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Energy-enhanced ALD for nano-manufacturing by Direct Spacer-Defined Double Patterning (D-SDDP)

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Energy-Enhanced ALD for Nano-manufacturing by Direct Spacer-Defined Double Patterning (D-SDDP)

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Abstract

Direct Spacer-Defined Double Patterning (D-SDDP) is a technique complementary to optical lithography that can be used to produce features in semiconductor technology at a scale smaller than can be realized with state-of-the-art 193 nm lithography only. In D-SDDP a spacer film is applied directly on top of a patterned photoresist, after which the structure is anisotropically etched and the photoresist is removed, leaving only the spacer sidewalls behind. The resulting feature width is determined by the spacer thickness, resulting in smaller mask features and a smaller pitch than attainable by 193 nm lithography.

The D-SDDP process is new to the PMP group and not extensively reported in the literature. In this explorative study the D-SDDP process is implemented using techniques available in the Nanolab @ TU/e cleanroom to identify the challenges related to this patterning technique. An essential step in the D-SDDP is the deposition of a conformal spacer film at low deposition temperature, so that the polymer-based photoresist layer is not affected. Therefore, energy-enhanced atomic layer deposition (EE-ALD) processes are developed for the deposition of $Al_2O_3$ and $SiO_2$ spacers at room temperature. During this project, these films were characterized in terms of processing properties and material properties, to test their suitability for application in the D-SDDP process.

Results obtained in this project show that $Al_2O_3$ spacers can be successfully deposited at room temperature using both ozone-based and plasma-assisted ALD. Both processes result in oxygen-rich films due to the incorporation of hydroxyl groups. Additionally, the ozone-based process results in a significant amount of carbon ($\sim 9$ at%) incorporated in the form of carbonates and formates. For $SiO_2$ only the plasma-assisted process was feasible at room temperature, resulting in films with incorporated -OH groups and $H_2O$. No growth was observed in the ozone-based process, which can be attributed to a low reactivity of $O_3$ with the remaining precursor ligands at room temperature.

During the realization of the full D-SDDP process, several challenges were encountered and identified. The most significant challenge was the outgassing of the PMMA (polymethylmethacrilate) resist, upon interaction with the e-beam during SEM imaging and as a result of ion bombardment during plasma-processing. This outgassing effect can result in deformation of the structures, which, consequently, affects the shape of the spacer sidewalls. Other challenges that were encountered include non-reproducibility of the photoresist pattern and deformation of the spacer sidewall during the resist removal step. Furthermore, different techniques for photoresist removal and anisotropic etching have been compared to optimize the process flow.

The results obtained during this explorative study are promising, showing free standing spacer sidewalls, suggesting that a successful D-SDDP process is within reach. Future work will have to focus on the optimization of the shape of the resulting structures, after which the distance between the spacers can be further minimized. Moreover, to scale down feature sizes even more, the application of two subsequent SDDP process (quadruple patterning) can be investigated. Eventually, D-SDDP can be studied for the fabrication of nano-devices.
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Chapter 1

General Introduction

This chapter is designed to provide the background information needed to understand the concepts discussed in this thesis and to be able to place this research project in a broader perspective. Section 1.1 will start off with showing what integrated circuits (ICs) are. Next, section 1.2 will explain that nano-manufacturing is a necessary tool in creating the present and next generation of ICs. For creating these ICs with ever shrinking components, lithography is an essential step that will be treated in section 1.3. Once a full background is provided, the concept of Spacer-Defined Double Patterning (SDDP) is introduced as a necessary technique in the world of modern day electronics (section 1.4). Section 1.5 will show that Atomic Layer Deposition (ALD) is a technique needed in the realization of a SDDP process. Finally section 1.6 will present the project goals and an outline of this thesis.

1.1 Integrated Circuits

Integrated circuits (ICs) have revolutionized the world of electronics and can be found in virtually all electronic devices used today. Typically, a piece of a semiconductor wafer, also called a chip, contains one or more ICs on which billions of miniaturized electrical components (mainly transistors and capacitors, sometimes with additional inductors and resistors) are fabricated. The ever decreasing production costs of ICs have made computers, mobile phones and other digital appliances, an inextricable part of modern society.

![Figure 1.1](image)

Figure 1.1 A typical modern device is a laptop computer. This device contains several chips or IC’s, as shown in the second inset. On a chip often a microprocessor can be found, built from small electrical components such as transistors and condensators constructed on a nanometer scale nowadays.

Figure 1.1 shows a laptop computer which contains several chips placed on a printed circuit
bord, as illustrated by the second inset of this figure. On some chips a microprocessor can be found, which is a particular kind of IC that is designed to perform logic operations executed by the connected components present on the chip (e.g. transistors and capacitors). The third inset of figure 1.1 displays these small electrical components, making the microprocessor the beating heart of a device.

In today’s technology driven world, electronic devices are becoming faster and more versatile with time. This is because chips are gaining processing power since more and more electrical components can be placed on a single chip. The electrical components on a chip shrink in size with every new generation of devices, which is the development described by Moore’s law. Around 1970 Gordon Moore made a prediction that stated that the number of transistors that can be placed on an integrated circuit would double approximately every two years. Figure 1.2 displays the number of transistors on commercially released microprocessors and the year in which the particular IC was introduced to the market [1]. The figure reveals that the so called Moore’s law (black solid line) has been valid up till today.

![Figure 1.2](image)

Figure 1.2 The number of transistors on commercially released microprocessors is displayed against the year that the particular IC was introduced to the market. The solid black line resembles Moore’s law, which represents a doubling of the transistor count every two years. (Figure from [1])

Initially Moore’s law was made in the form of an observation and forecast. However, the more widely it became accepted, the more it served as a goal for the entire semiconductor industry. Semiconductor manufacturers would greatly invest to meet the predicted specifications for an increase in processing power, as it was presumed that their competitors would also do so. In this regard, Moore’s law can be viewed as a self-fulfilling prophecy.

To keep up with Moore’s law, the semiconductor industry has to keep producing smaller sized transistors. According to figure 1.2 the amount a transistors per microchip is approaching the 3 billion, this number can be translated to a so called technology node that represents the half-pitch (i.e. half the distance between identical features) of a transistor in a microchip;
1.2 Nano-manufacturing

Currently the 32 nm technology node. This indication, using the concept of technology nodes was introduced by the International Technology Roadmap for Semiconductors (ITRS). This organization tries to identify knowledge gaps in the semiconductor industry and focuses research and development efforts to keep industry in pace with Moore’s law [2]. The term ‘32 nm technology node’ clearly illustrates that the fabrication of microchips has entered the realm of nano-manufacturing and in keeping up with Moore’s law nano-manufacturing will become even more important in the future.

1.2 Nano-manufacturing

The transistor is the most important electrical component used in chips that can be found in modern electronic devices. A transistor is used to switch electric signals, so that by connecting many of them in a specific way, logic operations can be executed. The most commonly used transistor is a MOSFET (Metal-Oxide-Semiconductor Field-Effect Transistor) which has three main terminals being the source, the gate and the drain. The electrical current which flows from the source to the drain can be switched by a voltage on the gate terminal. This voltage is used to create a conducting pathway in a doped (p- or n-type Si) semiconductor material between the source and drain by repelling charge carriers away from the gate channel region (see figure 1.3). In a n-type MOSFET electrons are transported through the created conduction pathway, a p-type MOSFET transports holes. Figure 1.3 depicts a n-type MOSFET. In this type of transistor, the negatively charged electrons are free to be transported between the source and the drain without recombining with the holes which were repelled provided that a positive voltage is applied to the gate and a voltage is present between the source and the drain. This basic operating principle is also illustrated in figure 1.3. The transistor can also be designed to repel electrons from the gate region by applying a negative voltage to the gate, letting a current created by positively charged holes connect the source and the drain.

![Figure 1.3](image_url) A transistor can be used to switch electric signals by applying a voltage to the gate terminal. The left figure has no voltage applied to the gate, therefore no current can be conducted between the source and the drain since charge carrier will easily recombine in the gate region. The right figure shows that a conduction pathway is created when a voltage is applied to the gate, by repelling the positively charged holes from the gate region.

The transistor, being the fundamental building block in electronics, has to shrink in dimensions to keep pace with Moore’s law. As stated in the previous section, microprocessors consist of many transistors all placed together on a chip with a half-pitch of 32 nm. Nano-manufacturing is thus needed to accurately create all the components of these transistors at a nanometer scale. Semiconductor nano-manufacturing can be described as the creation of small 3D structures typically on a silicon substrate. The most common process to do this involves three steps: 1) deposition of a uniform film of material on the substrate; 2) applying a photoresist layer and
executing a lithography step to transfer the desired mask pattern in the film; 3) an etch step to transfer that pattern into the target layer followed by the removal of the resist. These steps are depicted in figure 1.4.

![Diagram](image)

**Figure 1.4** The three basic steps involved in nano-manufacturing: 1) depositing a specific film (light grey); 2) applying a photoresist layer (orange) and patterning it; 3) an etch to transfer the pattern in the target layer followed by removal of the resist.

It should be noted that also another processing step can be defined, namely the implantation of ions to create the regions of excess holes or electrons which are necessary for a working transistor as seen in figure 1.3. To create these so-called doped regions on a specific location, a mask can be used. However the process of ion implantation will not be discussed here.

The first step, the deposition of a specific material (e.g. metal-oxide, semiconductor or metal) can be done by many different technologies such as chemical vapor deposition (CVD), physical vapor deposition (PVD) and atomic layer deposition (ALD). Since this thesis has a special focus on ALD, this method will be discussed in detail in section 1.5.

The second step of the nano-manufacturing process concerns the application of a photoresist layer and the execution of a lithography step to transfer a mask pattern into the resist layer by using light. Typically two types of resist are available, classed as positive, where exposure to light causes the resist to be removed after development, and negative, where exposed patterns remain after development. The basic principle behind the operation of a photoresist is the change in solubility of the resist in a developer upon exposure of to light. In the section that follows (section 1.3) the lithography step will be discussed more extensively.

The third processing step, etching, involves the selective and anisotropic removal of the material not protected by the photoresist. The goal of this step is to transfer the pattern of the resist into the target layer. The etch process is therefore selected to have the required etch selectivity, which is defined as the ratio of the film etch rate and the resist etch rate. Additionally, the selected etch process had to be anisotropic, meaning that the etch rate is directional. With isotropic etching, the etch rates are similar in all directions and this type of etching can thus lead to undercutting of the mask, which is often undesired in nano-manufacturing.

To fabricate a complete microchip these three basic steps of nano-fabrication have to be executed repeatedly, with different materials being deposited and with different patterns. At all processing steps careful considerations are made about the materials that have to be deposited and their properties. The material for instance has to have certain electrical properties to meet the performance requirements of a new microprocessor. The properties of the material can be dependent on the deposition temperature, adding demands for the depositions processes used. However, photoresist films can typically not withstand relatively high processing temperatures without undergoing significant unwanted changes. Therefore, in some cases inorganic hard masks are necessary and additional processing steps have to be
added to transfer the pattern in a polymer resist to a target layer that can act as a hard mask in further processing [3]. Furthermore, at each processing step the etch selectivity of the exposed materials has to be considered, this can possibly lead to the use of additional buffer layers to protect a certain film during an etch. Finally, also the total processing costs have to be considered, clearly making the fabrication of a complete microchip a complex process. Nowadays a chip even contains multiple levels and at each level the three basic steps of nano-manufacturing have to be executed. In the fabrication of a modern microprocessors this can lead to a total processing scheme that involves up to 24 lithography steps and well over 200 other processing steps.

1.3 Lithography

In following the path set by Moore’s law the biggest roadblock is lithography. The patterning step has to be able to produce patterns that can be used to construct transistors that become smaller with every new technology node. Several lithographic techniques are available. The technique most commonly used is projection printing [4], because this lithographic technique offers the highest resolution and the lowest defect densities. Therefore, projection printing is the standard lithographic technique in the semiconductor industry for producing chips at the 32 nm technology node.

The systems used for projection printing are very complex. This section will discuss the main features of optical lithography to provide a complete background for all research discussed in the upcoming chapters. Figure 1.5 shows a simplified schematic of an optical lithography system using projection printing.

![Figure 1.5 A simplified schematic representation of an typical optical lithography system using projection printing.](image-url)
A laser source is used to generate light at a specific wavelength and in state-of-the-art optical lithography machines used in production lines this is typically 193 nm. This light is guided through an illuminator. After being expanded, homogenized and condensed, the light passes the photomask, which contains a large version of the pattern to be imaged onto the wafer [5]. A complex projection lens then reduces the photomask by typically a factor of 4, and projects it onto the photoresist that chemically changes in the exposed areas, which allows for the production of the final pattern after the development of the photoresist layer. 

Advanced lithography systems image the photomask pattern onto each wafer many times, in a two-step process called ”step and scan”. During the ”step” the wafer moved is to a specific location where the pattern has to be applied. In the scanning part, portions of the photomask are imaged onto the wafer in a continuous scanning motion, until the whole photomask pattern is transferred to the wafer. Now the process of step and scan is repeated until the entire wafer is patterned.

The performance of the projection system is ultimately determined by the laws governing the propagation of electromagnetic waves. In lithography, the most important metric is the resolution, or the resulting pattern dimensions. As described by equation 1.1, the resolution depends on the patterning wavelength and the numerical aperture (NA). The NA is determined by the refractive index (n) of the medium that is in contact with the photoresist and the angle (θ) of the converging rays in the imaging system (see figure 1.5).

\[
\text{Resolution} = \frac{k_1 \lambda}{NA} = \frac{k_1 \lambda}{n \sin(\theta)} \tag{1.1}
\]

The \(k_1\) coefficient is a proportionality factor that convolutes the effects of optics and resist process capability [6]. In other words it resembles the difficulty in printing a given dimension with a given exposure system-photoresist combination [5]. The practical lower limit for \(k_1\) is considered to be 0.25 [6]. The resolving capability of the photoresist to make use of the image is an example of a factor influencing \(k_1\). Techniques like off axis illumination can be used to influence this \(k_1\)-factor [7].

In the quest to produce features for a future technology node, equation 1.1 indicates that the resolution (and thus the minimal feature sizes that can be produced) can be improved by reducing the wavelength, increasing the numerical aperture or decreasing the \(k_1\) value. A short discussion on the historic development and the current status of these three factors will now be discussed in the next three paragraphs.

**Reducing the wavelength**

In lithography history, industry has switched from broadband mask aligners (> 450 nm) to lithographic tools using Hg lamps and utilizing different spectral lines (436 nm, 405 nm and 365 nm), to DUV systems (< 300 nm) to current systems using ArF excimer lasers at 193 nm. The next generation for optical lithography is seen as extreme ultraviolet (EUV) lithography, utilizing a wavelength of 13.5 nm, consequently requiring complex multi-layer mirrors and vacuum optics. EUV lithography has the potential for high resolution imaging due to extremely small exposure wavelength. However, still many technological challenges are present that prevent these systems so far from being integrated in commercial semiconductor production lines [8]. For instance the intensity of the light source has to be improved to reach of sufficiently high throughput. Also the X-ray mirror optics and the required vacuum processing is preventing a high throughput. Because of these technological challenges, 193 nm tools are currently still the standard in producing patterns for the current 32 nm technology node, and also the next technology node (22 nm) is expected to be obtained using this wavelength.
1.3 Lithography

In stead of reducing the wavelength of the light source used, lithography systems can also employ electrons to chemically modify the resist. In principle optical lithography will always be diffraction-limited (whenever an object is imaged by an optical system, features smaller than half the wavelength of the light, are permanently lost in the image [9]). Electron beam lithography (EBL) does not have this limitation and resolutions below several nm can therefore be achieved. The principle of EBL is the basically the same as for optical lithography, only now a beam of electrons is focussed and used to write patterns. EBL is thus a maskless lithography technique and as a consequence more processing time is needed to write a pattern since the pattern cannot be exposed at once. EBL is therefore not very interesting for industrial applications, since the throughput will be very low compared to optical lithography. Several initiatives to enhance the throughput by using many electron beams simultaneously are however being developed for instance by Mapper[10]. Standard EBL can be convenient for prototyping though, since small features can be written without using a photomask.

Increasing the numerical aperture

Traditionally, after industry switched to a lower wavelength, research efforts focussed to increase the NA of the systems operating at that wavelength. DUV systems have been developed with a maximum NA of 0.8 and for 193 nm systems this was improved to a maximum of 0.93. For the current state-of-the-art 193 nm systems, an even higher NA can be obtained by using immersion lithography. Here, the air gap between the final lens and wafer is replaced with a liquid medium that has a refractive index greater than one (see equation 1.1). 193 nm immersion lithography is able to obtain a NA value of 1.35. For the first EUV systems that are operational, in test environments NA’s of 0.32 are reported [7].

Decreasing the value of $k_1$

Industry has progressed in time and found ways to decrease the $k_1$ values from 0.7 for ”g-line” (436 nm) lithography systems to values close to 0.30 for current processes at 193 nm. Double exposure techniques, where a photoresist is exposed twice to a lithography step, have added the capability to divide $k_1$ values by two, although patterning costs are doubled. Using this double exposure technique $k_1$ values down to 0.22 can be achieved [11]. Improvements in processing technology have facilitated the reduction in $k_1$ factors, along with more complex photomasks. However, also improvements in resist materials themselves and the use of additional assist layers, such as bottom antireflective coatings have contributed.

The current state-of-the-art lithography systems of ASML (the market leader in photolithography systems) operating at 193 nm, are able to obtain a resolution of 32 nm, when a NA of 1.35 and k1 of 0.22 is used (see equation 1.1). Reports on the EUV systems of ASML mention that a resolution of 16 nm can be achieved, which is sufficient to move to technology nodes below 32 nm. However, due to production issues these systems are not yet ready to be introduced to standard production lines. This means that for now 193 nm lithography remains the working horse to produce patterns at the 32 nm technology. More importantly, to keep up with Moore’s law the 193 nm systems also have to be used to reach the next technology node. The state-of-the-art systems however are limited to 45 nm if single exposures are used, so to reach the next technology node additional techniques have to be employed to extend the limits of optical lithography to the next node. A technique that is capable to do this isSpacer-Defined Double Patterning (SDDP).
1.4 Spacer-Defined Double Patterning

As discussed previously, lithography proved to be the biggest roadblock in keeping up with Moore’s law. Lithographic systems operating at 13.5 nm will be able to take that hurdle but they are not yet feasible. Therefore in the meantime, 193 nm lithography has to suffice and new technologies have to be used complementary to lithography to keep improving resolution and keep pace with Moore’s law. Spacer-Defined Double Patterning is such a technique that can be used to extend the limits of optical lithography [12]. A standard processing scheme for SDDP [3, 13], that also illustrates the basic concept, is displayed in figure 1.6.

![Figure 1.6](image.png)

**Figure 1.6** A conventional SDDP process scheme using a photoresist (orange) on top of hardmask (purple). The spacer (green) is deposited on top of the hard mask and the spacer sidewalls are utilized as a mask to etch patterns in the target layer (light grey).

