used resists are composed of a photon or an electron sensitive polymer, a solvent and some additives. The ultimate homogeneity of a resist layer is dictated by the structure of the polymer material itself. In most of these resists the steric compatibilities between the tactic sequences of the polymer molecules [19] and Van der Waals attractions [17] drives the smaller polymer molecules to diffuse and attach to the bigger molecules and make granules of about 20 nm big (figure 1).

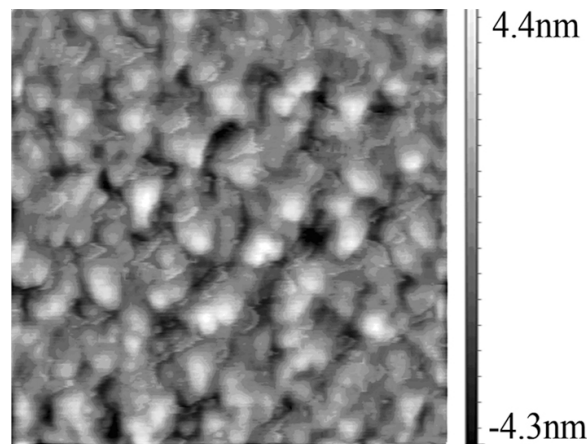


Figure 1. Granular Structure of Resist. 200x200 nm atomic force microscope (AFM) scan of a resist's surface is showing its granular structure resulted from agglomeration of polymer molecules. The resist is a commercial PMMA and coated on a silicon wafer in a standard process.

If the mentioned forces be enough strong, and the polymer chain be enough long and flexible; they can even make the polymer chain to collapse on itself. The diffusion rate of the developer is much faster between the granules and at their boundaries than inside the granules. In addition, these granules are much less soluble in the developer than the rest of the material. So, the resist material in the granules will not dissolve in the developer and these granules will be extracted and released one by one in to the developer.

Consequently, the size and solubility of these granules will limit the lithography resolution and line edge roughness (figure 2) [9, 19]. So, in order to increase the resist homogeneity, it is necessary to reduce the aggregation and formation of these granules; or choose a resist with less aggregation or smaller granules.

Generally, if the final resist layer will be much thicker than the length of the polymer chain; then, more rigid polymers with more 3-dimensional structures will result in less aggregation, e.g. if final resist layer be thicker than about 100 nm; surface roughness of hydrogen silses-

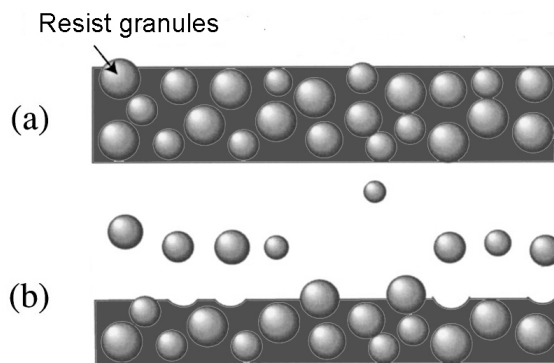


Figure 2. Effect of Resist's Granular Structure in Development. a) Schematic representation of a resist layer with granular structure. b) During the development the granules are being extracted and a rough edge is left behind.

quioxane (HSQ) or Calixarene be less than poly methyl methacrylate (PMMA), SAL[®] (Shipley Inc.) or ZEP[®] (Nippon Zeon Ltd.) [17]. In such conditions, smaller polymer molecules will result in smaller granules, e.g. Calixarene results in a smoother surface than HSQ if the resist thickness is more than about 100 nm. On the other hand, if the resist thickness is in the order of or less than the polymer length, more flexible and longer polymers will result in a more homogeneous surface, e.g. if the resist thickness be 20 nm, Novolac will result in a rougher surface than polyvinyl phenol [21].

Although, the existence of smaller polymer chains in a solution of longer polymers, prevents the resist layer from shrinking after removal of the solvent; they will increase the granule formation by diffusing into the bigger chains. So, the best polymer to make a very thin and homogeneous layer is a long and heavy polymer with a narrow molecular weight distribution and a one dimensional and flexible structure.

The other ingredient of a resist is its solvent which is a liquid that transfers the resist material to the substrate. This solvent should not degrade and should prevent the polymer molecules to reach each other and from particles. Because, if the resist molecules get very close to each other they will bind by the mentioned forces and make small particles or aggregations. To reduce the polymer aggregation, it is required to reduce the concentration of the polymer in the solvent. Hereby, the probability of two polymer molecules colliding to each other will reduce; but, to prevent partial coverage of the substrate by the resist layer and also to prevent the early aging of the resist and formation of particles, the polymer concentration should not reduce below a certain value. In addition, if a very low viscosity solvent be used and a thicker layer be required, it will be necessary to reduce the spin coating speed too much, which will increase the wafer level resist thickness variation.

To improve the surface coverage of the resist, other materials can be added to the resist solution to improve its adhesion to the surface. In some resists these are enhancing the sensitivity, dark erosion or contrast as well.

Potentially the most homogeneous resists are self assembled surface mono layers (SAM) [12, 15, 18, 2]. These are a few nanometer long molecules that can bind to the substrate's dangling bonds only at a specific site located at one end of the molecules (figure 3). In ideal case,

interaction between the molecules themselves and the substrate, results in a perfect 2-dimensional lattice of an arranged mono layer on the substrate.

Unfortunately, SAMs are very sensitive to the material beneath them. So, not only they are very sensitive to surface contamination, but also, it is not possible to use them on different materials. In addition, they have a very limited etch resistance. Hydrogenated dangling bonds have also been used as an atomic monolayer resist [16]. Although they may have potential of providing atomic resolution lithography, they are even more severely suffer from the lack of etch resistance and high sensitivity to the surface. Monolayer resists are mostly in the research stage and yet they have not found vast industrial applicability.



Figure 3. Schematic representation of a self assembled surface mono layer (SAM) resist. In this case linear resist molecules have made an arranged coating on the wafer.