The SDDP process starts with the application of a photoresist layer (orange) on top of the hard mask layer (purple). The hard mask is necessary since the polymer resist typically cannot withstand the temperatures needed during the deposition of the spacer material (green). Optical lithography or EBL can now be used to pattern the photoresist after which this pattern is transferred into the hard mask by an anisotropic etch. Next, a uniform and conformal spacer film is deposited on top of the patterns present in the hardmask, after which a second anisotropic etch and a hard mask removal step will be used to obtain a pattern based on the remaining sidewalls of the deposited spacer material. Now this pattern can be used as a mask to create the desired structures in the target layer. The half-pitch is reduced using this SDDP processing scheme as can clearly be seen by comparing step 4 and 7 of figure 1.6.

A conventional SDDP process involves a significant amount of processing steps, especially when additional films (such as antireflective coatings and buffer layers [3]) are utilized in order to obtain a better processing result. Since the amount of steps needed is directly related to the costs, the industry is constantly looking for techniques to reduce the number of processing steps.

With Direct-SDDP (D-SDDP) a few processing steps can be omitted. Figure 1.7 depicts the processing steps in a D-SDDP scheme.

In D-SDDP, the spacer material is deposited directly on top of the patterned photoresist, eliminating the deposition of the hard mask layer from the processing scheme and thus reducing costs. Another advantage of eliminating several processing steps is that in essence the chance of processing faults is reduced, which is beneficial for the accuracy that can be obtained. To execute a D-SDDP process the deposition of spacer material at relatively low temperatures (typically < 150 °C) is required, since the polymer resist layer cannot withstand higher processing temperatures.
In nano-fabrication at the current and future technology nodes, a deposition technique with nanometer control of the spacer thickness is desirable. At these technology nodes, a variation in spacer thickness of several nanometers can possibly affect further processing steps and in the end even the behavior of a device. Atomic layer deposition (ALD) is a technique that is suited for this objective as will be described in the next section.

1.5 Atomic Layer Deposition

Atomic Layer Deposition (ALD) is a technique for depositing high quality thin films with excellent control over the film thickness. Moreover, it has the ability to deposit uniformly over large wafer areas and conformally in non-planar structures. ALD has the possibility to control material properties on the atomic level, resulting in thin films of excellent quality [14, 15]. The concept of ALD is that thin films are deposited layer-by-layer by repeatedly executing two subsequent half-cycles. Each half cycle consists of self-limiting surface reaction, leading to a sub-nanometer control during deposition. Figure 1.8 illustrates the main principles of ALD.

As shown in figure 1.8, each half-cycle consists of a dosing and a purge step. In the first half cycle a precursor is dosed and adsorption of precursor molecules on the available surface groups takes place. The surface reactions are self-limiting, so after this a purge step is used to remove the volatile reaction products and the excess of precursor molecules from the reactor. The second half cycle starts again with a self limiting surface reaction, the surface is now exposed to a reactant that reacts with the adsorbed precursor. The half cycle is completed by another purge step to remove the volatile reaction by-products and the excess of reactant dosed. After one ALD cycle, typically a sub-monolayer of material is deposited and the surface groups are again similar to the ones at the start of the cycle. Now, the cycle can be repeated to eventually obtain a film with the thickness targeted.

ALD processes can be categorized in thermal ALD and Energy-Enhanced ALD (EE-ALD) processes. With thermal ALD, the reactant is a gas or vapor such as \( \text{O}_2 \) or \( \text{H}_2\text{O} \) and the surface reactions are driven by thermal energy obtained by heating the substrate. EE-ALD can refer to two types of processes, namely plasma-assisted ALD and ozone ALD. In both cases the reactant is "energy enhanced" by supplying power to it and generating more chemically reactive fragments (e.g. \( \text{O}_3 \)-radicals and \( \text{O}_3 \)). Plasma-assisted ALD uses radicals and ions created in a plasma in the reactant step, ozone ALD uses the reactive \( \text{O}_3 \) molecule. EE-ALD
Figure 1.8 Schematic representation of thermal ALD and plasma-assisted ALD. The first half cycle consist of an exposure to a precursor gas. In the second half cycle the surface is exposed to a reactant gas or to species generated by a plasma.
offers several merits for the deposition of ultra-thin films over thermal ALD and other vapor phase deposition techniques, the most important one being the high reactivity of the reactant species on the deposition surface during the EE-ALD process \[14, 15\]. This allows for uniform film depositions of excellent quality even at temperatures below 100 °C, making it an ideal deposition technique for D-SDDP.

1.6 Project Goals and Thesis Outline

So far this chapter has provided a background, steadily zooming in on the main subject of this thesis: Direct Spacer-Defined Double Patterning (D-SDDP). Double patterning techniques, including SDDP, but also double exposure techniques \[12\], are considered necessary to produce semiconductor structures for the 22 nm technology node using 193 nm lithography. There are even reports on using two consecutive SDDP processing schemes (quadruple spacer patterning) to already produce features at a 15 nm half pitch \[16\]. However, literature in this field is typically very focussed on demonstrating successful implementation of a SDDP technique \[12, 13, 16, 17\], rather than addressing specific processing issues that were encountered. This work will therefore focus on the realization of a D-SDDP process and on providing an overview of the significant specifications of each processing step and the challenges that are encountered. The main goal of this project is as follows:

Project Goal

- The realization and the exploration of the Direct Spacer-Defined Double Patterning process using energy-enhanced atomic layer deposition.

To realize a complete D-SDDP process as depicted in figure 1.7, multiple tools available in the Nanolab @ TU/e cleanroom will be used. Electron Beam Lithography (EBL), a patterning technique well suited for research and development since no photomask is required, will be used to obtain the starting pattern in the resist layer. Additionally, EBL has the potential to pattern smaller features compared to the optical lithography tools available in the cleanroom. This will allow for a demonstration of a D-SDDP process closest to the technology nodes (< 32 nm) where SDDP is currently employed to move beyond the limits of 193 nm lithography. For the deposition of the spacer material during the D-SDDP process, EE-ALD processes will be developed and employed. The development of the EE-ALD processes (i.e. ozone-based and plasma-assisted ALD) for the deposition of two spacer materials (Al₂O₃ and SiO₂) and the characterization of the films deposited using these processes are essential for a successful demonstration of a D-SDDP process. Therefore, the process development and film characterization are interesting and important topics to study. The ozone processes will have to be developed since an ozone generator was only recently installed on the ALD tool in the cleanroom. The plasma-assisted ALD processes for Al₂O₃ and SiO₂ are already available within the PMP group, however they have to be tuned to match the specifications needed for D-SDDP.

For the execution of the anisotropic etch step in the D-SDDP process, two different etching methods will be utilized, namely Ion Milling (IM) and Reactive Ion Etching (RIE). The resist removal step is executed using a plasma stripping process. Both the employment of the etching methods and the plasma stripping process are explorative in nature, since no practical knowledge of these techniques is present within the PMP group so far. It should be clear that many consecutive processing steps have to be integrated in to one D-SDDP process. Therefore, before a successful realization of a D-SDDP process, knowledge
on each individual processing step has to be gained. This is captured in the sub-goals of this thesis as follows, which can be divided into two main categories.

**Sub-goals**

- A comprehensive study of two energy-enhanced ALD techniques, including:
  - A evaluation of the merits of EE-ALD regarding the use in D-SDDP
  - The development of EE-ALD processes for deposition of different spacer materials
  - The characterization of the spacer films deposited by EE-ALD
  - A comparison of the spacer films and the EE-ALD processes

- Integration of all D-SDDP processing steps, including:
  - The obtainment of knowledge on each individual processing step
  - The identification of issues and challenges in the realization of D-SDDP

The structure of this thesis will be as follows. EE-ALD will be introduced in chapter 2. This chapter will also discuss the experimental setup used for EE-ALD and some preliminary experiments using the $O_3$ generator, of which the outcomes can be used for the development of $O_3$ ALD processes. Chapter 3 will discuss this development as well as the further development of the plasma-assisted ALD processes both at room temperature. The EE-ALD processes developed will be used to deposit $Al_2O_3$ and $SiO_2$ spacer films which will also be characterized in this chapter. Chapter 4 will continue with discussing all the individual processing steps and the integration of all the steps into a complete D-SDDP process. Furthermore, this chapter will show whether or not a D-SDDP process was realized successfully. The main project goal is thus extensively discussed in chapter 4. Finally, chapter 5 will return on the goals presented in this section and present the final conclusions and an outlook.

Enjoy reading!
Chapter 2

Experimental Setup for Energy-Enhanced ALD

This chapter is intended to provide a detailed background of EE-ALD. This technique will be compared with different deposition techniques including thermal ALD. Secondly, section 2.2 will contain a detailed description of the experimental setup and the basic operating principles of the plasma source and the ozone generator. Thirdly, section 2.3 will discuss some initial experiments regarding the optimization of the $O_3$ generator. Section 2.4 will give a short summary and highlight the findings that are of importance for future chapters.

2.1 Introduction

Miniaturization in the semiconductor industry has led to the requirement for atomic level control of thin film thickness during deposition. This idea was already expressed in section 1.2. Since the miniaturization entered the realm of nano-manufacturing, uniform and conformal film growth is in some cases essential. No other thin film deposition technique can approach the uniformity and conformality achieved by ALD, especially on high aspect ratio structures that are very common nowadays in the semiconductor industry [14]. Furthermore, the International Technology Roadmap for Semiconductors (ITRS) has recognized the importance of ALD for future applications. ITRS included this technique in the technology outlook for high dielectric constant gate oxides in transistor structures [2]. In addition, ALD has also met challenging requirements in other areas including the deposition of high quality dielectrics to fabricate trench capacitors for DRAM, illustrating the necessity of ALD in future applications [18, 19]. The ability of this technique to reach excellent uniformity, conformality and control at the atomic level originates from the sequentially executed self-limiting surface reactions as discussed in section 1.5. As a consequence of these self-limiting reactions the ALD film growth is not flux-dependent as long as sufficient precursor and reactant species are dosed and purge times between the doses are sufficiently long. Other depositions techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD) are flux-dependent and thus these techniques have more difficulty in achieving conformal growth [15].

As a consequence, ALD is the deposition technique of choice for applications that fall in the categorie of nano-manufacturing. In the last decades, ALD processes have been developed for many kinds of solid inorganic materials. From all different types of inorganic materials grown by ALD, oxides have been the type most often investigated [20]. ALD of oxides is quite straightforward contrary to e.g. catalytic metals [14]. Also in this thesis, two oxides will be investigated namely $Al_2O_3$ and $SiO_2$. Furthermore, the temperature at which these oxides are
deposited is of importance in this thesis, since the oxide layer will be deposited on a polymer
resist that cannot withstand relatively high processing temperatures. Traditionally, thermal ALD is
used for the deposition of oxides and typically \( H_2O \) vapor is used as reactant. However, typical
deposition temperatures are above 150\(^\circ\)C, mostly because higher temperatures lead to a increased
reactivity of the \( H_2O \) molecules with the substrate, since there is more thermal energy available
to drive the self-limiting surface reactions [21]. Deposition temperatures above 150 \(^\circ\)C can not be
used during the realization of a D-SDDP process, since the polymer resist that is used can not withstand
these temperatures. In the case of thermal ALD processes based on \( H_2O \) as the oxygen reactant, a second problem arises
at low temperatures namely the purging of \( H_2O \) [22]. Water has a tendency to stick to the
reactor or substrate surfaces especially at low temperatures. As a consequence, the necessary
purge time can increase drastically if the \( H_2O \) can be completely removed out of the reaction
chamber at all [23]. If \( H_2O \) molecules remain present in the reaction chamber during the
precursor dose, these molecules can cause unwanted CVD-like reactions [22].

It can thus be stated that thermal ALD is not the ideal candidate for depositions at low
temperatures, however EE-ALD can provide the right circumstances for growth at these low
temperatures. EE-ALD offers several benefits for the deposition of ultra-thin films over thermal
ALD and other vapor-phase deposition techniques, facilitated by the higher reactivity of the reactant species on the deposition surface during the EE-ALD process. This allows for
more freedom in processing conditions and for a wider range of material properties [15, 24].
Furthermore, the higher reactivity opens up possibilities in the precursor selection, EE-ALD can for instance be used to react with more stable metal precursors, such as \( \beta \)-diketonates [25]. The energy enhanced techniques used in this thesis are plasma-assisted ALD using an \( O_2 \) plasma and ozone ALD. These energy enhanced processes also provide advantages in process throughput compared to thermal ALD using \( H_2O \), since both processes employ very volatile species, which reduces the necessary purge times. Both techniques can thus provide the reactivity and throughput needed at low temperature processing, however there are also several differences between the two that should be addressed.

The first difference between ozone and plasma-assisted ALD is the complexity of the chemistry in the reaction chamber. A plasma contains many species such as electrons, ions, radicals and photons which can possibly all interact with each other but also with the surface. In plasma processing a plasma sheath is formed between the plasma and the substrate, which accelerates ions towards the substrate surface [15]. This ion bombardment results in additional energy that is provided to the deposition surface. This energy is locally dissipated by the surface species and can enhance surface reaction rates and processes such as surface diffusion [26]. However, the additional energy provided to the surface by ion bombardment can also result in damage [27]. The extent of plasma induced damage is determined by the specific implementation of the plasma source and the processing conditions. By altering processing conditions it is possible to control the level of ion bombardment. Chapter 4 will return on this subject, since it is crucial not to inflict any damage to the underlying film in a D-SDDP process. Next to ions also excited species can be created due to electron collisions, these species can emit in the ultraviolet region of the spectrum (resulting in vacuum ultraviolet photons) which can be sufficiently energetic to influence and induce (unfavorable) processes at surfaces or within thin films [15]. This should be kept in mind especially since resist layers can undergo significant changes due to radiation [28]. In ozone-based ALD only the surface chemistry with \( O_3 \) molecules will play a role. Ions and high energetic photons will be absent, since \( O_3 \) is generated remotely after which the ozone molecules are transported to the reactor. This might open up better processing conditions for depositions on photoresist layers.
The second difference between ozone and plasma-assisted ALD concerns the reactivity of the reactant. Plasma species and ozone molecules can both be used in the ALD surface reactions. The plasma species, however, are more reactive and can therefore in some cases be more effective to drive the surface chemistry in an ALD process than ozone [15]. This will also be demonstrated in chapter 3.

In plasma-assisted ALD, reactivity at the surface can often be provided almost independent of substrate conditions (e.g. temperature and material) [15]. Despite the high reactivity, the heat flux to the surface is low, which allows for low temperature processing. Also the energy provided to the surface by ion bombardment can contribute to the increased reactivity at the surface compared to other ALD techniques. In the case of $O_3$ ALD the reactivity is not completely independent of substrate conditions. Experiments discussed in chapter 3, have shown that in the case of $Al_2O_3$, the number of deposited Al atoms increases with increasing substrate temperature, illustrating a dependency of the reactivity on substrate temperature which is not observed for plasma-assisted ALD processes.

The next topic that should be addressed is the loss of the reactants due to surface recombination in EE-ALD. It has been shown that $O_3$ molecules can decompose or recombine at the surface of some catalytic materials (e.g. $MnO_2$ and $Rh_2O_3$), this can prevent $O_3$ molecules from reaching specific surface sites [29]. However, Knoops et al. show that ozone typically has a very low loss probability on most materials such as alumina and steel, especially at room temperature [30]. Therefore, they state that achieving conformality for ozone-based processes of most materials should be relatively easy. The effects of loss are however not negligible for high aspect ratio (HAR) structures.

Compared to ozone-based ALD, the recombination probabilities for the reactive species in a plasma-assisted ALD process are typically several orders of magnitude larger [30]. When plasma-assisted ALD is employed for deposition in HAR structures, radicals driving the essential surface reactions can be lost before reaching all surface sites located in the trenches, leading to non-conformal depositions. In specific cases, ozone based ALD might therefore offer some more possibilities for depositing in HAR structures than plasma-assisted ALD due to a lower loss probability of $O_3$.

A final comment in comparing ozone and plasma-assisted ALD should be made about the implementation. It is likely that the implementation of ozone ALD can be considered easier since $O_3$ can be created remotely after which only a single line has to be connected, feeding $O_3$ into the reaction chamber. Extreme modifications on existing setups are thus not necessary, consequently keeping costs relatively low, which can possibly also be an important consideration in scaling up ALD processes for industrial uses. Integrating a plasma source in an existing tool will typically require significant modifications to the setup, furthermore the chamber design in plasma-assisted ALD is far more critical, making plasma-assisted ALD a process harder to implement. Although the implementation of plasma-assisted ALD might be more difficult, the distinct advantages as noted in the discussion above, make it an important deposition tool in industry [31]. There is however also the possibility for radical-enhanced ALD, which is a technique that uses a remote plasma source to generate radicals that are then transported to the reaction chamber. The implementation of this technique is very similar to ozone-based ALD, however the radical losses in the lines to the reaction chamber are far greater than for ozone.

So far many considerations and merits of thermal ALD and EE-ALD have been discussed. Table 2.1 captures this discussion in a short visual summary.

This table illustrates that due to the increased reactivity at lower temperatures, EE-ALD is the ideal candidate for depositing spacer materials with a nanometer control on top of polymer photoresist layers in a D-SDDP process. EE-ALD is able to acces a parameter
Table 2.1 A visual summary of the comparison between thermal ALD and both EE-ALD techniques. Several characteristics of the deposition technique are ranked on a scale from: – (non-ideal) to ++ (excellent).

<table>
<thead>
<tr>
<th></th>
<th>Thermal ALD</th>
<th>(O_3) ALD</th>
<th>Plasma-assisted ALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactivity</td>
<td>0</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Choice of reactants</td>
<td>+</td>
<td>N/A</td>
<td>++</td>
</tr>
<tr>
<td>Easy purging at low temperature</td>
<td>-</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Process induced damage</td>
<td>0</td>
<td>0</td>
<td>(-)</td>
</tr>
<tr>
<td>Control over film properties</td>
<td>0</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Conformality</td>
<td>++</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Uniformity</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Integration</td>
<td>+</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Post-/pre-deposition treatment</td>
<td>0</td>
<td>0/+</td>
<td>++</td>
</tr>
</tbody>
</table>

space in materials processing which is not easily accessible with strictly chemical methods. Although process parameters in some cases have to be carefully selected in order to not damage underlying materials. The next section will continue with the details of the setup that is used to implement EE-ALD processes.

2.2 Experimental Setup

In this project, all EE-ALD depositions were executed in the FlexAL system of Oxford Instruments. Within the PMP-group a first and second generation FlexAL system, i.e. mark 1 and mark 2, is available, the reactors are basically identical, apart from slight differences in the delivery system responsible for precursor injection into the reaction chamber. To be conscientious in future sections with experimental data it will be stated which reactor was used. The FlexAL reactor of Oxford Instruments is a remote plasma reactor equipped with an ICP source, that is also suited for thermal ALD. The reactor has a load lock and is capable of handling substrate sizes up to 200 mm in diameter. A schematic representation and a photo of the setup can be found in figure 2.1, it is noted that the loadlock is not depicted in the schematic.