3. Resist storage and aging

The resist material should be stored in a clean low sodium glass, Teflon or HD-PE bottle. There should not be any plastic with a softener near the resist. The bottles can be cleaned in hot acetone and then in hot isopropyl alcohol (IPA) and should completely dry before putting the resist in it. After each refilling a waiting period of several hours is necessary to outgas air bubbles from the resist. The filled bottles should be stored in a dry and dark place, preferably inside the clean room. The storage temperature should be enough high to prevent particle formation and sedimentation, and enough low to prevent evaporation, degradation and decomposition of photo initiator. Usually the best storage temperature is between 5 °C to 10 °C.

Inappropriate storage or aging of the resist will result in formation of nitrogen bubbles, and particles and gradually conglomeration of them to bigger clusters. All of them will result in so called comet like inhomogeneity (figure 5.a). In an aged resist the photo initiator is lost. Therefore, development rate decreases and dark erosion increases. Aging also reduces the adhesion of the resist to the surface. This reduction will result in undesired undercuts, pill off of the resist during the development and will change the pattern dimensions. It is also recommended not to store partially used bottles for a long time. Because, the nitrogen can dissolve in the resist and the dissolved nitrogen can cause bubbles or popping during the baking or exposure. Frequent opening of the resist bottle will also result in evaporation of the solvent which will increase the resist viscosity and thickness.

4. Surface preparations of the substrate

Substrates should be cleaned before the resist coating. This cleaning decrease the surface roughness by removing particles and contamination; and also it will increase the resist homogeneity by removing contaminants and increasing the adhesion of the resist. Loss of adhesion may reduce the homogeneity by resulting in pill-off of the resist, or under cut in some parts. Contamination on the surface will result in pattern variations and homogeneity reduction as well.

In general the cleaning process will depend on the substrate's material. In the case of silicon substrate, an appropriate cleaning process can contain the following steps: first, dipping in piranha (H_2O_2 (25%) : H_2SO_4 (97%) 1:3 v:v) for more than 5min; hereby not only most of contaminants will dissolve in the solution, but also, SiO_2 will grow in to the silicon. So, the Si/ SiO_2 interface will be kept clean. Second, dipping in diluted HF (1-5%) will remove the oxide with all the remained contaminants attached to it. Third, dipping in SC-1 (H_2O_2 (25%) : NH_4OH (25%) : H_2O 1:1:5 v:v:v) for about 10 min at 75 °C; forth, dipping in diluted HF again. Fifth, dipping in SC-2 (HCl (30%): H_2O_2 (25%) : H_2O 1:1:6) for about 10 min at 80 °C; and finally, dipping in the diluted HF again and then blow drying with nitrogen. After this process the surface dangling bonds of the silicon should be hydrogenated (H-passivated), and consequently the resist will have a very good adhesion on it. If for any reason it does not be possible to completely remove the oxide from the surface, the surface will be hydrophilic to some degree. The resist will not have a good adhesion to a hydrophilic surface. In addition, a hydrophilic surface will easily absorb moisture. So, it is necessary to bake it for a few minutes at more than 120 °C (preferably in an oxygen free environment). This baking process will dehydrate the surface e.g. in the case of silicon it will remove the OH- groups from the silicon dangling bonds.

If for any reason it does not be possible to produce sufficient adhesion between the substrate and the resist material. It will be necessary to use an adhesion promoter. It is a material that coats the surface before resist coating. On one side it binds to the substrate and on the other side adheres to the resist layer which comes on top. For example, Hexamethyldisilazane (HMDS) binds to the SiO_2 surface, and then releases its ammonia. So, a methyl group remains bound to the surface (figure 4). Many resists have a very good adhesion to this methyl group. Possibly the HMDS coating will be thicker than a monolayer. Such a HMDS layer can release considerable amount of ammonia during the baking process. The released ammonia diffuses in to the resist material and crosslinks the resist molecules. In this case the complete development of the resist will be impossible. So, considering the fact that we need just a monolayer of the HMDS, thinner HMDS coatings are better. It is also necessary to dehydrate the substrate before HMDS coating. Another common adhesion promoter is TI PRIME ® (Microchemical Inc.); it works like HMDS; but, it automatically makes a monolayer by baking at 120 °C. So, it does not have the complications of the HMDS.

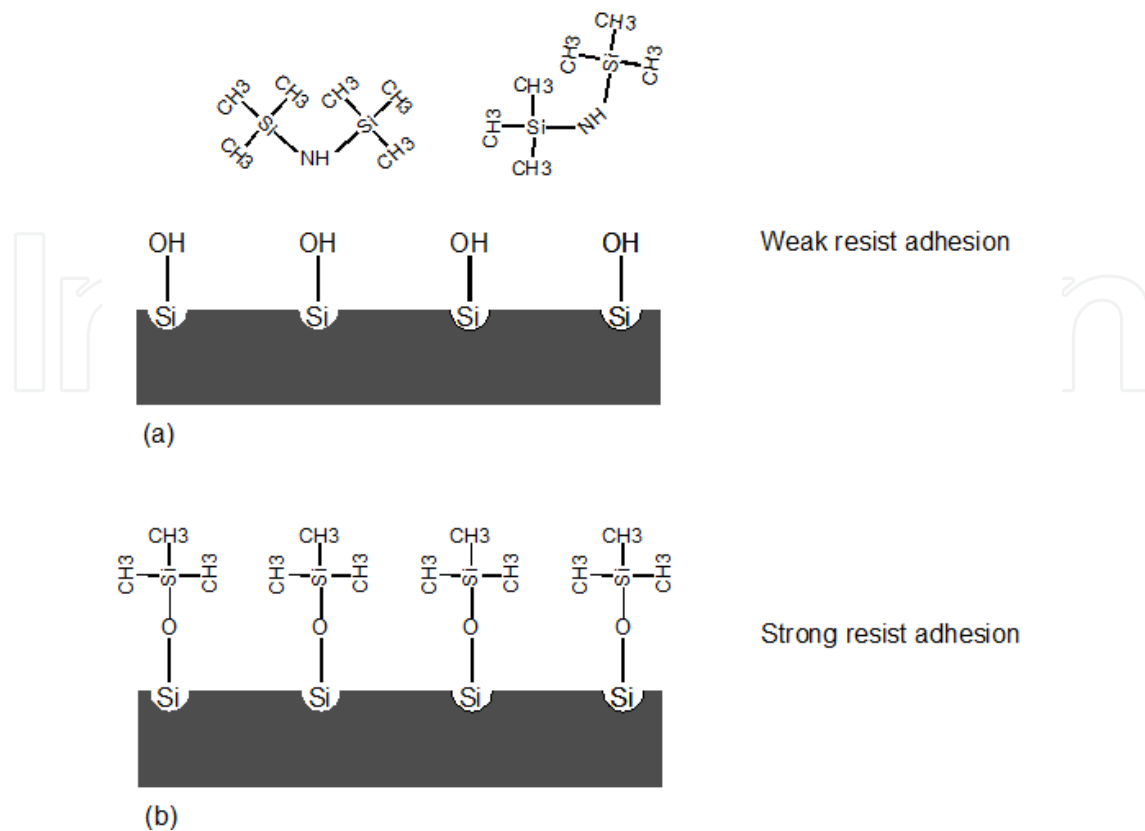


Figure 4. Schematic representation of chemistry of HMDS adhesion promoter working on a silicon substrate. a) Dangling bonds of silicon atoms and native oxide are occupied with OH groups, leaving a hydrophilic surface that cannot adhere to resists. b) HMDS molecules have left their NH group and bind to the silicon atoms on the surface, leaving a hydrophobic surface that strongly adheres to resists.

5. Resist coating

Some resists are available in rolled sheets of several centimeters by a few meters. These sheets can be laminated on the substrate. In the case of the liquid resists, it is possible to put a layer of the resist solution on the substrate by wetting a cylinder by the resist solution and rolling the cylinder on the substrate; but, the most widely used methods of resist coating are spraying the resist solution on the substrate; or dispensing it on the substrate; and then, rotating the substrate with high speed to obtain a very thin and homogeneous layer.

By rotating the wafer, the centrifugal force tries to spread the resist to the edges of wafer and eventually fling it off the edges of the wafer. On the other hand, the adhesion of the resist to the substrate and viscosity of the resist are trying to keep the resist on the substrate. At the same time, evaporation of the solvent gradually increases the resist viscosity and makes it impossible for the centrifugal force to move the resist material off the wafer. In ideal situation, the end result of these competing forces will be a homogeneous and thin layer of the resist material on the substrate.

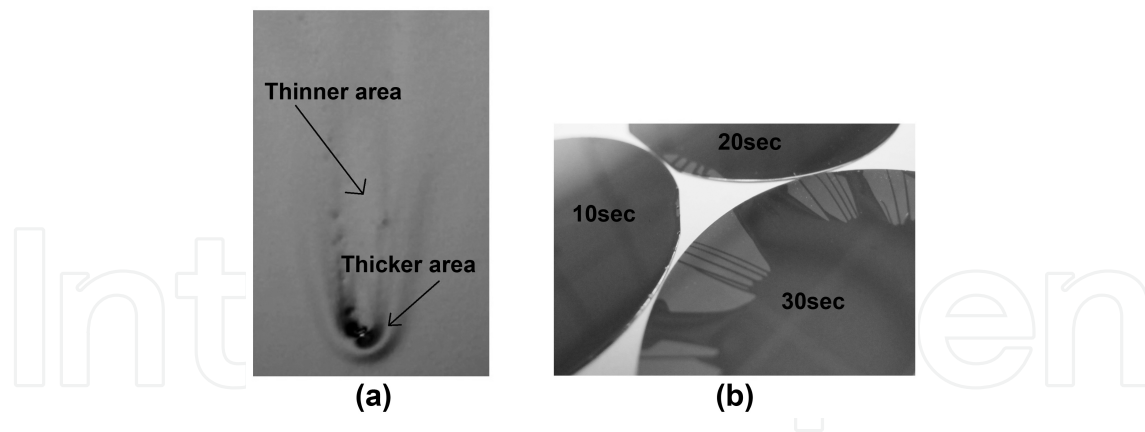


Figure 5. Resist Inhomogeneities Caused by Spinning. a) A comet inhomogeneity in the resist which is caused by a particle in the resist. b) Inhomogeneities caused by insufficient amount of dispensed resist and too long acceleration time. The lower wafer accelerated in 30 s, the upper one in 20 s and the left one in 10 s.

The spin coating consists of the following stages [14]:

1. At first small puddle of the resist is dispensed on the wafer near its centre. The amount of the dispensed resist usually is a few milliliters or less. For bigger wafers and more viscose solutions, more resist should be dispensed; and for less viscose resists and smaller wafers, less resist is needed. In many cases it is beneficial to dispense the resist through a micrometer sized filter to filter out the particles and bubbles. It is necessary to dispense the resist from close proximity of the wafer and prevent dropping off the resist on the wafer. Otherwise air bubbles may generate and cause comet shape thickness variations (figure 5.a). These so called comets can also be generated by bubbles or particles in the resist or on the wafer. If the amount of the dispensed resist be too small, depending on the acceleration, some triangular shaped areas with no resist will appear near the edges (figure 5.b).
2. Wafer should be accelerated to the final rotation speed and this acceleration should be precisely tuned. When the wafer rotates with a constant speed with no acceleration, the centrifugal force moves the resist outward on a radial direction. So, if there be some topographical features perpendicular to this radial movement, it will not be covered homogeneously by the resist. By the angular acceleration, the resist will make a spiral path instead of a direct radial path. This spiral movement during acceleration can increase the homogeneity of the coating on the topographical features. If the acceleration be too low (long acceleration time), some triangular shaped area with no resist will appear near the edges (figure 5.b). When the rotation speed of the wafer becomes enough high, aggressive expulsion of the resist from the wafer edges can be observed (figure 6.a). Due to the acceleration and the speed difference between the upper and lower layers of the resist, spiral vortices may be briefly visible. It is very important not to stop the spinning at this time. Otherwise, large resist thickness variations will remain on the wafer. By continuation of spinning, eventually the resist will be thin enough that the viscous shear drag exactly balances the rotational acceleration.