The reactor consists of a main deposition chamber to which a pump unit, a plasma source, a ozone generator and a load lock are connected through gate valves. A heater is located in the center of the deposition chamber that can be used to heat the substrate up to 400 °C. The chamber wall temperature can be controlled separately between room temperature and a maximum temperature of 120 °C. The chamber temperature is equal to the substrate temperatures during all experiments, however if the substrate temperature exceeds the maximum temperature the chamber is set to 120 °C. The base pressure reached in the chamber is in the order of \(10^{-6}\) Torr, operating pressures are typically set between 10 and 250 mTorr. The pressure during a deposition is regulated by an automated pressure controller (APC), which controls the angle of the bottom butterfly valve between 0° (closed) and 90° (open).

Liquid and solid precursors can be delivered into the process chamber by fast ALD valves from precursor pots located in independently heated modules close to the deposition chamber. The precursor delivery module and delivery lines from the module to the process chamber are heated (90 °C) to prevent condensation in the delivery lines. The precursor pots are connected to the same delivery line used to inject the precursors into the chamber, therefore this line
is continuously purged with argon (100 sccm), also during the dosing of the precursor. The precursors and also the $O_3$ are injected into the deposition chamber above the center of the substrate stage, just below the gate valve to the plasma source. As displayed in figure 2.1 diagnostic ports are present to allow for in-situ ellipsometry at 70 $^\circ$ to monitor thickness and film optical constants during or directly after deposition. An additional analytical port positioned above the wafer may be used for residual gas analysis using a quadruple mass spectrometer (MKS Vision 2000C).

### 2.2.1 Plasma-assisted ALD

In plasma-assisted ALD different plasma sources can be used [15]. Essentially all sources couple power into a gas, to generate the cold plasmas typically used for materials processing [32]. The coupling of power into a neutral gas is facilitated by electromagnetic fields. Any volume of a neutral gas always contains a few electrons, e.g. from cosmic radiation. These free charge carriers are accelerated by the electromagnetic fields and newly charged particles may be created when these charge carriers collide with atoms and molecules in the gas or with the surfaces of the electrodes. This leads to an avalanche of charged particles that is eventually balanced by charge carrier losses, so that a steady-state plasma develops.

The plasma utilized in the FlexAL is generated by a inductively coupled plasma (ICP) source operating at a pressure of typically 25 mTorr and power of typically 200 W. A schematic of an ICP source is displayed in figure 2.2, accompanied with a photograph of the ICP source.
on the FlexAL. In an ICP source, the plasma is ignited and sustained by the acceleration of free electrons by an electric field induced by the time-varying magnetic field produced by the alternating current through the coils [33]. The ICP source used on the FlexAL can deliver up to 600 W of radio frequency power (13.56 MHz) and is connected the coil through an automated matching network. The source consists of a three-turn water-cooled copper coil wrapped around a 65 mm alumina plasma tube. A wide range of gases (and mixtures thereof) can be connected to a common plasma source line, e.g. $H_2$, $N_2$, $O_2$, $NH_3$. In this thesis only $O_2$ will be used. The dominant radical and ion producing reactions that take place in an $O_2$ plasma at 25 mTorr are displayed in equation 2.1 and 2.2 [34].

\[ e + O_2 \rightarrow 2O + e \] (2.1)  
\[ e + O_2 \rightarrow O + O^* + e \] (2.2)

$O^*$ represents an excited state of atomic oxygen. If the $O_2$ plasma is generated at a higher pressure a third reaction displayed in equation 2.3, will start to play a role.

\[ e + O_2 \rightarrow O + O^- \] (2.3)

The plasma-generated radicals are used at the substrate surface in the second half cycle of the ALD process to regenerate the surface for the next precursor adsorption step (see figure 1.8).

### 2.2.2 $O_3$ ALD

Ozone can be generated in several ways, the main principles are UV-light [35], corona discharge [36, 37] and dielectric barrier discharge (DBD) [36, 37]. Ozone generation by dielectric barrier discharge is most commonly used because of greater sustainability of the generator, higher ozone production and higher cost effectiveness. The ozone generator attached to the
2.2 Experimental Setup

FlexAL also uses a DBD to generate $O_3$ molecules at atmospheric pressure. DBDs represent self-sustaining non-equilibrium electrical gas discharges between two electrodes. Typical configurations for a DBD are displayed in figure 2.3.

![Diagram of common dielectric barrier discharge configurations.](image)

**Figure 2.3** Common dielectric barrier discharge configurations. Industrial ozone generators typically use the cylindrical configuration.

DBDs are characterized by the presence of an insulating dielectric layer in the discharge gap. DBDs require alternating voltages for their operation since the dielectric barrier (being an insulator) cannot pass a dc current. To transport current in the discharge gap the electric field has to be high enough to cause electrical breakdown in the gas. During this breakdown, a growing electron avalanche develops into a streamer [38]. The streamer connects the two electrodes and charge accumulates on the dielectric surface which compensates the external voltage and ends the discharge. A new discharge will now occur when the voltage is reversed [37]. At atmospheric pressure a large number of microdischarges can be observed in the discharge gap. The gas in the gap is not completely ionized and serves as a reservoir to absorb the energy dissipated in the microdischarges and to collect and transport the long-lived species created in the plasma. The long lived species that are of interest here are ozone molecules.

Ozone can be generated by feeding oxygen gas into the discharge gap. The first step towards ozone generation is the dissociation of the $O_2$ molecules by impact of electrons created in the avalanche. See equations 2.4 and 2.5. Ozone is then formed in a three-body reaction involving $O$ and $O_2$, as displayed in equation 2.6.

$$e^- + O_2 \rightarrow O_2^+ + 2e^-$$  \hspace{1cm} (2.4)

$$e^- + O_2 \rightarrow e + O + O$$ \hspace{1cm} (2.5)

$$O + O_2 + M \rightarrow O_3 + M$$ \hspace{1cm} (2.6)

$M$ is a third collision partner, e.g., $O_2$, $O_3$ or $O$. The timescale of this last reaction to occur at atmospheric pressure is a few microseconds. The reactions displayed here are valid for a ozone generator where the gas inlet is pure oxygen. When air is used, $N_2$ molecules will also play a role in the chemistry, however this is not the case in our setup. The ozone generator is working at approximately atmospheric pressure, because of this pressure there are many third collision partners (see equation 2.6) present in the dielectric gap and hence $O_3$ generation is most effective. Although the timescale is only microseconds, competing side reactions come
into play, as described by equations 2.7, 2.8, 2.9 and 2.10.

$$e^- + O_3 \rightarrow e^- + O_2 + O$$ \hspace{1cm} (2.7)

$$O + O + M \rightarrow O_2 + M$$ \hspace{1cm} (2.8)

$$O + O_3 \rightarrow 2O_2$$ \hspace{1cm} (2.9)

$$O_3 + O_2 \rightarrow 2O_2 + O$$ \hspace{1cm} (2.10)

These undesired but unavoidable side reactions pose an limit on the degree of dissociation, the attainable $O$ concentration and finally on the maximum attainable ozone concentration. It is reported that ozone concentration can be increased by mixing $N_2$ in the discharge \[39\]. Simek and Clupek have described the chemistry in this situation \[40\].

The ozone utilized in the FlexAL is generated by an Atlas 25 Ozone Generator from Absolute ozone. A schematic of this ozone generator is displayed in figure 2.4 accompanied with a photograph of the $O_3$ generator. The generator has a variable power source with a maximum power consumption of 300 W. During an ALD process, the generator will be on continuously. Additionally, the $O_3$ generator should warm-up for approximately 15 minutes to reach a stable ozone output. Oxygen is fed into the generator at a pressure of 1.5 mbar (1.1 Torr) and a flow of 250 sccm, a gas mixture of oxygen and ozone leaves the generator. This mixture above atmospheric pressure, is led to an ozone destruct, after which it flows into the cleanroom exhaust lines. During the exposure of the reactant in the ALD cycle, the ALD valve inside the ozone generator is opened and an $O_3/O_2$ mixture will pass the needle valve and enter the delivery line to the reaction chamber. The stainless steel delivery line is approximately 1 m in length on the FlexAL mark 1 and 40 cm on the FlexAL mark 2. Just before entering the deposition chamber the $O_3/O_2$ mixture has to pass another fast ALD valve (also illustrated in figure 2.1). According to the manufacturer of the ozone generator, the ozone concentration of the output mixture is 12% by weight. Appendix A displays all performance data of the $O_3$ generator that was supplied by the manufacturer.

When using the reactor for ozone ALD, the top gate valve (in figure 2.1) is closed, isolating the ICP source from the reactor chamber and $O_3$ molecules are directly injected into the chamber.

2.3 Start-up Experiments and Results

Since the ozone ALD process is new within the PMP-group, this section will discuss some initial experiments that are essential in optimizing ozone ALD processes. Section 2.3.1 will start on the optimization of the ozone output. Section 2.3.2 will continue on the optimal operating pressure during an $O_3$ exposure step.

2.3.1 Optimization of $O_3$ generation

For the development of optimal ozone ALD processes first the $O_3$ output of the ozone generator has to be optimized, so that the duration of the surface reactions during the $O_3$ exposure can be minimized. The optimization experiments were carried out using a quadruple mass spectrometer (QMS) that is attached to the FlexAL mark 1, at a substrate temperature of 200 °C and a chamber temperature of 120 °C. A MKS mass-spectrometer was used to monitor the signals related to mass-to-charge (m/z) ratios of 16, 32 and 48, corresponding to signals
2.3 Start-up Experiments and Results

Figure 2.4 On the left side of this figure a schematic representation of the $O_3$ generator is displayed, the right side shows a photograph of the generator in the cleanroom.

originating from $O$, $O_2$ and $O_3$. The goal is to maximize the amount of ozone that enters the reaction chamber. This can not be realized by studying the absolute value of a signal related to $O_3$, because the behavior of the filament used to ionize species entering the QMS varies with time. However, by looking at signal ratios, of an ozone related signal ($m/z = 48$) to another signal, a simple optimization of the ozone output can be performed at a constant pressures. The signal ratio of $\frac{m/z = 48}{m/z = 32}$, referred to as $(O_3/O_2)$ and the signal ratio of $\frac{m/z = 48}{m/z = 16}$, denoted by $(O_3/O)$, will be studied. The setting resulting in the highest ratios will be used in further processing.

The $O_3$ generator has several variable parameters that might affect the ozone output namely: inlet pressure, inlet flow, position of needle valve and the power supplied to the generator. Changing the first three parameters within the limitations provided by the supplier of the generator, showed very little influence on the ratios observed. Therefore it was chosen to use typical setting provided by Oxford Instruments namely: 1.5 mbar, a flow of 250 sccm, and the position of the needle valve was set at 4. The power supplied to the generator however turned out to be an important parameter. The power was varied between 0 and 100% of 300 W. The $(O_3/O_2)$ and $(O_3/O)$ ratios as a function of power are displayed in figure 2.5.

Before the start of the experiments the $O_3$ generator was warmed-up for 15 minutes. The $(O_3/O_2)$ and $(O_3/O)$ signal ratios were monitored while slowly increasing the power and later again when decreasing the power. Although absolute values changed, both experimental series show a clear maximum at a power percentage of 50. In future experiments on both systems, FlexAL mark 1 and mark 2, the $O_3$ generator will be set to operate at 150 W.

2.3.2 Operating Pressure of $O_3$ ALD

Now that the output of the generator is optimized the next step is using ozone in an ALD process. As explained in section 1.5 an ALD process consists of four steps: the precursor dosing, the precursor purge, the reactant dosing and the reactant purge. The precursor and reactant dosing have to be sufficiently long enough so that all surface sites are covered. The
Figure 2.5 Power optimization curve for \( \text{O}_3 \) generation based on the ratio of QMS signals of \( \frac{m/z = 48}{m/z = 32} \), referred to as \( \text{(O}_3/\text{O}_2) \) and \( \frac{m/z = 48}{m/z = 16} \), denoted by \( \text{(O}_3/\text{O}) \).

Purge steps have to be long enough to ensure no CVD like processes occur. The first step in developing ozone ALD processes is to determine the typical ALD saturation curves. The saturation curves show the growth per cycle as a function of step time for all four ALD steps. The saturation curve that is of interest here, is the curve for the ozone exposure step. Obviously, when no ozone is dosed the GPC of any process will be zero. The exposure conditions of the ozone exposure step have to be optimized in order to reach a saturated GPC as quickly as possible. This is achieved by increasing the pressure in the chamber during the exposure step, so that the flux of \( \text{O}_3 \) molecules towards the substrate is as large as possible. Therefore, the optimal operating pressure is for the \( \text{O}_3 \) exposure is 250 mTorr, since this is the maximum processing pressure allowed in the FlexAL system because of a software limitation.

It might however be possible that during lower processing pressures, the flow of \( \text{O}_3 \) is still so large that no significant effect in the saturation curve can be observed. However initial, experiments have clearly shown that indeed this operating pressure during the \( \text{O}_3 \) exposure seriously affects saturation performance as expected based on the reasoning above. Appendix B displays a result of these initial experiments that shows the effect of operating pressure in the \( \text{O}_3 \) exposure step during an ozone ALD process.

In chapter 3 several \( \text{O}_3 \) ALD process will be developed and a full discussion is presented based on the saturation curves of those processes. However it is noted that all future ozone ALD experiments are executed with an \( \text{O}_3 \) exposure step at 250 mTorr.
2.4 Summary

Ozone-based ALD processes, using the newly installed Atlas ozone generator, have to be successfully developed before the implementation of such a spacer deposition technique is possible in a D-SDDP process. This chapter has revealed some important insights for achieving this objective. Section 2.3.1 showed that the operating power of the generator should be set to 150 $W$ in order to obtain the highest amount of $O_3$ in the reaction chamber. Furthermore, section 2.3.2 clarified that an $O_3$ exposure steps should be executed at 250 $mTorr$ to obtain the largest $O_3$ flux to the substrate surface, which results in a faster saturation of the $O_3$ exposure step. In the following chapter these settings will be adopted to further develop the EE-ALD processes used to deposit spacers for the SDDP process.
Chapter 3

EE-ALD of $Al_2O_3$ and $SiO_2$

This chapter will start with an introduction that provides some background on two candidate spacer materials ($Al_2O_3$ and $SiO_2$) to be used for the D-SDDP process. Section 3.2 will describe relevant additional details on the experimental setup which was extensively discussed in 2. Section 3.3 will discuss both the development of the EE-ALD processes of $Al_2O_3$ and $SiO_2$ and the characterization of the deposited films will be described. At the end of this chapter (section 3.4) the conclusions will be presented which are of importance for the integration of the spacer films in a SDDP process as will be described in chapter 4.

3.1 Introduction

The goal of this project was to realize a D-SDDP process. To attain this goal, EE-ALD techniques were required in order to deposit films at low temperature. Chapter 2 extensively described EE-ALD and its distinct advantages. It became clear that for realizing a D-SDDP process at a nanometer scale, ALD is the ideal candidate for the job. It can offer conformal growth with excellent control of thickness, which is required for nano-manufacturing. Secondly, the high reactivity of the ozone molecules and the oxygen radicals, facilitate the deposition of thin films with excellent properties and at relatively high growth rates, at low temperatures. The latter is needed since the spacers have to be deposited directly on top of a polymer photoresist.

The films that were deposited using EE-ALD have to act as a spacer layer in the D-SDDP process. In order to realize such a process successfully, the spacer layer has to have a certain mechanical strength, since these structures have to withstand several processing steps as shown in chapter 1 (figure 1.7). However, it is also important that the spacer material allows for all further processing steps to be executed. The third demand has a more practical origin, i.e. the process has to be available in the cleanroom. An objective of this work was to obtain a proof of concept for the full D-SDDP process during which all processing steps will be explored and difficulties/challenges will be mapped. In order to achieve this during a one-year project, ALD precursors that are already available have to be utilized. By doing so, existing ALD processes can be tuned to meet the requirements for application in a D-SDDP process and new ALD processes can be quickly developed. To summarize, at this stage the selection of the spacer material will be based on the following criteria:

- Deposition using EE-ALD Techniques
- Mechanical Strength/Stability
Chapter 3 EE-ALD of Al2O3 and SiO2

- Processing Possibilities
- Availability

In regard to the processing possibilities, in the ideal case processing should not only be possible, but also accurate, so that the features sizes that were aimed for can be obtained exactly. However, several processing steps will be new for our group and some combinations of material and processing technique are entirely new in the TU/e cleanroom. It is therefore hard to predict if a material can be processed with high accuracy. Therefore the selection criterium is just that the material has processing possibilities.

Two materials were selected based on the criteria just presented, namely Al2O3 and SiO2. In this chapter the EE-ALD processes for Al2O3 and SiO2 will be fully developed and characterized, after which they can be integrated in a D-SDDP process in chapter 4. Before continuing with the experimental setup however, a short background on Al2O3 and SiO2 will be provided in the next subsection.

Candidate Spacer Materials

Al2O3 is of interest for a wide range of applications, because of its unique material properties [41]. This material, has a relative high density (∼3.1 gcm⁻³), which contributes to its use as a wear resistive coating in for example microelectrochemical systems [42]. Additionally, its high density is exploited in moisture and gas permeation barriers [43, 44], that are of interest in emerging technologies involving organic electrical devices (e.g. flexible organic light emitting diodes (F-OLEDs)). Degradation of the OLED device has to be prevented by moisture permeation barriers. In chapter 4 the barrier properties of Al2O3 will be encountered. Probably the most investigated material properties of Al2O3 however, are its dielectric properties. Being a high-k material, Al2O3 is of interest to the semiconductor industry as a gate oxide in MOS-FETS (see also section 1.2) or as capacitor dielectric in DRAM. Al2O3 can be used in these applications because it combines a high dielectric constant (k ∼ 9), a low leakage current and a high breakdown electric field due to its large band-gap (∼9 eV) [45, 46, 47]. Since Al2O3 is of importance in many industries including in the semiconductor industry, many deposition processes are well studied and it is shown that a wide processing window exist for Al2O3, in which good material properties can be obtained. This also holds for the (EE-)ALD processes of Al2O3, which moreover, can have high growth rates if the highly reactive TMA precursor is utilized [21, 22, 48, 49]. Furthermore, Al2O3 also illustrates a very good chemisorption and growth behavior on various substrates (including polymers) using ALD processes at low deposition temperatures [46, 50, 43].

SiO2 is the most widely used material in the semiconductor. Therefore, also a lot of knowledge is available on this material and the techniques used to process it including EE-ALD processes [51, 52]. SiO2 is the material that has driven the revolution in microelectronics in to the realm of nano-manufacturing. The properties of SiO2, which include excellent insulating properties (when the layer is sufficiently thick), a good dielectric constant (k ∼ 4), a large band gap (∼9 eV), a high melting point, and a native, low defect density interface with Si, are in large part responsible for this revolution. These properties namely ensured the operation of MOSFETs, where traditionally SiO2 was used as the gate oxide [53]. Furthermore, in other applications in microelectronics, e.g. DRAM technology, spacer-defined double patterning processes are already used that employ SiO2 as spacer material [3]. Finally, also SiO2 can be used as a gas an moisture permeation barrier [54, 55].

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3.2 Experimental Setup

The experimental data that will be discussed in this chapter are based on $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ films deposited in the FlexAL mark 2 reactor from Oxford Instruments. A remote $\text{O}_2$ plasma at 25 mTorr, powered by 200 W, was used during the oxidation step in both plasma ALD processes that will be discussed here. In the ozone ALD processes, $\text{O}_3$ generated by a ozone generator from Absolute Ozone is led into the reaction chamber through a stainless steel pipe of approximately 40 cm long. As discussed in chapter 2, the oxidation step during ozone ALD will be executed at 250 mTorr. SAM.24 ($\text{H}_2\text{Si}[\text{N}(\text{C}_2\text{H}_5)_2]^2$) and TMA ($\text{Al(CH}_3)_3$) both supplied by Air Liquide were used as precursors in the EE-ALD processes. Both precursors exhibit a relatively high vapor pressure [51], as can be seen in figure 3.1.

![Figure 3.1](image)

**Figure 3.1** Vapor pressure of the SAM.24 and TMA precursor used for EE-ALD of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$, respectively, displayed as a function of the temperature [51]. The figure also shows a chemical representation of the precursor molecules.

The SAM.24 precursor was held in a stainless steel bubbler heated to 70 °C, the bubbler is connected to a dosing line at 90 °C that is constantly purged with argon since the TMA bubbler is also connected to this line (more details were described in chapter 2). The TMA bubbler is heated to 40 °C. The precursors, which are both vapor-drawn, mixed with the continuous flow of argon through the delivery line, are introduced into the reaction chamber by ultrashort doses (20 – 80 ms) using fast ALD valves. During the plasma-assisted ALD processes an $\text{O}_2$ flow was continuously present (50 sccm). This was possible since no evidence was found for reactions between the used precursors and $\text{O}_2$ under the conditions used for processing [51, 21]. During process development for both materials the substrate temperature was varied between 25 and 300 °C. Film characterization is done on samples deposited at 25 °C since this temperature will be set as the standard temperature at which all D-SDDP process steps are executed. The introduction of chapter 4 will shortly return on this. All films were deposited on 1 x 1 inch substrates, cut from a 4 inch n-type c-Si (100) wafer.

During process development and film characterization in- and ex-situ spectroscopic ellipsometry (SE) is used to obtain the film thickness, and consequently the growth per cycle (GPC), and the refractive index of the film. This is done using a Cauchy optical model that is used to fit the obtained SE-data [56]. A Cauchy model is typically used for modeling films that are transparent in the visible spectrum and it can thus be used for modeling both $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$. SE measurements are done using a J.A. Woollam, Inc. M2000U in the range of 190 – 1000 nm. For further film characterization also ex-situ absorption Fourier Transform InfraRed (FTIR) measurements were performed using a Bruker Tensor 27 FT-IR spectrometer. This was done...
to obtain information about the film composition. Also RBS (Rutherford Backscattering Spectroscopy) is employed to obtain quantitative information on the film composition. RBS analysis is performed by Acctec B.V. [57]. The information on the film composition and data obtained by an in-situ Quadruple Mass Spectrometer (QMS) of MKS (model: MKS Vision 2000C) will be used to comment on the reaction mechanisms of the EE-ALD processes. QMS can be used to study the deposition process by probing the species in the reaction chamber. The FTIR and QMS analysis will be discussed at the end of section 3.3, first the process development will be discussed.

3.3 Results and Discussion

3.3.1 Process Development

The development of an ALD process typically starts by studying the saturation behavior of the four steps during a full ALD cycle. Saturation curves are used to find the operating conditions where only self-limiting surface reactions occur. As discussed in previous chapters: the precursor and reactant exposures have to be long enough to ensure that all available surface sites adsorb the precursor or react with the reactant; the purges have to be long enough to avoid CVD-like reactions between the reactant and precursor. Figure 3.2 and 3.3 show the saturation curves for the EE-ALD process for $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ respectively, obtained at room temperature. Each curve displayed in these figures is made by fixing the other step times to a saturated value and by only varying the step time of interest. Perfect control of film thickness can be achieved when the ALD process is operated in saturated conditions. Figure 3.2 and 3.3 can thus be used to select the step times where the growth is saturated and when the process behaves truly like an ideal ALD process.

In figure 3.2, the black squares are related to the plasma ALD process and the blue circles to the ozone ALD process. When looking at the black squares it can be seen that if purging times are too short, CVD-like reactions come into play causing an increase in the growth per cycle (GPC). At this moment both precursor and reactant are present in the reaction chamber, causing gas phase reactions. It can also be seen that if the plasma exposure is too short not all surface sites are able to react resulting in a lower GPC. Based on these curves the following parameters will be chosen for the standard plasma ALD $\text{Al}_2\text{O}_3$ process: TMA dose 20 ms / TMA purge 2 s / Plasma exposure 3 s / Plasma Purge 2 s. To stabilize the process, an additional pre-plasma step of 1 s is added, that already brings the chamber to the pressure of 25 mTorr at which the plasma is ignited. All saturation curves were obtained using this pre-plasma step. Figure 3.4 captures the standard operating conditions for all EE-ALD processes that will be used for spacer deposition.

When looking at the blue dots in figure 3.2 it is important to note the relative slow saturation of the $\text{O}_3$ exposure step compared to the $\text{O}_2$ plasma exposure step. When extending the $\text{O}_3$ exposure time to 30 s an GPC of 1.21 Å/cycle can be obtained. Even longer dosing times were not tested. This behavior clearly shows that the surface reactions include a component that has a relatively long reaction time. This might be related to a relatively low ozone flux towards the substrate surface, since the ozone generator is not able to get a flow with a high $\text{O}_3$ concentration into the chamber. By further increasing the operating pressure the amount of $\text{O}_3$ molecules interacting with the surface during the exposure step can be increased, possibly leading to a faster saturation. Due to software limitations it is however not possible to increase the pressure above 250 mTorr. A dosing time of 30 s is highly impractical, therefore it was chosen to fix the standard $\text{O}_3$ exposure time to 5 s. In 5 s the GPC saturated to approximately 86% of the GPC obtained at 30 s and thus after a 5 s exposure a further increase of exposure
3.3 Results and Discussion

Figure 3.2 Saturation curves of each step in the ALD cycle for both EE-ALD processes of $\text{Al}_2\text{O}_3$ at room temperature.

time will only result in a very small increase of the GPC. Again the operating conditions for the standard ozone ALD process of $\text{Al}_2\text{O}_3$ are displayed in figure 3.4. This figure shows an additional process step, namely a second purge after the $O_3$ purge step due to practical reasons. During the $O_3$ exposure and consecutive purge step there is no argon flow going through the precursor dosing line, this is to ensure that no argon enters the reaction chamber in order to obtain the highest amount of $O_3$ in the chamber at the limited maximum chamber pressure of 250 mTorr. This additional purge step establishes an argon flow through the precursor dosing line, so that in the precursor dosing step the precursor can be delivered into the chamber without any problems.

The black squares in figure 3.3, show that a plasma-assisted ALD process can be successfully established allowing for the use of SiO$_2$ spacers in a D-SDDP process. Again, it can be seen that a too short plasma exposure will result in a lower GPC. A small difference compared to the $\text{Al}_2\text{O}_3$ process is observed for the saturation curve of the plasma purge in the SiO$_2$ process, i.e. no increase in GPC is observed for the purge times tested. The standard conditions that were selected for the plasma ALD process of SiO$_2$ based on the saturation curves in figure 3.3 are displayed in figure 3.4. Also in this plasma-assisted ALD process an additional pre plasma step is added.

Figure 3.3, reveals that an ozone ALD process with the SAM.24 precursor results in very low growth rates ($< 0.015 \text{ Å/cycle}$), as displayed by the blue dots. There are reports of successful ALD processes using SAM.24 as precursor and $O_3$ as the reactant [52], however in these cases deposition temperature was always well above 100 °C. Apparently, the resulting surface chemistry at room temperature of the SAM.24 $O_3$ process is not leading to film growth. Section
Figure 3.3 Saturation curves of each step in the ALD cycle, for both EE-ALD processes of SiO$_2$ at room temperature.

3.3.2 will return on this subject. The ozone ALD process of SiO$_2$ is considered non-feasible and will thus not be investigated any further.

Figure 3.4 Schematic representation of the three EE-ALD processes developed in this chapter. The settings of each individual ALD step are displayed. In the purge steps an argon flow of 100 sccm is used. Note that 90° denotes the fully opened position of the butterfly valve.
3.3.2 Film Characterization

In the previous section the development of three EE-ALD processes at room temperature has been discussed, for the deposition of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ spacers in a D-SDDP process. This section will characterize the three films deposited at room temperature using these developed EE-ALD processes. However, before focussing on the films deposited at 25 °C, a temperature series for all films is made to provide more insights in the EE-ALD processes of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$. The operating conditions displayed in figure 3.4 were used to deposit films at different substrate temperatures and the GPCs were obtained using SE and displayed in figure 3.5. Also an attempt was made to establish an $\text{O}_3$ ALD process for $\text{SiO}_2$ at 200 °C, this resulted in a process with a GPC of 0.16 Å/cycle when an $\text{O}_3$ exposure time of 30 s was used (also plotted in figure 3.5. Since the GPC was still relatively low and the exposure time long, further experiments using ozone ALD of $\text{SiO}_2$ were canceled. However, to comment in a more detailed way on the low GPC of the ozone $\text{SiO}_2$ process a comparison is made with EE-ALD processes using SAM.24 developed at ASM Microchemistry in Helsinki by Haukka et al. [58].

This data of an ozone and plasma-assisted ALD process using SAM.24 is also plotted in figure 3.5.

Figure 3.5 reveals the trend of a decreasing GPC as temperature increases for all plasma-
assisted ALD processes. Literature has shown that these trends can be explained by an decrease in the number of deposited Si or Al atoms per cm$^2$ per cycle and a increase of film density as temperature increases. This is shown by RBS measurements on films deposited under comparable conditions for SiO$_2$ [51] and Al$_2$O$_3$ [21, 48]. The reason for the reduction in the amount of Si or Al atoms deposited per cm$^2$ per cycle with increasing temperature originates from a loss of -OH surface groups due to thermally activated dehydroxylation reactions [20, 49, 59]. The -OH surface coverage is a key parameter in the growth rate of the plasma-assisted Al$_2$O$_3$ and SiO$_2$ processes, since the -OH surface group is the location where the precursor adsorbs and thus film growth starts [51, 49]. Later in this section the reaction mechanisms for the Al$_2$O$_3$ and SiO$_2$ processes are discussed in more detail, where also this importance of -OH groups is illustrated.

In the case of ozone ALD of Al$_2$O$_3$, the RBS results presented in table 3.1, obtained from samples deposited using the standard O$_3$ process shown in figure 3.4, show a different behavior in the amount of deposited Al atoms per cycle compared to the plasma-assisted processes.

With O$_3$ ALD the number of Al atoms deposited per cycle increases as temperature increases. This can considered to be an indication that the O$_3$ ALD process is affected more by substrate temperature than the plasma process. As the substrate temperature increases more thermal energy is available and Al atoms are deposited more easily since precursor ligands can be more easily removed by O$_3$. As temperature decreases, however, the carbon content and incorporation of -OH groups rises significantly, causing the film density to drop. This is supported by the clear increase in carbon and hydrogen content illustrated by table 3.1. The incorporation of -OH groups is also seen in FTIR absorption spectra which will be discussed momentarily in this section. Due to these phenomena, the GPC tends to stabilize above 100 °C, since both effects are balancing each other. Below 100 °C the GPC increases as the temperature decreases, apparently in this regime the incorporation of carbon and -OH groups (decrease in density) has a greater effect on the GPC than the decrease in Al atoms deposited.

In the case of ozone ALD of SiO$_2$ the GPC is relatively low for temperatures below 250 °C, above this temperature the GPC drastically increases to a value close to 1 Å/cycle [58]. Apparently, the surface chemistry at lower temperatures is not leading to the formation of -OH groups (or other groups) that can be used to initiate film growth.

Again indicating that the substrate temperature plays a role in ozone ALD. The thermal energy provided by the substrate has a significant influence on the surface chemistry and consequently on the SiO$_2$ film growth. The end of this section will shortly return on the changes in the surface chemistry that affect the film growth.

### Table 3.1 Results of RBS analysis of Al$_2$O$_3$ samples deposited by O$_3$ ALD at different substrate temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Al atoms deposited (10$^{14}$ atoms cm$^{-2}$ cycle$^{-1}$)</th>
<th>Density (g cm$^{-3}$)</th>
<th>Atomic Percentage [C] (at. %)</th>
<th>Atomic Percentage [H] (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>2.64</td>
<td>3.1</td>
<td>–</td>
<td>4.81</td>
</tr>
<tr>
<td>200</td>
<td>2.24</td>
<td>3.0</td>
<td>–</td>
<td>8.13</td>
</tr>
<tr>
<td>100</td>
<td>1.99</td>
<td>2.8</td>
<td>7.47</td>
<td>13.2</td>
</tr>
<tr>
<td>25</td>
<td>1.94</td>
<td>2.4</td>
<td>9.03</td>
<td>20.8</td>
</tr>
</tbody>
</table>
In order to continue this section on the film characterization in a structured way a division will be made between the two spacer materials. This section will first fully discuss the $\text{Al}_2\text{O}_3$ processes, after which the characterization of the $\text{SiO}_2$ films will be discussed. Both subsections will start by returning on the trend in the GPC with respect to the substrate temperature and linking it to the refractive index. The refractive index ($n$) is often correlated to the atomic density of the film, the higher $n$, the higher the density. Next, both subsections will discuss FTIR measurements to directly obtain information about the film composition and indirectly on the reaction mechanism. In the subsection on $\text{Al}_2\text{O}_3$ also performed QMS measurements will be discussed. The QMS data also contains information that can be used to obtain insight into the reaction mechanism.

Characterization of $\text{Al}_2\text{O}_3$ films deposited by EE-ALD

Figure 3.6 summarizes the GPC as a function of temperature of the EE-ALD processes for $\text{Al}_2\text{O}_3$ developed in the FlexAL. In this case also the refractive index ($n$) is plotted. $n$ shows a clear increase as temperature increases for both processes, indicating that the density is increasing as was already confirmed by RBS results of comparable samples. The refractive index datapoint of the $\text{O}_3$ process at 25 °C however, shows a deviation from this trend. It is important to note that careful considerations have to be made in directly relating the density of a film to a refractive index obtained by an optical model (in this case a Cauchy model). An optical model can typically fit any spectra by adjusting many fit parameters, but a physical meaning of the parameters can be lost in the fitting process if the model does not take into account the correct material characteristics [60]. The deviating refractive index data point will be discussed later in this section. First the trend in the refractive index with temperature will be discussed in more detail.

In the case of films deposited by ozone ALD, RBS results at low temperature showed a significant incorporation of carbon and -OH groups which reduces the $\text{Al}_2\text{O}_3$ film density. For plasma ALD, no significant carbon content was observed using RBS, i.e. the carbon concentration is below the detection limit of about 5 at%, a significant incorporation of hydrogen was however observed [21]. The trends in refractive index of figure 3.6 can therefore be explained by an increase in the incorporation of -OH groups which is reported before in depositions at low temperature [48, 21]. As a result, the density and the refractive indices decrease. FTIR measurements of samples deposited at room temperature, displayed in figure 3.7 and 3.8 for plasma-assisted and $\text{O}_3$ ALD processes respectively, indeed show the incorporation of hydroxyl groups.

Let us now return on the deviation in the trend of the refractive index for the $\text{O}_3$ process at low temperatures. As stated in the previous section, the saturation of the $\text{O}_3$ exposure step was slow, as a result the 5 s of exposure used in the standard $\text{O}_3$ process did not lead to full saturation. This can possibly have an influence on the film properties, e.g. its refractive index. Therefore, a film was grown using an $\text{O}_3$ exposure of 30 s and the GPC and refractive index were determined by SE. Figure 3.6 also displays these data points using a crossed open marker. The refractive index data point obtained by this experiment falls within the expected trend based on the RBS results i.e. it is lower which correlates with a lower film density. Apparently, the composition of the film is altered, allowing the refractive index obtained by the Cauchy model to follow the decreasing trend in $n$ for decreasing temperatures. In the previous case, using 5 s of $\text{O}_3$ exposure, the refractive index and density did not correlate for depositions at low temperature. It can be hypothesized that the films deposited using a 5 s $\text{O}_3$ exposure contain more absorbed water. The density of the films deposited at room temperature is relatively low, which might be an indications of voids present in the film. Water
Figure 3.6 The GPC (black) and refractive index (blue) as a function of the deposition temperature for both EE-ALD $\text{Al}_2\text{O}_3$ processes. The closed markers represent data of the standard plasma-assisted ALD process and the open markers represent data of the standard $\text{O}_3$ ALD process. The crossed open markers at 25°C represent data of an $\text{O}_3$ ALD process with an $\text{O}_3$ exposure of 30 s.

can possibly access and get incorporated in the bulk film through these voids post deposition. Since the refractive index of water ($n = 1.33$) is higher than that of air ($n = 1.00$), this might cause an increase in the refractive index of the film obtained by a Cauchy model. In the case of the deposition using a 30 s $\text{O}_3$ exposure step, the exposure was long enough to result in a more closed lattice (less voids) causing less $\text{H}_2\text{O}$ molecules to penetrate in the bulk film, resulting in the lower refractive index.

So far the FTIR data presented in figure 3.7 and 3.8 has been used to prove that carbon and hydroxyl groups are incorporated in the standard EE-ALD processes developed in the previous section at room temperature (figure 3.4). What is illustrated in these figures are the FTIR absorption spectra of $\text{Al}_2\text{O}_3$ films deposited using different reactant exposure times (both for saturated and unsaturated ALD reactions). The purpose of these figures is to show that and speculate on how the carbon is incorporated in the film (i.e. in what way the carbon is bound) and possibly gain insights into the reaction mechanism by comparing the FTIR spectra of samples deposited using saturated conditions and unsaturated conditions. Figure 3.7 shows the FTIR absorption spectra of $\text{Al}_2\text{O}_3$ deposited by plasma-assisted ALD with different plasma exposure times. The absorption spectra of the sample deposited using conditions below saturation clearly display a larger absorption peak in the region between 1250 and 1750 $\text{cm}^{-1}$. The absorption in this region is due to carbonates and formates that
3.3 Results and Discussion

![FTIR spectra of Al₂O₃ samples deposited by plasma-assisted ALD using different plasma exposure times (in & below saturation). All samples had a thickness of 26 ± 2nm, therefore the absorption spectra are not corrected for film thickness. The most prominent absorption peaks/regions have been assigned.](image)

Figure 3.7 FTIR spectra of Al₂O₃ samples deposited by plasma-assisted ALD using different plasma exposure times (in & below saturation). All samples had a thickness of 26 ± 2nm, therefore the absorption spectra are not corrected for film thickness. The most prominent absorption peaks/regions have been assigned.

are incorporated in the film [22]. The peaks correspond to symmetric and asymmetric OCO modes of bound formate and carbonate species. Some of the absorption is also caused by methoxy species which has absorption features around 1475 and 1100 cm⁻¹ [22]. By extending the plasma exposure time these carbon containing species in the film are reduced, however even in saturated conditions the carbon species, mainly in the form of formates and carbonates cannot be eliminated completely. The spectra also reveals that -OH groups are incorporated in the film using a 3 s plasma exposure as well as 0.5s exposure, indicated in both cases by a broad absorption band ranging from 2700 to 3700 cm⁻¹ related to unassociated hydroxyl groups [22, 48, 49]. Verlaan et al. reported on comparable absorption features for Al₂O₃ films deposited by plasma-assisted ALD in an OpAL reactor from Oxford Instruments [48].