3. In this stage, wafer rotates with a constant speed and the resist rotates with the same speed meanwhile the resist thickness gradually reduces. The resist thickness is almost uniform at this stage (figure 6.b), and gradual change of interference colors of the whole surface of the resist due to reduction of its thickness is often visible. If a relatively thick resist layer is desired, it is possible to stop the spinning at this stage; but, in order to have high reproducibility and lower wafer to wafer thickness variation, usually the spinning is continued for a longer time. In addition, edge effects are more pronounced at this stage. Because, the fluid flows very gradually outward to edges, this flow is not enough strong to instantaneously make the resist to fly off the edges. Infact the resist is gathered on the edges and only when a significantly thick layer forms on the edges, small amounts of resist can fly off the wafer in small droplets or thin fibers. This thicker resist layer on the edges is called edge bead. The edge bead not only reduces the useful area of the wafer but may cause sticking to the mask. The edge beads are inversely proportional to the spinning speed.

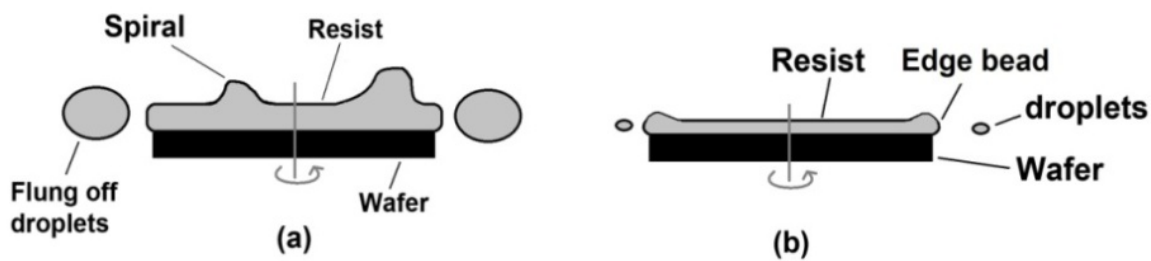


Figure 6. Formation of Edge Bead during the Spinning. a) Schematic representation of the second stage of spin coating when resist explodes from the wafer edges. b) Schematic representation of the third stage of spin coating when resist flies off the wafer in very small amounts and edge bead forms.

4. By continuation of spinig flow of resist on the substrate reduces to zero. At this stage most of the thickness reduction is due to the solvent evaporation. This evaporation is enhanced by the flow of air due to the rotation. This stage happens at the relatively flat tail of the spin-curve (figure 7). The best time to stop the spinning is during this stage when the highest homogeneity and reproducibility is achievable. The overall spinning time required to get to this point depends on the resist viscosity and the spinning speed. For more viscose resists it takes more time to get to this point and the final resist layer will be thicker. By using higher spinning speeds, this time will reduce as well as the resist thickness.

If C be the polymer concentration, η the intrinsic viscosity, ω the number or rotation per minute and K , γ , β and α fitting constants; the final resist thickness obtained by spin coating will be:

$$T = \frac{KC^\beta \eta^\gamma}{\omega^\alpha} \quad (1)$$

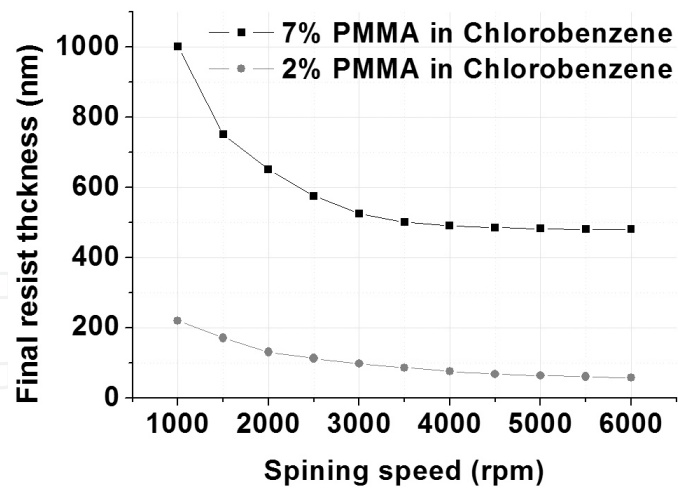


Figure 7. Spin speed curves for 2 and 7% PMMA in chlorobenzene.

6. Baking

After spin coating of thick resist layers, it is usually beneficial to wait for few minutes. This waiting time allows the resist to relax on the surface. Thus, the edge bead and other thickness variations will reduce. Then the resist should be baked. The baking is a process in which the wafer is heated to 50 °C to 250 °C before exposure. This process is necessary to evaporate the solvent content and harden the resist to prevent formation of nitrogen bubbles, sticking to the mask, improving the resist adhesion and minimizing the dark erosion. After spin coating the solvent content of the resist is usually about 20 to 40%. During the baking process this solvent content reduces by diffusion from depth to surface and evaporation of the solvent at the surface. So, the solvent content of the resist at the resist top surface is less than areas deep in the resist. By increasing the baking time the solvent content decreases (figure 8).

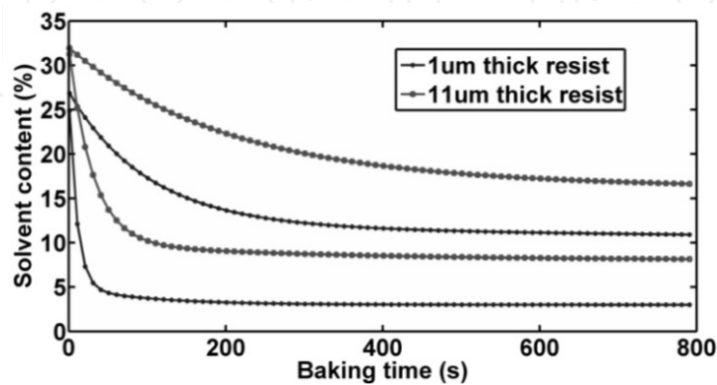


Figure 8. Solvent content of a PMMA based resist as function of time for two different resist thicknesses. Baking was done on a hot plate at 90 °C.