In the case of the ozone ALD process of Al₂O₃, the same carbon containing species (formates, carbonates and methoxy species) were observed, only to a larger extent. Figure 3.8 shows that even if long ozone exposure times are used, the broad absorption band between 1250 and 1750 cm⁻¹ remains. Based on this figure it is seen that the carbon content can not be significantly reduced using longer exposure times. Possibly, there is not enough energy available at this temperature for the reactant to remove a formate group and thus this specie is incorporated in the film. In the case of plasma-assisted ALD, the more reactive radicals are able to break these C-O bonds, possibly aided by the energetic ions. Increasing the substrate temperature
during the $O_3$ ALD process can provide the energy needed to break the C-O bonds as was clearly seen by the RBS results displayed in table 3.1 that showed that the $C$ content was below the detection limit for deposition temperatures above 200 °C.

![Figure 3.8 FTIR spectra of $Al_2O_3$ samples deposited by ozone ALD using different ozone exposure times (in and below saturation). All samples had a thickness of 16 ± 2 nm, therefore the absorption spectra are not corrected for film thickness. The most prominent absorption peaks/regions have been assigned.](image)

The $Al_2O_3$ samples deposited by ozone ALD also reveal a broad absorption band due to the absorption of OH groups. However, when looking at the red line in figure 3.8 two peaks can be distinguished in this region namely around 2960 and 3520 cm$^{-1}$. The blue spectra only shows the peak around 3520. It is reported that methyl groups bound to alumina can have absorption features around 2850 cm$^{-1}$[22], so it is possible that the carbon content is slightly reduced by longer exposure times due to a decrease in the concentration of the methyl groups.

In addition to the FTIR absorption measurements, QMS measurements were performed to gain further insight into the reaction mechanism. For the plasma-assisted ALD of $Al_2O_3$ the QMS results are plotted in figure 3.9. This figure shows the signals of several mass to charge (m/z) ratios related to species present in the reaction chamber during a full ALD cycle. For the first step in the ALD cycle, the dosing of the TMA precursor, the QMS signal shows a steep rise related to the mass to charge ratios of 15 and 16 in figure 3.9. Both signals correspond to a release of $CH_4$. At this stage, the TMA precursor reacts with -OH surface groups present on the surface to form $CH_4$ (methane). The signals decrease to base level during the purge step. In the plasma exposure step, signals related to the reactant ($O$ & $O_2$)

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3.3 Results and Discussion

**Figure 3.9** Signals obtained by QMS during a plasma-assisted ALD process of Al$_2$O$_3$ in FlexAL mark 1. In the ALD process shown in this figure, no pre-plasma step was executed as utilized in the standard ALD process reported in this section. However, it can be expected that although the process is slightly different, the surface reactions remain the same and insights obtained from this figure can be applied to the standard plasma-assisted ALD process for Al$_2$O$_3$.

and signals related to the reaction byproducts (H$_2$O & CO$_2$) dominate. Based on this information combined with the corresponding findings of other studies on the reaction mechanism in the plasma-assisted ALD of Al$_2$O$_3$ [49, 61], it can be postulated that the second half cycle consists of a combustion like reaction between the remaining CH$_3$ ligands and the O$_2$ plasma species. In this step the surface is regenerated for a next ALD cycle. The dominant reactions in the plasma-assisted ALD of Al$_2$O$_3$ are described by equation 3.1 and 3.2 [49, 61].

\[
Al + OH^* + Al(CH_3)_3(g) \rightarrow AlO + Al(CH_3)_2^* + CH_4(g) \quad (3.1)
\]

\[
AlCH_3^* + 4O(g) \rightarrow Al - OH^* + CO_2(g) + H_2O(g) \quad (3.2)
\]

The asterisks in these equations designate the surface species, the volatile/gas-phase species are indicated by '($g$)'. Besides this dominant reaction scheme, it is possible that in the second half-cycle reactions occur with other oxygen-containing species e.g. O$_3$ and H$_2$O present in the reaction chamber, also resulting in the regeneration of the surface. So there are probably many more, and more complex reactions that take place.

As detected by FTIR absorption spectroscopy, see figure 3.7, carbon can be incorporated when the CH$_3$ ligand is not fully removed during the second half cycle. As a result a carbonate group is formed. The carbonate species contain -OH groups which can be used as adsorption sites in the next cycle for the precursor molecule [62], thus incorporating carbon in the material. The incorporation of carbon in the lattice is more pronounced in the case of ozone ALD, as shown by the FTIR absorption spectra. The O$_2$ can thus be considered more effective in
oxiding all the ligands. To study the $O_3$ process further also QMS analysis was performed, the results are displayed in figure 3.10.

**Figure 3.10** Signals obtained by QMS during a ozone ALD process of $Al_2O_3$ in FlexAL mark 1. In the ALD process shown in this figure, no pre-plasma step was executed as utilized in the standard ALD process reported in this section. However, it can be expected that although the process is slightly different, the surface reactions remain the same and insights obtained from this figure can be applied to the standard ozone ALD process for $Al_2O_3$.

The start of the ozone ALD cycle is equal to the start of the plasma-assisted ALD process. Also, in the second half-cycle the same signals as for the plasma-assisted dominate. It is therefore postulated that the overall dominant reaction mechanism is in principle the same as for plasma-assisted ALD, so equation 3.1 and 3.2 can be applied. However, the difference in figure 3.10, between the QMS signal peak of the $CO$ and $CO_2$ signals in the beginning of the $O_3$ exposure step and the signal level at the end of this step is significantly smaller than was the case during the plasma-assisted ALD process. This suggests that $O_3$ is less effective in the removal of the precursor ligands. Possibly, the surface reactions are slower, and/or more complex (i.e. different oxidation pathways are followed) in the case of ozone ALD. The significant amount of carbonates and formates observed in the FTIR absorption spectra are likely indicative that these species play a role in the reaction mechanism. The reason for the significant increase in carbon incorporation in the case of ozone ALD, is possibly related to a different reaction pathway. Reports by Goldstein et al. [22] and Rai et al. [62] have proposed several possible reaction pathways during the second half cycle of ozone ALD. Figure 3.11 captures the possible surface reaction that can take place during ozone ALD.

This figure shows that either through formates, carbonates or C-H insertion the surface is regenerated to form hydroxyl groups. However, in ALD using $O_3$ as the reactant, the large amount of carbon in the films probably originates from that fact that some of the carbonate groups remain and its -OH groups acts as an precursor adsorption site, thus incorporating formate species in the material [62].
Both the ozone-based and the $O_2$ plasma-based ALD processes, for $Al_2O_3$ rely on combustion-like reactions during which the methyl-groups are oxidized into $H_2O$ and $CO_2$. The $O_2$ plasma is however more effective than $O_3$ in oxidizing the ligands, so that the films deposited by plasma-assisted ALD contain less carbon. Which is not surprising considering that oxygen radicals are more reactive and ions in the plasma provide additional energy to the reaction surface, reducing the chance that carbon species remain during the second half cycle.
Characterization of SiO$_2$ films deposited by EE-ALD

The SiO$_2$ films deposited by plasma-assisted ALD were characterized in a way analog to the Al$_2$O$_3$ films in the previous section. The final discussion on the reaction mechanism at the end of this section will however be based on QMS data measured and published by Dingemans et al. [51]. Figure 3.12 displays the GPC and $n$ as a function of temperature for the SiO$_2$ films deposited by plasma-assisted ALD.

![Figure 3.12](image)

**Figure 3.12** The GPC (black squares) and refractive index (blue circles) as a function of the temperature for the standard plasma-assisted ALD process of SiO$_2$.

For films deposited at temperatures of 75 °C and higher, this figure reveals the same trends as for the Al$_2$O$_3$ films deposited by plasma-assisted ALD. The refractive index increases with increasing temperature since films are becoming more dense. The densification is in this case not expected to be related to the decreasing amount of carbon in the lattice. This assumption is based on RBS analysis of similar SiO$_2$ films deposited by plasma-assisted ALD, which showed that the amount of carbon was below the detection limit (< 5 at%) [51]. Furthermore, the FTIR absorption spectra, that will be discussed later in this section, show no indications of carbon in the lattice. The densification with increasing temperature, indicated by the increase in refractive index in figure 3.12, is related to a reduced amount of -OH groups in the SiO$_2$ lattice. Higher deposition temperatures result in a highly cross-linked SiO$_2$ lattice, since the cross linking is less distorted by the incorporation of -OH groups.

At temperatures below 75 °C, the amount of incorporated -OH groups is relatively high, for which it has been reported that they could induce voids in the SiO$_2$ lattice [63]. Water
molecules can form hydrogen bonds with the -OH groups present in the film. These molecules can originate from the reaction chamber as a byproduct of the ALD process, or from the atmosphere to which the film is exposed after venting. As a result of a significant amount of water in the SiO$_2$ films, the refractive index can be influenced [63]; a phenomenon that could explain the increasing trend in the refractive index for temperatures below 75°C in figure 3.12.

Figure 3.13 confirms that OH-groups are incorporated in the lattice at room temperature. This figure compares two SiO$_2$ films deposited using a different O$_2$ plasma exposure time. The most interesting difference can be found in the 3000 – 3600 cm$^{-1}$ range, which is related to the absorption by OH-groups. Isolated silanol (Si-OH) groups in a film typically appear above 3600 cm$^{-1}$ [49, 64, 65]. This absorption feature shifts and appears as a broad absorption band between 2700 and 3700 cm$^{-1}$ when the concentration of OH-groups is so high that neighboring Si-OH groups influence each other due to the large polarity of the O-H bonds [48, 49]. These interacting OH groups are referred to as associated -OH groups.

![FTIR spectra of SiO$_2$ samples deposited by plasma-assisted ALD using different plasma exposure times (in and below saturation). All samples had a thickness 19±2 nm, therefore the absorption spectra are not corrected for film thickness. The most prominent absorption peaks/regions have been assigned.](image)

Figure 3.13 FTIR spectra of SiO$_2$ samples deposited by plasma-assisted ALD using different plasma exposure times (in and below saturation). All samples had a thickness 19±2 nm, therefore the absorption spectra are not corrected for film thickness. The most prominent absorption peaks/regions have been assigned.

In under-saturated conditions the peak of the -OH absorption feature is slightly increased and shifted towards the lower wavenumbers, as shown by the black line in figure 3.13. It is believed that this change is related to an increase of absorbed H$_2$O molecules in the film,
because the SiO₂ lattice is more porous in the case of the 0.5 s plasma exposure [63]. H₂O molecules namely have a distinct absorption feature around 3400 cm⁻¹ [66]. If the plasma exposure time is extended the SiO₂ lattice has more time to reach a higher degree of cross linking within the lattice, reducing the porosity and leading to less absorbed H₂O molecules. At the end of section 3.3.1 it was already postulated that the reaction mechanism of the plasma-assisted ALD process of SiO₂ was governed by surface reaction involving -OH groups. Figure 3.13 clearly illustrated the presence of these surface groups. In the reaction mechanism it is therefore likely that the N(C₅H₅)₂ ligands of the precursor react with the surface OH groups, producing volatile HN(C₅H₅)₂. This leads to a similar reaction mechanism proposed by Burton et al. for the SiH(N(CH₃)₂)₃ (tDMAS) precursor [67], which is comparable to the SAM.24 precursor used here. It is likely that the dominant surface reactions are captured by equation 3.3 and 3.4 that display the two half reactions.

\[ Si - OH^* + H₂Si[N(C₅H₅)₂]₂ \rightarrow SiO - SiH₂[N(C₅H₅)₂]_2 - x + xHN(C₅H₅)₂ \]  

\[ SiH₂N(C₅H₅)₂ + O \rightarrow Si - OH^* + H₂O + COₓ + N - containing species \]  

The second half cycle is dominated by combustion-like reactions during which H₂O and COₓ is formed, similar to the reaction mechanism of plasma-assisted Al₂O₃. As stated earlier, the QMS data that will be used to clarify and demonstrate the surface reaction is obtained from Dingemans et al. [51]. The original graph of the QMS measurement of a plasma-assisted ALD process utilizing SAM.24 as published in [51], is displayed in figure 3.14 and shows the release of N(C₅H₅)₂ and HN(C₅H₅)₂ during the precursor dosing step and a release of H₂O and CO₂ during the plasma exposure. This is in agreement with the reaction mechanism proposed in equation 3.3 and 3.4.

Figure 3.14 QMS analysis performed by Dingemans et al. for the plasma-assisted ALD process of SiO₂ using SAM.24 as precursor at a substrate temperature of 250 °C. The figure shows an increase in the signals corresponding to N(C₅H₅)₂ (m/z=72) and HN(C₅H₅)₂ (m/z=73) during the first cycle. In the second half cycle a combustion like reaction is confirmed by an increase in the signals related to H₂O (m/z=18) and CO₂ (m/z=44).
The ozone-based ALD process for $\text{SiO}_2$ proved to be unfeasible at low temperature due to a low reactivity of $O_3$ with the precursor ligands. Haukka et al. attributed this low reactivity to the fact that the SAM.24 precursor adsorption is more bifunctional and thus tends to leave more Si-H bonds on the surface instead of alkyl-amide ligands [58]. Figure 3.15 illustrates the proposed adsorption possibilities for the SAM24 precursor.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures/3.15}
\caption{SAM.24 precursor adsorption: (a) shows a precursor adsorption on a single surface site, leaving an alkyl-amide ligand; (b) shows a bifunctional precursor adsorption that only leaves Si-H ligands.}
\end{figure}

The Si-H bond is less reactive towards $O_3$ at low temperatures, leading to a non-feasible ozone process at these low temperatures. This was already illustrated by the low growth per cycle of the $O_3$ ALD process for $\text{SiO}_2$ at low temperatures, as shown in figure 3.5.
3.4 Conclusions

In this chapter, the process and material properties were discussed for three EE-ALD processes to fabricate spacers at room temperature. The \( \text{Al}_2\text{O}_3 \) films could be deposited using \( \text{O}_3 \) molecules and \( \text{O} \)-radicals as the reactant, whereas \( \text{SiO}_2 \) only showed reactivity with \( \text{O} \)-radicals. The three successfully developed processes show a relatively high GPC (\( > 1 \text{ Å/cycle} \)) at room temperature.

This high GPC originates from a high -OH surface coverage at room temperature and the high incorporation of OH species in the film for \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) films. As a result, the films deposited at room temperature also showed a lower density compared to films deposited at high temperatures. This lower film density was also connected to the possible presence of water in the film at room temperature.

The reason for the development and characterization at room temperature of the \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) films, is its implementation in a D-SDDP process, where both the high GPC and relative low density of the films offer advantages. While still providing excellent control of the film thickness, an ALD process with high GPC reduces the number of cycles needed to achieve a specific spacer thickness, reducing the deposition time. The lower density can possibly offer advantages in the anisotropic etch step of the D-SDDP process. In previous studies the etch rate and film density have shown a correlation [68], spacers with a relatively low density can possibly be processed faster.
Chapter 4

Direct Spacer-Defined Double Patterning (D-SDDP)

This chapter will focus solely on the exploration and realization of a Direct Spacer-Defined Double Patterning (D-SDDP) process. It should be expressed once more that this chapter is very explorative in nature, since almost no knowledge of the D-SDDP process was present within the research group. Moreover, SDDP literature only provides a very limited scope by typically only demonstrating that a SDDP can be realized to reach a certain technology node and not describing the specific challenges that are encountered.

Section 4.1 will start with a short summary of the relevant information on D-SDDP that was discussed in the previous chapters and it will continue with some more background information on all individual process steps involved. Section 4.2 will provide specific experimental details of all processing steps and systems that were used in realizing a D-SDDP process. The results will be discussed and presented in section 4.3 and the conclusions will be presented in the final section. The last paragraph in this chapter will provide an outlook for the D-SDDP research possibilities at the Nanolab @ TU/e.

4.1 Introduction

The next generation of optical lithography, i.e tools that use EUV light with a characteristic wavelength of 13.5 nm, is not ready yet to replace the current lithography tools. This is mainly the result of throughput issues, related to the low power output of the EUV sources available and intensity losses at EUV mirrors [8]. Consequently, 193 nm tools will have to be used to fabricate devices at the 22 nm technology node, to keep technology in pace with Moore’s law. However, section 1.3 showed that the resolution that can be obtained with state-of-the-art 193 nm lithography tools alone is not sufficient to reach this technology node. Therefore, the limits of optical lithography have to be extended and this can be done by double patterning techniques [12], including SDDP that is of interest in this project. The price for a higher resolution is, however, that SDDP requires additional processing steps. The number of processing steps can again be reduced by using D-SDDP, in which the need for a hard mask is eliminated by depositing the spacer material directly on the resist. By utilizing EE-ALD, spacer material can be deposited at the relatively low temperatures required, on top of the polymer resist layer, without damaging it. The goal of the D-SDDP process is to obtain a masking layer from free-standing spacer sidewalls that reduces the resolution compared to a mask that can be obtained solely using optical lithography. Figure 4.1 illustrates which processing steps are required to achieve this goal.
Chapter 4 Direct Spacer-Defined Double Patterning (D-SDDP)

Figure 4.1 The Direct-SDDP process scheme where a photoresist layer (orange) is applied directly on top of the target layer (light grey). The spacer layer (green) is then deposited on top of the patterned photoresist at relatively low temperatures. After an anisotropic etch and a resist removal step, the spacer sidewalls are utilized as a mask to etch patterns in the target layer.

Spacer-defined double patterning does not allow for unlimited freedom in creating patterns that can be used as a mask. This is because the spacer sidewall on each side of the patterned photoresist is utilized in further processing. Therefore the possibilities offered by SDDP can be exploited best when a repetitive pattern is required. Because of this, the first application of the SDDP method are memory cells. Next generation memory devices of DRAM [3, 18] and NAND flash [69] are currently fabricated using SDDP processes. Figure 4.2 displays an example of a state-of-the-art NAND flash memory cell of Hynix fabricated using SDDP processes, the figure also clearly illustrates the repetitive features that are common in memory application. However, there are also reports of the use of SDDP in the fabrication of FinFETs [70, 71].

Figure 4.2 A SEM image of a NAND flash memory cell produced by Hynix, created using an SDDP process [69]. The repetitive structures in the memory cell, which make it ideal to employ SDDP processes, can clearly be seen.

To successfully adopt a SDDP process in a device, such as the one shown in figure 4.2, full control over the five steps displayed in figure 4.1 is necessary. The next sections in this introduction will provide some additional background on these five essential processing steps.

4.1.1 Applying the photoresist film

The first step in the SDDP process (see figure 4.1) is the application of the polymer photoresist film, which is done by spin-coating [72]. Using this technique uniform thin films can be applied to a flat, clean substrate, by rotating it at high speed, on which an excess amount of photoresist solution is placed. The device used for this is called a spinner or spin-coater. The photoresist solution consists of at least two compounds: a polymer solution and a casting solvent. The
polymer dissolved in the casting solvent forms the base resin which changes upon exposure to UV light, x-rays, EUV light, electrons or whatever exposure follows. A third compound, the sensitizer, can be added to influence the photochemical reactions resulting from an exposure [73]. Two types of resist are available; positive resists where the exposed areas will be removed after development and negative resists where the exposed areas remain after development.

During spin coating, the photoresist solution on the substrate is spread by a centrifugal force and evenly spun of the substrate, until this force is balanced by the viscous drag forces in the solution. During this balancing act, the net fluid flow due to viscosity effects decreases with time. Gradual evaporation of the volatile solvent species will become the dominant process occurring in the coating. The resulting film thickness is dependent on the centrifugal forces (spin speed) applied, the viscosity of the fluid and the evaporation behavior the fluid. The evaporation behavior can be influenced by the ambient conditions. A high ambience solvent saturation in the spinner will for instance reduce the attained thickness of the resist due to a suppressed solvent evaporation from the resist.

After applying a photoresist film to the substrate, patterns have to be created in the resist by exposing the film to light or other radiation and exploiting the changes that this exposure imposes on the polymer base resin. Here, two key resist properties play an important role, namely sensitivity and contrast. The sensitivity of the resist describes which radiation dose, or electron dose is needed to cause sufficient chemical change in the resist so that desired patterns can be fully developed so that all resist material is removed on the desired locations. The development of a photoresist can be based on chemical changes such as: a change in reactivity or changes in molecular weight (cross linking or chain scission of polymers), causing changes in solubility. The second important aspect is contrast, which is a measure of a resists response to dose variation. Figure 4.3 (a) illustrates the concept of contrast. The dotted line in this graph shows the exposure dose that is needed to cause sufficient chemical change in the resist so that it can be developed. The position on the horizontal axis of this line is determined by the sensitivity. The contrast of the resist in principle describes the behavior of the resist around this point. In the ideal case (infinite contrast) the development rate will remain zero for every dose below the dotted line. Real photoresist however, will already shown an increase in the development rate for an exposure dose below the dotted line. Contrast plays an important role in determining how vertical the sidewall of the resist will be after an exposure. During an exposure always some light or electrons are backscattered in the underlying film, this causes areas that were supposed to remain unexposed to be exposed to a low dose. If the contract is low, the areas which were under-exposed by backscattering undergo chemical changes. This can affect the sidewalls of the patterns created in your resist, as displayed on the right in figure 4.3 for the case of a positive resist.

4.1.2 Patterning the resist by EBL

The second step in the D-SDDP process is the patterning of the resist by EBL, a form of maskless lithography that uses a focussed beam of electrons to write patterns in a resist layer. An EBL tool extracts electrons from an electron source and accelerates, focusses and directs them to the sample by electric fields [74]. The electron beam is focussed to a small spot (2−3 nm in diameter) on the substrate by a set of lenses, consisting of magnetic or electric fields. The electron beam can also be deflected by magnetic and electric fields applied perpendicular to the trajectory of the beam and in this way the focussed electrons can be scanned over an area (the write field), therefore no mask is required. The beam can also be deflected entirely off axis onto a beam stop, which is done by a beam blanker and basically turns the beam on and off. Patterns of any shape can thus be written. Large area patterns can be created by
stitching together multiple write fields, this is done by moving the sample stage after each write field.

When an electron beam enters a material, electrons collide (elastically and inelastically) with the resident atoms. As these primary electrons slow down as a result of inelastic collisions, much of their energy is dissipated in the generation of secondary electrons. These secondary electrons, which have a range of only a few nanometers, are responsible for the actual resist exposure process. The rest of the electrons collide elastically, most of them being scattered forward through small angles causing a broadening of the beam as illustrated in figure 4.4. This beam broadening and not the beam size, limits the resolution. Some of the electrons experience large angle backscattering which causes them to return toward the surface. These backscattered electrons also cause exposure of the resist at locations far from the focus point. The scattering can extend over several micrometers, depending on the electron beam energy, meaning that closely spaced patterns will receive electrons from the exposure of their neighbors. This is known as the proximity effect and is illustrated in figure 4.4. This figure shows the simulation result (Casino v2.42 software) of an electron beam entering a PMMA layer of 250 nm thick on top of a silicon substrate. The electron beam was modeled to have an acceleration voltage of 30 keV and a width of 1 nm. The red lines represent pathways of backscattered electrons, the blue lines of electrons scattered forwards.

The figure illustrates that the electron beam only slightly broadens inside the PMMA layer, meaning that a fairly good resolution can be obtained. By increasing the acceleration voltage and reducing the thickness of the resist, in principle this broadening can be reduced even further and the resolution can thus be improved. The figure also clearly illustrates that backscattered electrons expose the PMMA several micrometers away from the entrance location of the e-beam. Models such as the one used to generate figure 4.4 can be used to reduce unwanted effects related to the proximity effect, by simulating the pathways of the electrons and consequently adjusting the dose of each pattern considering the dose from backscattered electrons due to neighboring patterns.
4.1 Introduction

Figure 4.4 Simulation result of an electron-beam at 30 keV entering a PMMA film on top of a silicon substrate. The blue lines represent electrons scattered forwards, the red lines represent backscattered electrons that return to the PMMA layer and can also induce chemical change in the resist layer.

4.1.3 Depositing the spacer material

The third step in the D-SDDP process is the deposition of the spacer material (step 3, figure 4.1). In this project the spacer will be deposited on a polymer resist and therefore the deposition has to be executed at relatively low temperatures. EE-ALD is an ideal technique to realize this, offering high reactivity at low temperatures while also providing excellent uniformity, conformality and thickness control. EE-ALD processes can however also influence the underlying polymer resist film and the patterns, as explained in chapter 2. Therefore, the deposition parameters have to be carefully chosen to avoid affecting the patterns in the resist. Section 4.3.1 will continue on this subject. Since the deposition of the spacer material itself has already been discussed extensively in the previous chapters, no further information will be provided.

4.1.4 Anisotropically etching the spacer

The fourth step of the D-SDDP process is the etch step, during which the spacer material is anisotropically etched so that the spacer sidewalls and the resist material between the sidewalls remains. Etch processes can be divided into two categories: wet etching and dry etching [75]. In wet etching, substrates are immersed in a reactive solution and by chemical reactions or by dissolution material is removed. The reaction products have to be soluble and are carried away by the etchant solution and during the post-etch rinse. With dry etching, substrates are exposed to a reactive gas, a beam of energetic ions or electrons or a plasma which may combine both. Material is now removed by chemical reactions and/or by ion bombardment. The reaction products must be volatile and are carried away in the gas stream. Three basic etching mechanisms can be identified in wet and dry etching processes, as captured in figure 4.5.
Figure 4.5 Basic etching mechanisms: (a) chemical etching, (b) physical etching or sputtering and (c) reactive ion etching (RIE). Chemical etching mechanisms are typically isotropic, undercutting the etch mask. The other etching methods are considered anisotropic.

In wet processes only a chemical etching mechanism is present and commonly an isotropic etch is the result, meaning that the etch rate is constant in all directions. (Anisotropic wet etching can be realized by exploiting the crystal planes of a material [76]). With D-SDDP (figure 4.1) an isotropic etch is clearly unwanted since this will not result in the standing spacer sidewalls needed for further processing. Wet processes can therefore not be used. In this thesis, two available dry etching processes will be used in realizing a D-SDDP process namely, ion milling and reactive ion etching. The etch mechanisms of these process are depicted in figure 4.5 as (b) and (c) respectively. For an extensive report on other dry etching processes the reader is referred to [75].

**Ion Milling**

With ion milling or ion beam etching [75], no chemical reactions with the etch species are involved, since ions from noble gasses (typically argon) are used. In such a process generally a plasma source is used to generate the argon ions. A grid with an external voltage applied to it (the beam grid), is used to extract the argon ions after which they are accelerated by another grid (the acceleration grid) towards the substrate. Here the bombardment by ions results in an etch process by “knocking” out atoms of the targeted layer during collisions. Additionally, low energy electrons are injected by a filament, to prevent charging of the substrate. Figure 4.6 shows an illustration of a typical ion miller, including the plasma source, the beam and acceleration grids and the filament used for the injection of electrons.

Two key characteristics of ion milling are its directionality and applicability. The ion beam is directional due to the fact that the ions are accelerated by a strong electrical field, that is oriented perpendicularly with respect to the substrate. When the chamber pressure is sufficiently low ($\sim 10^{-5}$ mbar) no collisions between ions and atoms occur in the gas phase. As a result, the directionality of the ions is almost completely perpendicular with respect to the substrate holder as it hits the target.

When a beam of energetic ions collides with the surface of a solid, energy and momentum are transferred from the incident particles to the lattice which leads to the ejection of atoms at the surface [77]. As long as the ion flux and ion energy are sufficient, virtually any material can be etched. The etch rates obtained for ion milling will be dependent on the ion energy and ion flux. An increase in these parameters will result in an increased etch rate. Moreover, the etch rate will also be dependent on the material (and its lattice) that is bombarded by ions. An increase in the atomic density, decreases the etch rate, since a higher amount of energy is needed to eject an atom out of a closely packed film. Additionally, also crystallographic orientation can be a material properties that can influence the etch rate [77].
4.1 Introduction

Figure 4.6 Schematic of an ion miller. A collimated beam of energetic ions generated by an ICP plasma, is formed by the beam and accelerations grids and used for etching. The neutralizer ensures that there is no charge build-up by emitting electrons.

The ability of ion milling to etch virtually any material is also one of its disadvantages, because the etch selectivity of the ion milling process to spacer material and underlying photoresist or silicon is generally close to 1:1. A second drawback is the throughput, since ion milling processes generally are single-wafer processes [78].

Reactive Ion Etching

For progress in the semiconductor industry, RIE processes have proved to be crucial, responding to a need for higher etch selectivity and providing increased dimensional and shape control necessary for nano-manufacturing. Ion milling has a low selectivity, however a RIE process that utilizes the synergism of ion bombardment and chemical reactions can provide the required selectivity [79]. This synergism was first described by Coburn & Winters in 1979 in a publication, where etching of silicon using an $\text{XeF}_2$ gas was studied [80]. Figure 4.7 displays their results, illustrating that the etch rates increase significantly when chemical etching and ion bombardment are combined.

This was basically the start for the development of reactive ion etching (RIE) processes for many different materials. A RIE process commonly combines two elements: reactive neutrals (radicals) present in the plasma that chemically etch the target film and a significant flux of energetic ions arriving at the surface simultaneously with the reactive neutrals. Optionally, a sidewall protecting film can be deposited preventing isotropic etching by the radicals. This optional element is not always necessary, if the required etch anisotropy is already provided by the other two elements [81]. All three elements can be recognized in figure 4.8. This figure also depicts a parallel plate reactor, that is typically used for RIE processes.

A plasma is produced in the parallel plate reactor by applying a RF-voltage between the electrodes. After the plasma is ignited, space charge layers (plasma sheaths) will form between the electrodes and the plasma, originating from the higher mobility of the electrons compared to the ions [24]. In the plasma sheath ions are accelerated to the substrate surface. The voltage over the sheath can be enhanced by applying a bias voltage, influencing the energy of the ions arriving at the surface [15, 24]. Depending on which material is to be etched, specific
Figure 4.7 Etch rate of silicon determined by Coburn & Winters [80] using different etching methods. Etching rates are enhanced when chemical etching is combined with ion-bombardment.

gasses providing the correct plasma chemistry are fed into the reaction chamber. Radicals, created in the plasma, that arrive at the film surface will chemically etch the film (leading to isotropic etching). The effect of ions, accelerated towards the surface due to the plasma sheath, is to: 1) enhance the adsorption of the reactive neutrals by creating “active” sites; 2) assist the chemical reactions by breaking bonds; 3) and cause desorption of the etch product by sputtering it from the surface [82].

This last effect causes a renewed exposure of the surface, after which new radicals can come in and repeat the process, so that the synergy between the chemical etching component and the ion bombardment is fully exploited. This leads to etch rates that are larger than the sum of the contributions of the two individual components.

To suppress the isotropic radical-induced etching of the sidewalls of a pattern, a RIE process often employs a sidewall protecting film. This protective film can be deposited during the etch process or after the etch step just described if etch and deposition step are subsequently executed (the Bosch process [83]). In either case a anisotropic etch is the result, in the latter case this result is obtained by repeating the etch step and the step where a protective film is deposited. The protective film will basically cover the whole sample surface, inhibiting etch reactions everywhere, however due to the energetic ions in a RIE process the protective film can be removed by sputtering. Since these ions are directional (as a result of the plasma sheath), the protective layer on the sidewalls of the features remains intact. The right inset of figure 4.8 summarizes all processes occurring at the sample surface that were just described. On the left side of this figure a schematic of a typical RIE reactor is shown.

In this project a RIE process will be employed to etch SiO$_2$ using CHF$_3$. The resulting plasma chemistry to etch SiO$_2$ is purely based on fluorocarbon gasses. During the process, CHF$_3$ dissociates primarily into CF$_2$ and HF species [79]. According to Abe et al. the basic RIE reaction process occurring on the surface of SiO$_2$ films can be formulated according to equation 4.1.

\[
CF_x + SiO_2 \rightarrow SiF_x + CO_2 \tag{4.1}
\]

The protective sidewall film that ensures the anisotropy in this RIE process is a thin polymer film (C$_x$F$_y$) that is formed in the plasma by carbon containing fluorine species. According to Jansen et al. the CF$_2$ intermediates are responsible for the polymer formation on surfaces [79].
4.2 Experimental Details

Figure 4.8 On the left a parallel plate reactor is displayed that is typical used for RIE processes. The inset on the right schematically displays the chemical component in the etching process, the role of ion bombardment and the role of the sidewall protective film during RIE.

4.1.5 Removing the resist

The final step in the D-SDDP process is the removal of the resist layer. The resist used in this work, PMMA, can be removed/stripped in several ways [84]. Cleanroom solvents such as acetone can be used, but also plasma etching (ashing) can be used. In the semiconductor industry a major change in manufacturing occurred when there was proof that plasma ashing technologies could be applied successfully. Within a fairly short period conventional wet processes were replaced by dry plasma-based techniques for resist removal, since dry techniques reduced the number of processing steps and clearly enhanced the chip yields, therefore reducing the manufacturing cost of the devices made [68].

The switch from wet to dry plasma stripping techniques also triggered innovations in the design of photoresists. Nowadays, plasma ashing technology is able to remove modern photoresists at a high rate in a process with low plasma dust (monomer-type dust) generation and without leaving any residue on the substrate.

The introduction of plasma stripping has also led to a more simple, cleaner and safer process compared to the previously used wet processes, which used hazardous chemicals and had problems with accuracy and reproducibility.

Plasma stripping processes are typically carried out in a barrel-type reactor that is equipped with a CCP or ICP plasma source. Polymer resists are typically stripped using an oxygen-based plasma. The stripping process due to oxygen radicals can be represented by the most prominent reaction described by equation 4.2.

\[ C_xH_y + O^* \rightarrow CO + CO_2 + H_2O \]  \hspace{1cm} (4.2)

Since oxygen radicals are responsible for the removal of the resist, this plasma stripping process is considered to be a chemical, combustion-like process resulting in an isotropic etch of the resist.

4.2 Experimental Details

In this section, the experimental details of all processing steps will be discussed. All processing steps reported in this thesis are executed at room temperature, to reduce thermal effects and
to protect the resist. Only during the plasma stripping step the processing temperature could not be actively controlled, which resulted in a higher processing temperature.

4.2.1 Resist Spinning and Electron Beam Lithography

The polymer photoresist that is used to realize a D-SDDP process is PMMA (polymethyl methacrylate), a high resolution positive resist for EBL that has many variations where the molecular weight or the percentage of solids can be varied. In this project PMMA A4 and PMMA A2 are used, both formed with a 495,000 molecular weight resin in an anisole solvent. "A2" or "A4" represents the percentage of solids that is dissolved in anisole, which is 2 or 4% respectively. Both polymer resists are applied in an open spinner that is set to spin for 60 seconds at 4000 rpm. The spin speed is ramped-up as slow as possible (setting 9) to the final speed, so that minimal center-to-edge thickness variations occur [85] and thus a larger uniform area can be used to locate the patterns. The PMMA thickness that is obtained under these conditions is 250 ± 2 nm for the PMMA A4 and 80 ± 2 nm for PMMA A2, as confirmed by spectroscopic ellipsometry using a Cauchy model for optical modeling [84]. After the resist is applied, the samples are baked at 180 °C for 1 hour in a standard convection oven (by Heraeus electronic). It is important to note that the PMMA A4 resist had expired at the time of use and as a result the photo active compound might have gradually decomposed, affecting the required exposure dose [86].

After the baking step, an exposure step is executed by electron beam lithography (EBL) in a RAITH150-TWO system. The electron extractor was set to 30 keV, the aperture used was 10 µm. The written patterns were all gratings, consisting of 5 exposed lines of 40 µm long, where the linewidth was equal to the space between the lines. The linewidth was varied between 100 and 2000 nm. The results in this thesis will however only focus on the 100 nm grating, since in this case the feature size is closest to current technology node. The standard 100 nm grating is displayed in figure 4.9. This pattern was repeated multiple times with different area exposure doses varying between 400 µC/cm² and 60 µC/cm². Consecutive patterns are 25 µm apart. The size of the write field was 100 µm, the area step size was set to 0.01 µm.

Figure 4.9 Pattern applied by EBL (approximately on scale)

The choice of the pattern design, was completely based on practical considerations: this grating pattern was a default design included in the EBL software and could therefore be implemented fastest. To obtain a proof of concept, this design is sufficient, however usually the pattern has to be designed in a way that equally spaced spacer sidewalls can be obtained. A basic mathematical description and some considerations on pattern design can be found in [16].

After the EBL exposure, the patterned samples were developed using a developer based on a 1:3 ratio of MIBK (methyl isobutyl ketone) to IPA (isopropanol) for 60 seconds. Chain scission has occurred in the exposed areas, allowing the developer to dissolve the PMMA in these areas. To stop any slow further development of unexposed PMMA, the samples were placed in a bath of isopropanol for 60 seconds before they were blow dried by N₂. The 100nm patterns are now resolved and are ready for further processing.
4.2 Experimental Details

4.2.2 Spacer Deposition

The next processing step is the deposition of the spacer material. In chapter 3 the EE-ALD processes of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ were discussed extensively and these materials will be used for spacer deposition. Important to note is that these processes were developed on silicon substrates. As discussed in section 2.1, one needs to take into account that ozone, radicals and/or ions can possibly influence the underlying film, especially when the film is a polymer. In the next section of this chapter, section 4.3, it will be shown that the standard $\text{O}_3$ process developed for $\text{Al}_2\text{O}_3$ does not influence the polymer resist, whereas the plasma-assisted processes do. By altering the plasma parameters, however, the influence of the $\text{O}_2$ plasma on the resist can be minimized. This is shown in an experiment where the resist is exposed directly to an $\text{O}_2$ plasma, under different plasma conditions (i.e. power and pressure).

The deposition parameters used during this project for the deposition of spacer material are shown in figure 4.10.

![Figure 4.10](image)

**Figure 4.10** The deposition parameters of the three different EE-ALD processes, used for spacer deposition in the D-SDDP process. In the purge steps an argon flow of 100 sccm is used. Note that $90^\circ$ denotes the position of the butterfly valve.