In order to have a more reproducible process, the baking time should be in the flat region of the figure 8. To have a homogeneous resist layer the solvent content of the resist should be less than a few percents. To increase the throughput it is desired to reduce the baking time by increasing the baking temperature; but, too high baking temperature may introduce cracks in thicker resists and eventually degrade the resist material. Too high temperature or too long soft bake will also decrease the development rate and contrast.

Baking can be done on hot plates or in nitrogen oven (in a state of the art process that will be described in the last section a rapid thermal processing system should be used). Usually baking in nitrogen oven takes more time than hot plate, but, it can result in a better resist homogeneity. Regardless of equipment used for baking, temperature gradients on the wafer and in different parts of the equipment should be minimized.

During the baking process, water content of the resist layer reduces. While a certain amount of water in the resist layer is necessary to have a reasonable development rate. Considering the fact that the water is absorbed from ambient on the surface, some time after baking is needed to let the water to penetrate deep in to the resist layer. So, if the exposure done immediately after the baking, development rate will be different in different depths in the resist. Such an inhomogeneity will change the pattern's cross section profile (figure 9). The time needed to have a homogeneous rehydration, is varying between a few seconds to tens of minutes depending on the resist thickness and other parameters. If the humidity of the yellow room be less than 45% the resist will not be able to absorb enough water, and if the humidity of the room be more than 55% the resist adhesion will decrease by absorption of water on the substrates surface. The best condition for the yellow room is 22 °C and 45% relative humidity.

Since most of the resist materials are sensitive to ultraviolet, UV free yellow light is used in areas of the clean room where lithography is done; so, lithography rooms are also called yellow rooms. Although the resist coated substrates can be stored for months in yellow room conditions without chemical degradation of resist material, any unnecessary elongation of the lithography process is not recommended and can reduce the homogeneity.

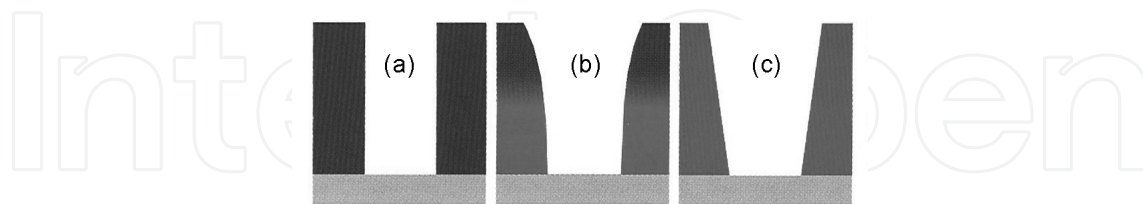


Figure 9. Effect of resist rehydration on the pattern cross section after development. a) Rehydration was complete. b) Rehydration was happened in the upper half of the resist layer. c) There was no rehydration.

7. Exposure

In order to have a homogeneous pattern in ultraviolet (UV) lithography, the exposure dose variation should be less than 10% along the wafer. In addition, the exposure should be done

on an anti vibration table. The wafer and the mask should be precisely aligned to the lenses or mirrors. The exposure tool and especially the mask should be clean and free of particles. If the chromium mask has defects in the form of small holes or cracks, using lower exposure dose will reduce their effect. In other words, although increasing the exposure dose increases the contrast, it can reduce the homogeneity. Reducing the gap between the mask and the wafer will enhance the resolution as well as the homogeneity. However, this reduction usually increases the probability of mask contamination and may damage it, and shortens mask's longevity. Variation of the reflection coefficient of the substrate beneath the resist can also cause inhomogeneity in the UV exposure.

In the case of electron beam lithography it is recommended to put the samples at the centre of the sample stage directly under the column. Because, for exposing the areas away from the centre, the beam should bend more; and this bending increases the beam noise by coupling the electrical noise of the deflector; enlarges the spot size, and increases the effects of aberrations. The electrical and acoustic noise should be minimized during the electron beam exposure. Turning off the lights of the lithography room, especially florescent lights during the exposure decrease the noise level. Any electrical inhomogeneity, edge or thick insulator layers on the substrate can introduce randomized beam fluctuation. This fluctuation is caused by charging, and inhomogeneous or fluctuating electrical fields near the wafer.

8. Development

Frequent opening or exposure of the developer to air leads to carbon dioxide absorption by the developer and after exhaustion of its buffer; it will result in lower development rate. In addition, by using a developer for lot of wafers, concentration of the developed resist in it will increase. Consequently, the development time will increase too. As a rule of thumb, if the resist content of a developer reaches one tenth of a percent, the development rate will decrease about ten percent. Very low development rate usually is accompanied by reduction of contrast and increase of dark erosion. Consequently it will pronounce the effect of resist thickness variations and inhomogeneities. On the other hand, if the development time be too short; reproducibility and homogeneity will reduce. Because, it will be difficult to produce a repeatable and homogeneous flow of the developer on the substrate, in a very short time compared to the development time. Also strong developers tend to roughen the resist's surface and decrease the resolution by making a thick gel like layer between the developer and the resist (these effects will be further discussed in the next section). Usually preferred development time is between 30 s to 3 min. Development time is a function of temperature, concentration and exposure dose. So, it is necessary to precisely control the temperature of the developer and keep it homogeneous by constant stirring. Development rate increases with the exposure dose to some point and then it remains constant (figure 10). Thus, to have a better repeatability and homogeneity, the exposure dose should be in the flat region of figure 10's curve. Substrate compatibility of the developer should be considered too. For example alkaline developers attack aluminum and its alloys.

Some times after the development the wafers are baked again. This application of high temperature after development is called hard bake. Although hard baking can increase the stability of the resist layer and its adhesion to the substrate; but, it can also result in cracks, rounding of the edges, reflow of the resist and consequently reducing the resolution.

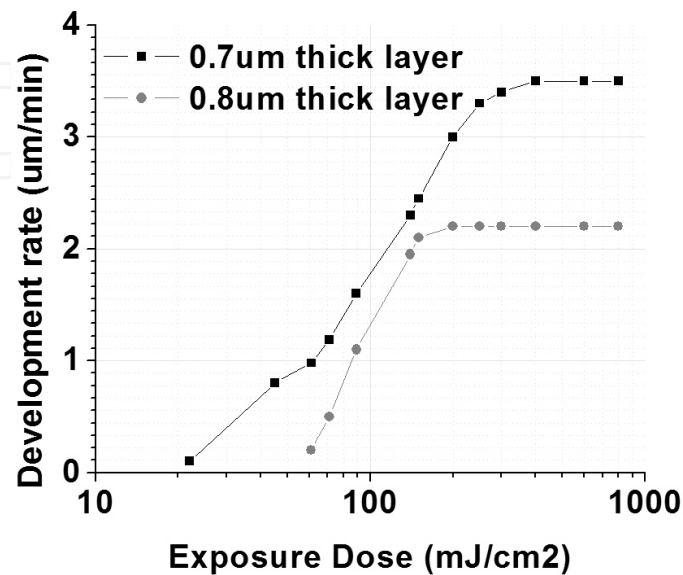


Figure 10. Development rate versus exposure dose for a UV resist (AZ 9260) that baked for 10 min at 100 °C.

9. Resist homogeneity in nano lithography

As it mentioned earlier in this chapter, the most important problem that limits the ultimate resolution of industrial lithography can be granular structure of the resist material (figure 1). The formation mechanism of these granules is:

After spin coating and during backing process, bigger polymer molecules fold on themselves; due to the attraction between the monomers on the same chain. Hence, end-to-end distance of the polymer reduces to much shorter than its length. Moreover, solvent evaporation reduces the radius of gyration. During the solvent evaporation, the big polymer molecules immobilize sooner, while the smaller molecules are still highly mobile and because of the intermolecular attractions, these small molecules penetrate to the long molecules. This aggregation makes about 20 nm to 60 nm big granules.

Because the development is much faster at the granule boundaries, granules release one by one into the developer instead of dissolving (figure 2). This effect increases the RMS of surface roughness to more than 250 pm and the RMS of line edge roughness to more than 2 nm, and determines the smallest patternable structure. An approved method to reduce this problem is a very short time thermal processing, which does not give enough time to the short polymer molecules to penetrate into the longer molecules, while using higher temperature to evaporate

all of the solvent in the limited time. A detailed study of using this method to obtain a very homogeneous layer of PMMA and making patterns smaller than 5 nm by electron beam lithography (EBL) follows.

As a typical substrate, p-type <100> silicon is used in this study. Usually it is needed to pattern a thin film on the substrate. This thin film may be a part of the final device or maybe used as a mask to make patterns in other layers. Here, a thin film of ruthenium is used on the substrate. Ruthenium has high ion milling etch rate, so, it does not need a thick layer of resist to hold up the etching process; ruthenium has high conductivity, so, the charging effect during the electron beam exposure will be minimum; it has small grain size, so, it can make a thin, continuous and smooth film which will not increase the resist inhomogeneity; ruthenium has compatibility with different surfaces [24], and the possibility to be used as a mask to etch other material beneath the ruthenium. In addition, ruthenium activates C–H and C–C bonds and benzene decompose on ruthenium at 87 °C, thus it helps the solvent to outgas during baking, while there is no dehydrogenations bellow 277 °C. Thus, it will not damage the PMMA in the backing process, while PMMA has good adhesion on it. To make the ruthenium layer; after RCA cleaning of the substrate, 10 nm ruthenium sputtered on the samples. In order to improve PMMA adhesion and uniformity, samples annealed at 400 °C. Hereby, the contact angle of PMMA solution on the substrate’s surface reduced to less than 5 °C.

Samples were coated with 2% 950K PMMA in chlorobenzene by spinning at 6000 rpm for 50 s with 1s acceleration and 10 s deceleration time. This long deceleration time increases the resist homogeneity. The best thermal processing for this process found to be: increasing the sample temperature from 21 to 250 °C in 1 s and keeping it in that temperature for about 15 s and cooling it down to 21 °C in 1 s (figure 11).

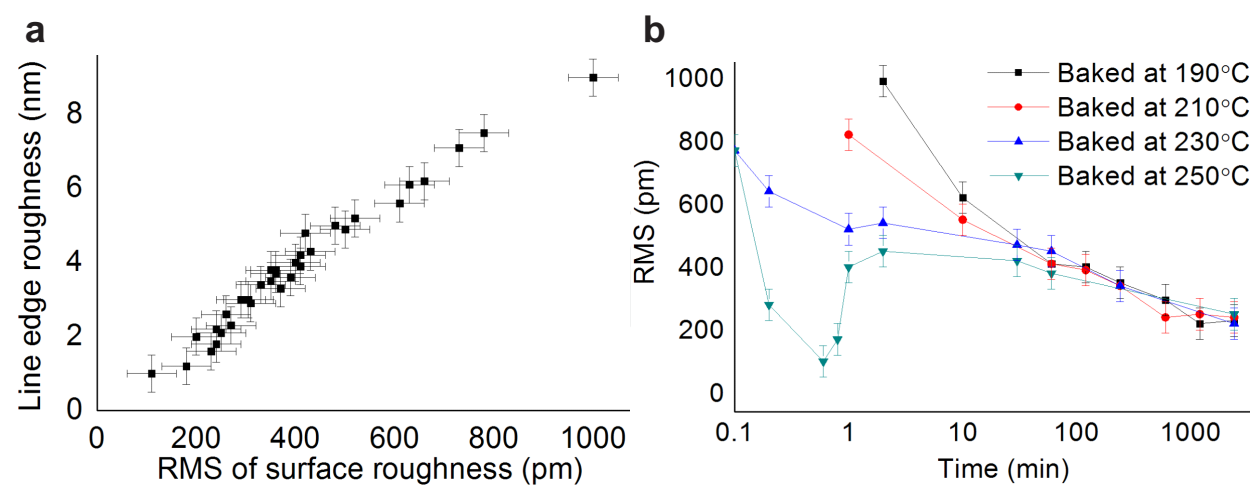


Figure 11. Effects of Different Baking Processes on Line Edge Roughness. a) RMS of surface roughness versus line edge roughness; obtained by baking the resist in different thermal processes. b) RMS of surface roughness versus baking time for different baking temperatures.