The duration of the pre-plasma step was increased compared to the plasma-assisted ALD processes described in chapter 3. The increase in step time from 1 s to 2 s was needed, to obtain the higher pressure of 200 mTorr in the reaction chamber (compared to 25 mTorr in chapter 3) at which the consecutive plasma exposure step has to be executed.

4.2.3 Anisotropic Etching and Resist Removal

After the spacer material is deposited in step 3, an anisotropic etch is executed. In this project, this etch was executed in two different systems, one based on ion milling whereas the other employs reactive ion etching. In section 4.3 the results of both processes will be compared. A standard protocol developed by the FNA group at the TU/e, is used to etch the $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ spacer material in the ion miller (Roth & Rau Unilab system). In this protocol two argon flows are set: mass flow controller 1 (MFC 1) is set to an argon flow of 3 sccm and MFC 2 is set to 1.3 sccm. The Ar ICP plasma is powered using a Hüttinger RF power source (PFG 300 RF) set to deliver 120 W. Ions are extracted and the beam of ions is conditioned by two hardware boxes indicated by "Beam" and "Accelerator" which are set at 402 V / 0.01 mA and 500 V / 0.38 mA respectively. These settings result in a ion beam with a current density in the range of 840 – 940 $\mu$A/cm$^2$ and an ion energy of $\sim$ 1 keV. To prevent the sample from charging, the neutralizer is switched on to reduce the net current density reaching the sample to zero. To obtain this value the input parameters of the neutralizer i.e. $I_E$ and $I_H$ are set to 0.80 mA and 10.4 A respectively. The sample that is to be etched is attached
using silver paste to a substrate holder rotating at 20 rpm to minimize any effects of slight deviations from vertical ion impact. Ion milling starts when the substrate holder is tilted in position and a shutter is manually removed. The etch time is monitored by a stopwatch and when the required etch time has progressed the shutter is placed back again to block the ion beam. For additional background on the ion miller and the FNA protocol that is followed, the reader is referred to the bachelor thesis of T. Weekenstroo (TU/e) [87].

The RIE process is executed in an open-load Plasmalab System 100 by Oxford Instruments. A standard recipe developed by the PhI (photonic integration) research group at the TU/e is used for the etching of SiO$_2$. This recipe is based purely on a CHF$_3$ chemistry. The etch step is executed at 15 mTorr, the CHF$_3$ flow is set at 60 sccm and the plasma power is 50 W. Before and after the etch step, several pumping and purging steps are added to ensure stable and reproducible processing conditions.

Before the execution of a complete D-SDDP process, the etch rates of both the ion milling and RIE process have to be obtained for all spacer materials that will be used. This process characterization will be described in the first part of section 4.3.

After the anisotropic etch, the spacer material on top of the resist is removed (see figure 4.1) and the resist can therefore now be removed in the final D-SDDP processing step. The resist is stripped in a PVA Tepla 100 Plasma system. The stripping process that is used in this barrel etcher employs a 300 W plasma used for 30 minutes at 1.0 mbar. The oxygen flow, required to achieve this pressure is 55 ml/min. No characterization experiments were performed regarding this process step since it was assumed that a 30 minute exposure was sufficiently long to completely remove all the resist. Possibly, the exposure time can be reduced, however, considering the focus and available time for this project this was not investigated. The resist stripping process was the final step in D-SDDP process. Subsequently, the resulting patterned samples will be studied using scanning electron microscopy (SEM).

4.2.4 SEM Imaging

In a scanning electron microscope (SEM) a focussed beam of electrons is used to produce images of a sample surface. In a SEM, an electron beam is created in the same way as in an EBL system described in 4.1.2. The main difference is that during SEM imaging the electrons typically have a lower energy (~ 5 keV) compared to EBL (30 keV). In section 4.1.2 it was also explained that when an electron beam penetrates the sample, secondary electrons are created due to inelastic scattering of the primary electrons. In SEM imaging, special detectors are used to collect the signals of these secondary electrons generated at the surface which contain information about the morphology of the sample. Using these signals, a SEM can produce very high-resolution images of the sample surface, revealing details < 20 nm in size.

In this thesis a Nova 600i Nanolab Dualbeam workstation (FEI company) will be used to capture high-resolution SEM images of samples at different stages in the D-SDDP process. This tool can thus provide the images confirming whether a processing step has been executed correctly. Based on the information obtained, additions or improvements can be made in the D-SDDP process to obtain a better overall result. This dualbeam workstation is also equipped with a focussed ion beam (hence the term dualbeam), which will be used to etch a trench in the sample so that a side-view (or cross sectional view) of the spacer sidewalls can be obtained. To do this the following protocol is used: first the SEM is used to locate the area where the 100 nm gratings were produced by EBL and where consequently spacer sidewalls can be observed as a results of an EE-ALD process. When these features are located a protective platinum film is deposited on top by electron beam induced deposition (EBID), using a gaseous precursor
molecule containing platinum \((MeCpPtMe_3)\) \cite{88}. Then, the sample is tilted 52 degrees, so that the ion beam is positioned perpendicular to the sample. The ion beam utilizes ions originating from a Ga liquid metal ion source. Now, a trench is etched by the FIB using a predefined patterning method (cleaning cross section) in order to obtain the best possible etch result. A side-view SEM image can now be obtained showing the features in the D-SDDP process, since the SEM is under an angle of 52°. These cross sectional views will be displayed in the results section (section 4.3). Figure 4.11 schematically illustrates the configuration of the dualbeam workstation used to obtain a side-view of the D-SDDP features.

![Dualbeam workstation](image)

**Figure 4.11** Dualbeam workstation, illustrating how the ion beam and electron beam are located and how side-views of the D-SDDP features are created. The stage whereupon the sample is located can be tilted so that the SEM can also be used for generating top-view images.

### 4.3 Discussion and Results

This section will start (section 4.3.1) with the results obtained during two characterization experiments required to realize a full D-SDDP process. Firstly, the effect of \(O_3\) and \(O_2\) plasma on PMMA will be evaluated. Secondly, the etch rates of the different etch processes will be determined. After both topics are discussed, section 4.3.2 will continue with the results obtained during the realization of the full D-SDDP process. SEM images obtained at different stages during the process will be displayed.

#### 4.3.1 Final Process Characterization

**Plasma and \(O_3\) exposure of resist**

As mentioned in chapter 2, the reactant exposure during an EE-ALD process can possibly affect the resist (e.g. due to interaction with oxygen radicals or by ion bombardment), which is clearly unwanted during the D-SDDP process. To verify whether these effects occur, experiments were performed during which substrates covered with PMMA were exposed to a number of exposure cycles. Such a cycle consists of a 5 second \(O_2\) plasma or \(O_3\) exposure, after which a 5 second argon purge takes place, mimicking a normal ALD process but with no precursor dosing.
Chapter 4 Direct Spacer-Defined Double Patterning (D-SDDP)

Figure 4.12 shows the results of a first experiment where the PMMA resist was exposed to several exposure cycles of $O_3$ and $O_2$ plasma. Both experiments were executed in the FlexAL mark 1, where the plasma exposure was executed at 15 $mTorr$ with 200 $W$. The thickness of the resist was monitored in-situ using spectroscopic ellipsometry (SE). A Cauchy model was used to extract the thickness of the remaining photoresist layer from the SE data. Such a model can typically be used to model materials that are transparent in a large part of the visible region such as PMMA [60, 84]. Figure 4.12 displays the evolution of the resist thickness for the tested exposure conditions, as a function of the number of exposure cycles.

From figure 4.12 two things can be deduced. First and foremost an $O_3$ exposure does not affect the resist. Secondly, an $O_2$ plasma exposure results in a linear etch process, which is temperature dependent. The higher etch rate at higher temperature can be explained by the fact that there is more thermal energy available in the layer. As a consequence, bonds can be broken more easily by chemical reactions with the oxygen radicals present in the plasma (in other words: the reaction is thermally activated), possibly the process is also assisted by ion bombardment. The fact that an $O_2$ plasma has a greater effect on the resist thickness at higher temperatures, contributed to the choice for the execution of all D-SDDP processing steps at room temperature.

In developing an accurate, stable and repeatable SDDP process it is not desirable that the resist is significantly affected during the deposition of the spacer material. Therefore, under the conditions shown in figure 4.12 plasma-assisted ALD processes have to be carefully designed to meet specific requirements for implementation in a D-SDDP process. On the other hand,
plasma processes also open possibilities for the trimming of features in the resist [89] which is, however, not investigated in this project.

As mentioned before, some plasma parameters might minimize ion bombardment and radical production, which could both affect the PMMA film. Another experiment was therefore carried out to investigate the behavior of PMMA during plasma exposures at different pressures and powers. A total number of 50 exposure cycles is used and the thickness of the resist is determined before and after the exposure. The conditions for the 5 s plasma exposure were varied and the experiment was now only performed at room temperature in the FlexAL mark 2. The conditions used and the results are displayed on the horizontal axis in figure 4.13.

![Figure 4.13](image_url)

**Figure 4.13** Rate of the resist removal during 50 plasma exposures of 5s each. The plasma conditions (i.e. pressure and power) were varied.

Figure 4.13 clearly demonstrates that the rate of resist removal can be minimized at room temperature by increasing the pressure and decreasing the power.

By increasing the pressure during the plasma exposure to this extent, the amount of collisions in the plasma will increase, which will reduce the influence of ion bombardment on the PMMA film, because the plasma sheath became more collisional [27]. Also a lower plasma power contributes to this reduction since the ion flux is reduced [27]. The role of ion bombardment (or ion-radical synergism) in the removal of the PMMA resist will thus be minimized by an increase in pressure and decrease in power.

By changing these parameters, the contribution of the oxygen radicals to the resist removal is also expected to change, as described in a study by Gudmundsson et al. [34]. In that study
it was demonstrated by modeling experiments that an increase in pressure results in a slight increase in the density of atomic oxygen, whereas a decrease in power is likely to result in a more significant decrease of the density, which could also be the case here. Therefore, by reducing the power and increasing the pressure, the radical and ion flux to the surface is reduced, leading to a lower etch rate. The net effect of increasing the pressure to 200 \text{mTorr} and decreasing the power to 100 W is that etch processes can be eliminated completely, as shown by figure 4.13 for 50 exposure cycles. Furthermore, during an actual ALD process material is deposited each cycle, which will partly shield the PMMA from the plasma when the film closes. It can therefore be expected, that the PMMA film thickness is not reduced during the actual plasma-assisted ALD process at 200 \text{mTorr} and 100 W. These settings will therefore be used during deposition of spacer material.

**Determination of the etch rates of ion milling and RIE**

The second topic addressed in this section is the characterization of the etch processes (ion milling and RIE) used for the D-SDDP process. Before these techniques can be implemented, the etch rates of the different spacer materials have to be known. To do this for ion milling (IM) and RIE, samples with 100 nm of spacer material were deposited on a silicon substrate. \(\text{Al}_2\text{O}_3\) was deposited by ozone and plasma-assisted ALD, whereas \(\text{SiO}_2\) was only deposited by plasma-assisted ALD. The standard deposition parameters of these three deposition processes were discussed in section 4.2.2. The thicknesses and refractive indices of the 100 nm spacer samples were determined by SE, using a Cauchy model [60], before loading the samples in the etch tools. After the samples were etched for a specific amount of time (using the settings described in section 4.2.3), the thicknesses and refractive indices were again determined by SE. Figure 4.14 shows the reduction in thickness of the samples after etching (i.e. the amount of etched material) versus the etch time, for \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\). The etch rate was determined by fitting a linear curve through the data points, which intersects the origin of the graph. The etch rates for the spacer films deposited by different EE-ALD processes are displayed in the left top corner of figure 4.14. The etch rates of the IM process are approximately 0.1 – 0.2 nm/s and the differences can be mainly attributed to differences in film density. Section 4.1.4 already described that the etch rate was a function of the density of the material. As pointed out in chapter 3, the density can be represented by the refractive index (\(n\) increases if film density increases). The refractive indices of \(\text{Al}_2\text{O}_3\) deposited at room temperature were found to be 1.63 and 1.59 for the plasma-assisted and ozone ALD process respectively. This difference in \(n\) corresponds with the different etch rates of the \(\text{Al}_2\text{O}_3\) films deposited by ozone-based and plasma-assisted ALD, i.e. the etch rate increases as \(n\) decreases.

It is finally noted that, the refractive indices of the spacer materials determined after the IM process, showed a slight increase compared to the values measured before the IM process. The refractive index of the plasma-assisted deposited \(\text{Al}_2\text{O}_3\) film increased by 0.2%, for the ozone deposited \(\text{Al}_2\text{O}_3\) this increase was 0.6% and for the plasma-assisted \(\text{SiO}_2\) films this was 0.3%. This observation might be related to a film densification as a result of the penetration of Ar ions in the spacer layer [90]. The next section will discuss the results of the realization of this D-SDDP process.

**4.3.2 Realization of the D-SDDP process**

In this section the results of the realization of the D-SDDP process will be presented, to do this in a structured way, each processing step will be discussed individually (figure 4.1 shows all the processing steps). At each step the challenges will be discussed by evaluation of the available
Figure 4.14 Characterization of the two anisotropic etch processes, i.e. ion milling (IM) and reactive ion etching (RIE), that will be used in the D-SDDP process.

results. The first step that will be discussed is the patterning of the resist by electron beam lithography (EBL). With each step, the “step number” will be provided. which corresponds to the process flow diagram in figure 4.1.

Step 1 & 2: Application and patterning of the resist

After the PMMA photoresist film is spincoated on a sample, patterns are written on it by EBL, after which the resist is developed. Both the A4 and A2 PMMA resist can be used for the patterning. The PMMA A2 resist results in thinner resist films, causing the electron beam used in EBL to broaden less in the PMMA, so that in principle a higher resolution can be obtained. This does not play a significant role in producing the 100 nm grating, however when smaller features should be written this will become important.

The goal of the patterning and developing procedure is to produce 100 nm gratings with perfectly straight sidewalls, as seen in figure 4.15 (a). The electron dose required to produce such a pattern on Si/PMMA sample is unknown. Multiple patterns were therefore written at different electron doses to later locate the patterns with vertical sidewalls. Figure 4.15 schematically illustrates the pattern profile that is obtained if the electron dose is either too low (b) or too high (c). Due to the gaussian shape of the electron beam, an underexposure will result in sidewall profiles that are slightly tilted and resist material that is not completely removed during developing where it should have been. Overexposure can also result in tilted
sidewalls, in this case however the width is largest on the bottom due to the additional dosing by backscattered electrons.

![Figure 4.15](image)

**Figure 4.15** Schematic illustration of the possible sidewall profiles as a result of under- and overexposure during EBL.

Before continuing to the next D-SDDP processing step, the patterns produced by EBL have to be checked and the electron dose that results in vertical sidewalls has to be determined so that the ideal exposure conditions can be fixed for future sample creation. Figure 4.16 shows a top-view SEM image that confirms that a 100 \( \text{nm} \) grating is transferred to the PMMA with an accuracy that is sufficiently high to realize a D-SDDP process at this scale.

![Figure 4.16](image)

**Figure 4.16** A top-view SEM image of the 100 \( \text{nm} \) grating used as the standard pattern for the realization of a D-SDDP process.

The sidewall profile can, however, not be checked using this SEM image, because to do this a side-view is needed that includes a FIB etch as explained in section 4.2.4. Unfortunately, the FIB etch drastically influences the polymer resist layer and causes deformation of the sidewall profile. This effect even occurs when a protective Pt film is applied before the FIB is used. Therefore, at this stage no information about the sidewall profile can be obtained. After the spacer material is applied however, it is possible to obtain this information. The inorganic spacer material provides some mechanical support, helping the resist to maintain its original shape during the FIB etch.
4.3 Discussion and Results

The side-view SEM images made after spacer deposition, which could provide information about the sidewall profile, revealed some problems concerning the reproducibility of the starting pattern in the PMMA. It turned out that in some cases, only an electron dose of 400 \( \mu C/cm^2 \) resulted in the complete development of the PMMA A4 layer, while in other cases a dose of 200 \( \mu C/cm^2 \) was already sufficient to remove the resist after the development. Possibly, the fact that the expiration date of the PMMA A4 had passed, might be of influence on the results after EBL. However, the reproducibility issue might also originate from the resist baking step. Slight deviations in the bake temperature might result in different behavior of the PMMA upon electron exposure.

Due to this reproducibility issue it was not possible to establish the electron dose required for the production of patterns with vertical sidewalls. Therefore, multiple patterns that had received different electron doses will be studied during SEM imaging. The patterns with the most vertical sidewalls will be used to generate the final SEM images that are displayed in the upcoming sections.

**Step 3: Depositing the spacer materials**

After the deposition of a spacer film (\( Al_2O_3 \) or \( SiO_2 \)) on either patterned PMMA A4 or A2, problems were encountered during successive SEM imaging. While imaging, blister growth was observed in real-time. Frequently, such a blister continued to grow until it burst, during which spacer material was scattered across the sample surface. Figure 4.17 displays a SEM image showing some blisters before and after they had burst for the case of a \( Al_2O_3 \) spacer film applied on top of PMMA A4. For \( SiO_2 \) as the spacer material similar effects were observed.

![Figure 4.17](image)

*Figure 4.17* A top-view SEM image showing blisters that are produced due to outgassing of the resist during SEM imaging. In some cases the blisters burst, scattering spacer material across the sample. The figure shows a SEM image of a sample with PMMA A4 where a \( Al_2O_3 \) was applied as spacer material by O\(_3\) ALD.

The blister formation is expected to originate from a combination of a high vacuum during SEM imaging (\( \sim 10^{-5} \) mbar) and the interaction of the PMMA with the electron beam. The e-beam might induce chemical changes in the resist which results in the release of gaseous products (possibly \( H_2 \) and \( CH_4 \)), which are "pulled out" due to the high vacuum. Additionally, a high vacuum alone might already facilitate evaporation of any remaining solvents in the
PMMA layer, causing the outgassing issues. The presence of some solvents in the layer, might be related to a ineffective baking step. This issue should be addressed in future research.

Due to the gas-barrier properties of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$, these gasses can not escape to the surface and as a result a pressure is built up beneath the spacer material [43, 44, 55]. This causes de-attachment of the spacer film with the PMMA layer and consequently a blister is formed. The blisters that form during SEM imaging can grow to over 500 $\mu\text{m}$ in diameter. Clearly, this can have an effect on a single pattern that has smaller dimensions. Figure 4.18 displays a SEM image at a higher magnification, also showing a single pattern.

![Figure 4.18](image)

**Figure 4.18** Two side-view SEM images providing an overview of the sample. Its surface is drastically affected by the outgassing of the resist. Deformation of the resist occurs as a result, which can affect the sidewall profile of the pattern. This is a SEM image of a sample with PMMA A4 where a $\text{SiO}_2$ was applied as spacer material by plasma-assisted ALD.

This figure illustrates a piece of spacer material that was scattered across the sample. Furthermore, the SEM image on the right shows possible deformation-effects as a result of the outgassing process. Outgassing results in stress within the PMMA layer and might therefore cause deformation of the PMMA layer. This effect could cause attached sidewalls to be forced out of their original location.