Highest resolutions and smallest patterns in industrial lithography have been achieved by using electron beam to pattern PMMA. By using PMMA as the electron beam resist; lines as

thin as 5 nm [23, 3, 22] and 10 nm gaps [7, 13] have been reported. 5 nm pillars have been achieved by etching thicker pillars [5, 10]; but, without using the described method to solve the problem of resist aggregation, holes smaller than 10 nm had not achieved [8, 1, 6].

Unlike patterning lines, in patterning holes, there is a very confined space for developer to penetrate through the exposed area. In addition, there is a very small space for the dissolved resist to diffuse in to the bulk developer. So, to overcome this problem, and to overcome the intermolecular force between the unexposed walls and the exposed PMMA, ultrasonic agitation should be used.

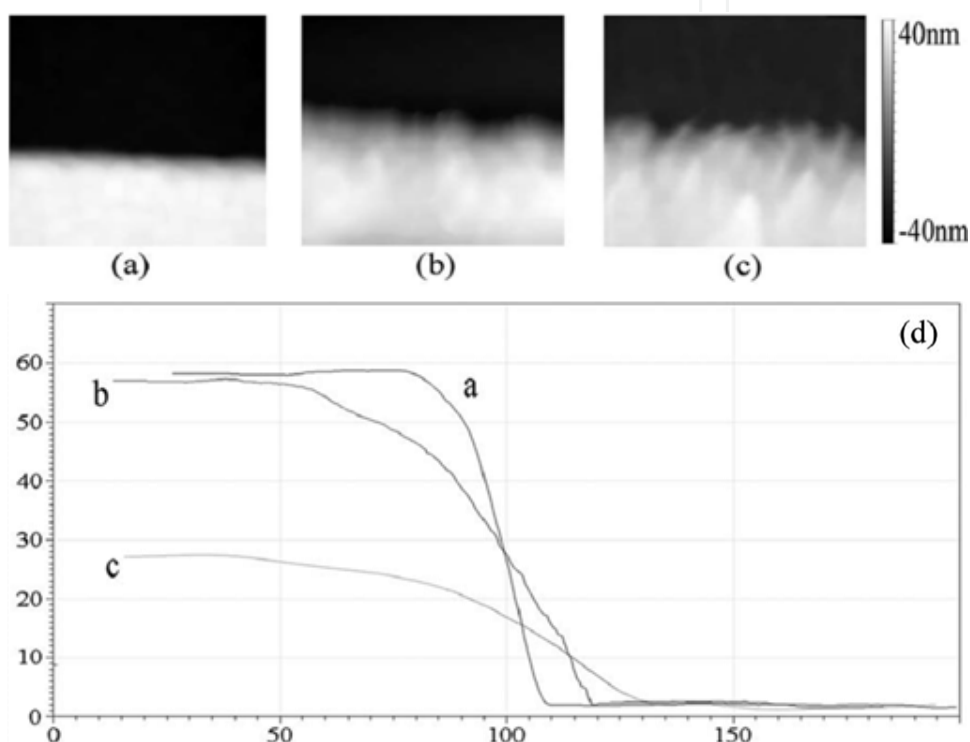


Figure 12. AFM Investigation of Effect of baking process on Line Edge Roughness. a) Line edge of a PMMA that baked for 15 s at 250 °C. b) Line edge of a PMMA that baked for 3h at 165 °C. c) Line edge of a PMMA that baked for 10 s at 300 °C. d) Cross section profile of a, b and c; axes are scaled in nanometers. Lowest line edge roughness and highest contrast are obtained in sample a, while in sample c the resist is degraded.

Other problems in patterning small holes are the gel thickness at the interface between the exposed resist and the developer (related to the radius of gyration) and developer induced swelling. To overcome these problems a weak developer, and cold development, should be used. This process is successfully used to make sub 5 nm patterns. For making such a small pattern, the only available industrial lithography process is electron beam lithography (EBL). In this study, electron beam exposure performed by Vistec VB_6HR with 50 keV acceleration voltage and 150 pA current (by increasing the acceleration voltage and decreasing the current, spot size reduces). Optimized development condition is 7:3 v:v isopropyl alcohol (IPA) in water in ultrasonic bath at 12 °C. After the development, ion milling for about 65 s at 80 mA beam current with 375 V acceleration voltage used to transfer the PMMA pattern to the

ruthenium layer beneath. Then, the resist residue striped by 1, 2-dichloroethane:acetone 1:1 v:v to completely remove the PMMA without affecting the underlying surface [11].

The almost linear relation between the surface roughness and line edge roughness (Figure 11.a) substantiates a common source for both of them and the mentioned theory of PMMA granules. In samples which have been baked at temperatures lower than 230 °C, surface roughness and line edge roughness are improving by increasing the baking time (Figure 11.b). This improvement is due to reduction of solvent content in the resist by evaporation. By baking in higher temperatures for a very short time, a significant improvement in surface roughness and line edge roughness appears. By baking at 250 °C for 15 s the lowest surface roughness and line edge roughness are obtained which are about 100 pm (figure 11.b) and 1 nm (figure 12.a), respectively. By reducing the baking time, PMMA molecules do not have enough time to diffuse and form the granules, while due to the high temperature all the solvent evaporates. By further increasing the baking temperature, resist thinning and line edge rounding increases considerably, which is an indication of losing the contrast and degradation of the resist material (figure 11.b).

If ultrasonic agitation do not be used for development, small holes will not completely develop, no matter for how long they were developed (a partially undeveloped hole could not result in a highly visible object in SEM image after ion milling). Doing the development in higher temperatures takes much shorter time but in higher or lower temperatures or stronger developers (such as methyl isobutyl ketone:IPA 3:1 v:v), contrast will be much lower and pattern edge roughness will be much higher that patterning small holes will not be possible. However, by using the mentioned optimized development process, holes smaller than 5 nm were obtained on the PMMA (figure 13).

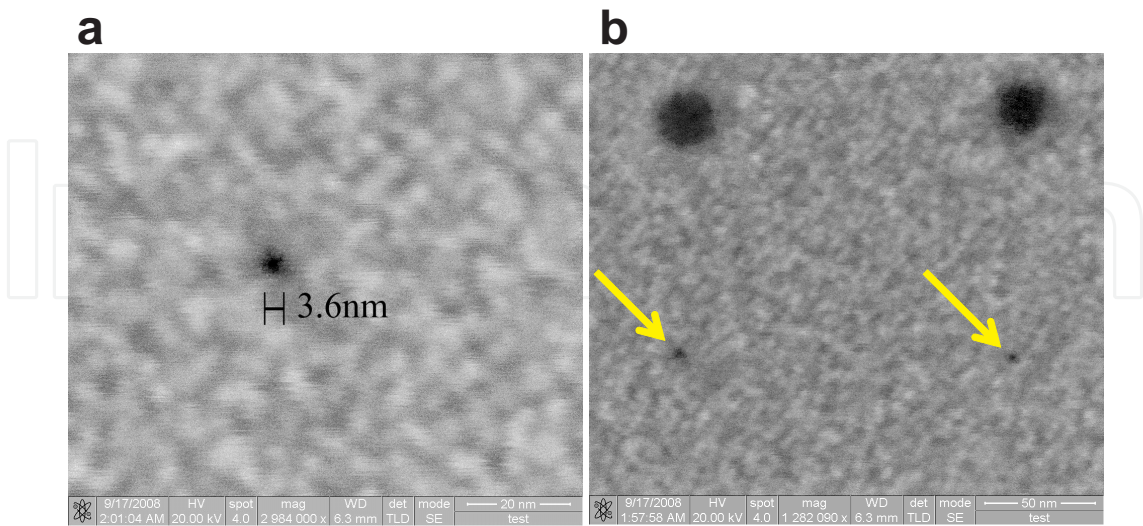


Figure 13. Patterned Holes in PMMA. a) High magnification SEM image of a small hole patterned on the PMMA layer. b) An array of the patterned hole with different diameters. Arrows are showing the small holes. The PMMA was spun at 6000 rpm on a 10 nm thick layer of ruthenium. Then, backed at 250 °C for 15 s, exposed by 50 keV electron beam, and developed in IPA:H₂O 7:3 v:v at 12 °C.

By baking the samples at 250 °C for 15 s, the development time was more than 2 min, but for the samples baked in lower temperature for longer time, it is less than 1 min. The reason is, if the PMMA has granular structure, the development rate at the boundaries is much higher than in the granules. So, the granules release during the development. However, by using the fast baking process, resist is homogeneous. So, there is no granule boundary and it takes a longer time for the PMMA to gradually dissolve in the developer.

The resist thickness in this process is about 58 nm and before and after the development, there is no measurable change in the resist thickness. The resist can hold up for about 70 s in the mentioned ion milling process. So, it can be used as a mask for etching 20 nm of copper, 15 nm of aluminum, ruthenium, tantalum, or some other materials in ion milling. Hereby, open holes smaller than 5 nm obtained on the ruthenium without significant pattern enlargement during the etching process (figure 14). It worth to mention that the etch rate of the ruthenium layer in SF_6/O_2 plasma in typical reactive ion etching (RIE) processes is almost zero. Therefore, the ruthenium thin film can be used as a mask for RIE of silicon, silicon dioxide or nitride.

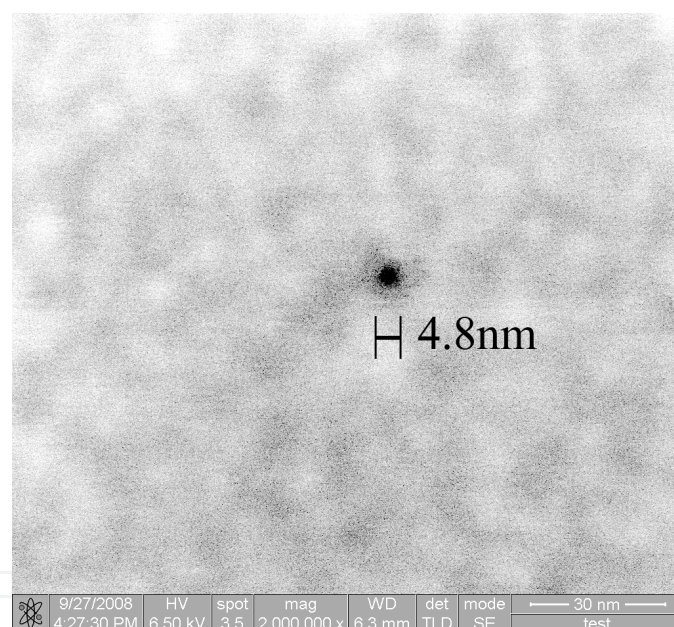


Figure 14. High magnification SEM image of a hole patterned in the ruthenium layer by transferring the PMMA pattern to it by ion milling.

10. Conclusion

Wafer level homogeneity of resist layer is crucial to minimizing product variation and it is also one of the most important factors in having a high production yield. This chapter provided the guidelines for increasing the wafer homogeneity. In order to precisely optimize the process parameters, it is necessary to perform a range of experiments in the framework of a design of

experiment (DOE). The guidelines and trends provided here will be useful to find the optimum condition in a shorter time. These guidelines can also be used as a troubleshooting tool for solving common lithography problems. In the last section, nanometer scale inhomogeneity of the resist which is a consequence of polymer agglomerations, described. Overcoming the problem of these nanometer scale inhomogeneities is important in nanolithography, especially to improve the resolution and making small patterns. A state of the art process to solve this problem described in details. This process has resulted in some of the smallest patterns ever made in an industrial lithography. However, polymer resists have their own intrinsic homogeneity limitations. For atomic resolution lithography, further research in using surface monolayers or crystalline resists for making patterns; and application of atomic layer deposition instead of etching, will be valuable.

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