For instance, one of the four spacer coated features in the center of the right SEM image in figure 4.18 shows a deviating shape compared to the other features and shows a void in its interior. It is likely that this deformation of the spacer and formation of the void is the result of outgassing effects. Furthermore, on the left and right of the etched trench similar voids in the PMMA can be observed, which might be related to a deformation of the most outer spacers sidewall, which seem to be pulled down towards the PMMA side.

Figure 4.17 and 4.18 illustrate that imaging can be considered as destructive and therefore these samples were not used for further processing. It might be possible to reduce or even eliminate the effect of outgassing by executing a vacuum baking step before the spacer material is deposited, however care should be taken that heating the patterned PMMA does not result in a change of the applied pattern.

Despite the effects of outgassing, side-view SEM images could be obtained of a 100 nm grating coated with spacer material. Careful considerations have to be made however when interpreting these images. Figure 4.19 displays two side-view SEM images obtained after (a) a $\text{SiO}_2$ spacer deposition on patterned PMMA A4 by plasma-assisted ALD and (b) a $\text{Al}_2\text{O}_3$ deposi-
tion by ozone ALD on patterned PMMA A2. Both SEM images show that the spacer film
applied by both EE-ALD techniques is deposited uniformly and conformal.

![SEM images](image)

**Figure 4.19** Side-view SEM images of a single 100 nm grating coated with spacer material: image (a) displays PMMA A4 with SiO$_2$ as spacer deposited by plasma-assisted ALD; image (b) displays PMMA A2 with Al$_2$O$_3$ as spacer deposited by ozone ALD.

Figure 4.19 (a) shows that unexposed PMMA A4 has maintained its original thickness, confirming that the plasma did not facilitate in resist-removal during deposition. The shape of the features is however unexpected. It is not likely that this "hour-glass" shape is a result of the plasma exposure since the results so far confirmed that the PMMA was not affected by the O$_2$ plasma in the deposition process. Furthermore, if plasma processing would have any effect on the features, some rounding of the top corners would be expected in stead of this curving [18].

A possible explanation for this hour-glass-shape might be twofold. First, the shape could be related to the manner in which outgassing took place. The most right feature in figure 4.19 (a) shows a void in the center which is possibly a result of outgassing. It illustrates that the manner of outgassing can have an impact on the shape of a feature, if the outgassing process does not result in a void in the interior it might in the end result in the hour glass shape.

Secondly, the EBID Pt deposition, part of the procedure for making the cross-sectional SEM images, might have affected the features. Possibly, the EBID of Pt resulted in stress in the PMMA feature coated with spacer material. Forces as a result of stress might not be balanced at the center of the vertical spacer sidewalls because of the difference in material properties of the Pt and PMMA that surround the sidewall. The spacer-coated PMMA feature behaves like an empty plastic bottle, which can easily be deformed in the center since the edges provide the most mechanical strength. The void in the most right spacer-coated PMMA feature (figure 4.19 (a)) could possibly have contained trapped gas, which might have exerted a force that resulted in a different deformation of the spacer sidewalls.

In the case of figure 4.19 (b) the first thing to be noted about this SEM image, is that the
thickness of the PMMA A2 decreased from its original thickness of 80 nm to approximately 50 nm. The Al₂O₃ spacer was applied by ozone ALD, for which an effect of O₃ on the spacer material has already been excluded. The exact same experimental procedures were used for the different PMMA A4 and PMMA A2 resist. This might have caused the reduction in thickness and the experimental procedures (e.g. electron doses, development time and length of isopropanol bath) have to be altered for the thinner A2 resist. It might also be possible that this behavior is typical for PMMA and that the effect is less pronounced in the A4 resist as a results of its expiration. Nevertheless, this behavior is noted, but not investigated any further.

Finally, it is noteworthy that no peculiar feature profiles were observed in figure 4.19 (b), although in top-view SEM images similar to figure 4.17, outgassing was also observed for samples based on PMMA A2. It can be argued that since the features are significantly smaller, the inorganic spacer provides more mechanical stability preventing deformations.

**Step 4: Anisotropically etching the spacer**

The etch rates determined in section 4.3.1 for IM and RIE, were used to calculate the required etch time during execution of the etch step in the D-SDDP process. It was found however, that the actual etch rate of the IM process had increased when integrated in the D-SDDP process flow. This effect is illustrated by figure 4.20 (b), which shows that the height of the spacer is approximately 160 nm while the original resist thickness was 250 nm. Moreover, figure 4.20 (a) shows blister patterns similar to what was observed in figure 4.17 and 4.18. This result indicates that also the ion milling process might induce outgassing.

The difference between the etch rate found in section 4.3.1 and the actual etch rate is likely to originate from the fact that the characterization experiments were not performed using spacer films deposited on PMMA. Actual etch rates might have been enhanced by stress at the PMMA-spacer interface due to the outgassing during IM.

Furthermore, the redeposition of spacer material after blisters have burst open due the outgassing of the underlying PMMA film, is problematic with respect to further processing. After redeposition the scattered spacer material acts as an additional etch mask, which causes the blister patterns to be transferred into the PMMA layer or silicon substrate during the etch process. Additionally, redeposited spacer material can cover the complete 100 nm gratings that are of interest for the D-SDDP process, making it impossible to successfully realize the process.

It is likely that the outgassing during the IM process, results in a deviation of the actual etch rate compared to the etch rate determined in the characterization experiment. A combination of a high vacuum (∼10⁻⁵ mbar) during ion milling and impact of energetic particles that can induce chemical changes in the PMMA, might be the cause of the outgassing issue. This was observed during SEM imaging as well, as described in a previous section. As a result of the outgassing, the IM process can not be characterized accurately, i.e. deformations of the spacer sidewalls can occur and it is not possible to control the etch depth.

The spacer sidewalls of samples that were created using PMMA A2, as seen in figure 4.19 (b), were completely lost after ion milling as a result. The height of the features in this figure was simply too small, so that the overetching (as a result of the increased actual etch rate) resulted in the removal of all spacer material as illustrated by SEM images presented in appendix C. Therefore, it was decided to only use PMMA A4 in further experiments. The A4 resist allowed for inaccurate etching times, since the spacer sidewalls were higher. Ideally, the PMMA A2 resist would be preferred since figure 4.19 showed that due to the smaller thickness the spacer sidewalls are less influenced by deformations of the patterned photoresist.
4.3 Discussion and Results

Figure 4.20 The top-view SEM image (a) illustrates that due to the scattering of spacer material as a result of outgassing, blister patterns remain after the anisotropic etch step. The side-view SEM image (b) shows a single 100nm grating after Al₂O₃ spacer deposition and an anisotropic etch by ion milling.

For Al₂O₃ as the spacer material, ion milling was the only etching process available. For the SiO₂ spacer however, a RIE process could also be used, which could possibly provide a solution for the outgassing during the IM process. A RIE process has a more chemical nature compared to ion milling and the ion energies during RIE are considerably lower (< 500 eV), which could lead to different processing results. Due to availability issues however, the utilization of this technique was very limited. Only the final paragraph that discusses the results after a full D-SDDP process will present some results obtained using RIE.

The side-view SEM image in figure 4.20 (b), clearly shows that the spacer sidewalls were not aligned vertical. Instead, they are tilted inwards, with the top towards the side where the PMMA is located. The spacer material in this case was Al₂O₃ deposited by ozone ALD. It was not possible to locate a single 100nm grating with vertically aligned sidewalls. In all cases in which the PMMA was completely developed the spacer sidewalls were tilted towards the PMMA side.

It should however also be noted that the width of the tilted spacer is approximately 21 nm as determined from the SEM image and remains constant for the entire spacer. This
is in good agreement with the 20 nm that was deposited as determined by SE performed on a similar reference sample (only without patterns) on which the $\text{Al}_2\text{O}_3$ spacer film was deposited simultaneously. This suggests that it is plausible that during most of the milling time the sidewalls were standing approximately vertical. Otherwise the width of the spacer sidewall would have decreased, since a tilted sidewall would be exposed to the vertical ion bombardment used to anisotropically etch the spacer. It might be possible that the angle of the spacer sidewalls did not start to deviate immediately after the milling process had started. Possibly, deviations only occur, once the horizontal part of the spacer on top of the PMMA is etched, since then the feature has lost some mechanical strength. If the etch could be stopped exactly at this moment, vertical sidewalls might be obtained. This did not happen, however, because the actual etch time was based on the flawed etch rates obtained in the characterization experiment. Therefore, ion bombardment continued while the vertical free-standing sidewall was surrounded by PMMA on one side and no material on the other side. Since PMMA is less dense than $\text{Al}_2\text{O}_3$ it etched faster during ion milling (see section 4.1.4).

It is hypothesized that this different etching behavior resulted in stress in the feature consisting of the remaining PMMA and the attached sidewalls, causing the top of the spacer sidewalls to tilt towards the PMMA. Also in the next paragraph this deviation of the spacer sidewall towards the PMMA side will be discussed.

When sidewalls are tilted as drastically as in figure 4.20, they can not be used as an etch mask to etch down in a target layer. Furthermore, it might be difficult to completely remove the remaining resist under the tilted sidewall. Despite this result, samples where the full D-SDDP process was performed using $\text{Al}_2\text{O}_3$ as spacer material will still be studied in the next paragraph to gain insight in the final processing step, the resist removal. That paragraph will also display the results of a full D-SDDP process using $\text{SiO}_2$ as spacer material.

**Step 5: Removal of the resist**

In figure 4.21 and 4.22 SEM images are shown of two attempts that were created after execution of the full D-SDDP process implementing an ion milling process for the anisotropic etch step. Figure 4.21 shows a sample that utilized: PMMA A4 as the resist; an $\text{Al}_2\text{O}_3$ spacer deposited by ozone ALD; ion milling for the anisotropic etch and a 30 minute $\text{O}_2$ plasma strip to remove the resist.

The first thing that should be addressed when analyzing this figure is the contrast with figure 4.20 (b). The only difference in terms of processing conditions was the execution of the resist removal step by plasma stripping. Apparently, this step caused the spacer sidewalls to bend, in order to form a closed circular feature. The deviation of the spacer sidewall is towards the side where the PMMA used to be. This direction is in agreement with the SEM image in the previous paragraph which showed tilted sidewalls (figure 4.20 (b)). The difference is, however, that the spacer sidewall is now curved. This effect could only be caused by the plasma stripping procedure.

The plasma stripping process has a duration of 30 minutes and in this period the sample is exposed to an oxygen plasma at 300 W. During this processing step it is not possible to actively control the substrate temperature, whereas it is expected that the temperature will increase due to plasma radiation, ion bombardment and chemical surface reactions [91]. After the plasma stripping process an increased sample temperature was indeed noticed during manual handling of the sample.

It is expected that the curving of the spacer sidewalls might be a result of the increased processing temperature. In the initial stages of the plasma stripping step, the $\text{Al}_2\text{O}_3$ spacers were
4.3 Discussion and Results

Figure 4.21 A top-view (a) and side-view (b) SEM image of a sample after the full D-SDDP process had been executed. During the process $Al_2O_3$ deposited by ozone ALD was used as the spacer material and ion milling was used for the anisotropic etch.

in contact with a significant amount of PMMA. A difference in thermal expansion behavior of the PMMA and the attached spacer sidewall, could have caused strain in the system during processing, which might have resulted in the curving of the spacer sidewall.

A similar effect is shown in figure 4.22, although to a smaller extent. This figure shows a sample for which PMMA A4 was used as the resist; an $SiO_2$ spacer deposited by plasma-assisted ALD; ion milling for the anisotropic etch and a 30 minute $O_2$ plasma strip to remove the resist.

The side-view SEM image shows that, the spacers are tilted towards the location where the PMMA used to be, which is in agreement with comparable SEM images discussed so far. The curving of the $SiO_2$ spacer sidewalls is less apparent than for $Al_2O_3$ however, and free standing spacer sidewalls can be observed in the top-view SEM image in figure 4.22.

Finally, results will be shown of a full D-SDDP process where a RIE etching process was used, instead of ion milling. As mentioned in the previous paragraph, the issues related to redeposition and outgassing might be less significant, due to the more chemical nature of the etch and the lower ion energies. It should also be noted that the RIE process is executed at a significantly higher pressure ($\sim 10^{-2}$ mbar) compared to the IM process and the pressures during SEM imaging. This might also seriously contribute to a minimization of any outgassing issues.

Furthermore, another change was made in the D-SDDP process compared to the D-SDDP processes used for figure 4.21 and 4.22. A 10 minute acetone bath at room temperature was used to remove the remaining resist, instead of the plasma stripping process. The result of this full D-SDDP process is displayed in 4.23, which for completeness also utilized PMMA A4 as the resist and a $SiO_2$ spacer deposited by plasma-assisted ALD.

The top-view SEM image (figure 4.23 (a)) shows that free standing spacer sidewalls were obtained in this full D-SDDP process. During imaging no blister patterns could be observed.
Figure 4.22 A top-view (a) and side-view (b) SEM image of a sample after completion of the full D-SDDP process. This process used a SiO$_2$ spacer deposited by plasma-assisted ALD and ion milling for the anisotropic etch.

as also seen in the top-view image. This confirms that no outgassing issues occur during a RIE process as a result of the lower vacuum and the lower energy of ions impacting on the surface. Additionally, no top-view SEM images showed any PMMA remnants, indicating that an acetone bath can be employed to successfully remove the PMMA. However, the quality of this resist removal step has to be confirmed by future experiments also using this resist removal technique. Possibly, some issues regarding this technique might reveal itself.

The side-view SEM image in figure 4.23 (b), also confirms that free standing SiO$_2$ spacer sidewalls can be successfully obtained with a close to vertical alignment. Most spacers tend to show a very small deviation to the side where originally the PMMA was located. In the previous discussion such deviations were linked to stress in the feature consisting of the PMMA and the attached spacer sidewalls, that could originate from ion bombardment or increased processing temperatures. I could therefore be possible that this small deviation might be an affect of the RIE process, during which ion bombardment takes place and temperature might increase due to the transfer of energy from the plasma to the substrate. Compared to all other results presented so far the deviation of the spacer sidewall from vertical alignment is small and therefore, the full D-SDDP process illustrated in figure 4.23 is considered to be the most successful.

The darker areas between the spacer sidewalls observed in figure 4.23 (b), are probably a result of the Pt EBID process that was used to deposit a protective layer so that a side-view SEM image could be obtained. It was not possible to conformally coat/fill the trench by EBID and consequently a void is created that causes the darker area.

Finally, the height of the spacer sidewalls is approximately 250 nm, as was expected since this was the thickness of the PMMA A4 on which the starting pattern was created. The actual etch rate during a D-SDDP process did not deviate from the etch rate determined during the
4.4 Conclusions

This chapter described the realization of the complete Direct Spacer-Defined Double Pattern-ing process and the exploration of all involved processing steps. This section will first discuss all individual processing steps in the D-SDDP process, after which some conclusions will be presented on the fully executed D-SDDP processes in this work. Finally, an overview will be given on the challenges that were encountered during the individual process steps and during the complete process. In this overview also some recommendations will be provided.

The starting pattern for the D-SDDP process was created by electron beam lithography (EBL). It was shown that a 100 nm grating, could be successfully transferred in both PMMA A4 and A2 resists. Two types of EE-ALD processes (ozone-based and plasma-assisted) were used to

Figure 4.23 A top-view (a) and side-view (b) SEM image of a sample after the full D-SDDP process has been executed using SiO₂ deposited by plasma-assisted ALD as the spacer material, RIE for the anisotropic etch and a acetone bath for the resist removal.

process characterization described in section 4.3.1.
Chapter 4 Direct Spacer-Defined Double Patterning (D-SDDP)

successfully deposit a conformal spacer film on top of the patterned resist layers. When the deposition parameters were chosen well, it was shown that the deposition process did not affect the PMMA film. An ion milling process was utilized to anisotropically etch both $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ spacers. For the $\text{SiO}_2$ spacer however, also a reactive ion etch (RIE) process could be successfully employed. Results indicated that the PMMA remaining after the etch step could be removed by a plasma stripping process provided that the remaining spacer sidewalls did not completely enclose any PMMA. It was also shown that an acetone bath can be used to remove the PMMA resist.

After individual optimization and exploration, the individual steps were integrated to realize a full D-SDDP process. The full process was executed three times under different processing conditions. It can be concluded that at this moment the encountered issues in the realization of a D-SDDP process using $\text{Al}_2\text{O}_3$ as spacer material could not be overcome when a 100 nm grating was used as the starting resist pattern. No free standing spacer sidewalls were observed when PMMA A4 was used. SEM images after $\text{Al}_2\text{O}_3$ spacer deposition on PMMA A2, however proved to be promising. In this case unfortunately the inaccuracy in the etch rate of the ion milling process as a result of outgassing prevented the realization of a full D-SDDP process.

The realization of a D-SDDP process using $\text{SiO}_2$ as spacer material and ion milling to perform the etch step, could however be considered successful. Results have shown that free standing spacer sidewalls could be obtained. Although, the alignment was not completely vertical, these sidewalls can in principle be used as a mask to etch in a target layer.

The third and final full D-SDDP process that was executed utilized $\text{SiO}_2$ as spacer material and employed RIE as the etch method. In this process the resist was removed by an acetone bath. Results show that free-standing vertically aligned spacer sidewalls could be obtained. This process could therefore be considered as the most successful attempt, and actual proof of a successful realization of D-SDDP.

During realization of a full D-SDDP process several issues were encountered that can have a significant effect on the result of the process. These issues are summarized in the overview that will be provided momentarily. Also a number of specific challenges can be formulated as a result of the knowledge that was obtained for each individual processing step. These challenges will also be incorporated in this overview, as well as several recommendations.

**Issues / Challenges / Recommendations**

- *Reproducibility of the starting pattern:*
  The first issue that was encountered concerned the reproducibility of patterns created in the PMMA resist by EBL at different electron doses. For the PMMA A4 resist, it was not possible to establish the electron dose needed to obtain a developed pattern with vertical sidewalls. Possibly, this is related to the expiration of the A4 resist. For the PMMA A2 resist (which was not expired) the reproducibility was not investigated since only one exposure by EBL was performed. In order to confirm whether the reproducibility is related to the expiration date of the resist, it recommended to test the reproducibility using the PMMA A2 resist. Furthermore, it is also possible that the reproducibility issue originates from slight differences in the resist baking step. Since the baking step was possibly also connected to the outgassing future work should look into this.

- *Outgassing of the resist:*
Both PMMA resists used suffer from outgassing issues as a possible result of high vacuum processing and impact of energetic particles (electrons and ions). Outgassing was shown to lead to deformation of the resist and consequently of the spacer sidewalls. As a result, the final result of a D-SDDP process is seriously affected. The fact that the spacers of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ that were used in this work, possess gas-barrier properties could have led to an additional amount stress in the system during outgassing, which proved not to be beneficial for the D-SDDP process. Outgassing could possibly be reduced by adjusting several experimental procedures, especially the resist baking step should be investigated in more detail. An ineffective baking step might leave some solvents in the PMMA layer, which might cause outgassing issue during high vacuum processing. It is recommended that the addition of a hard-bake step after the development of the resist is investigated, since this can possibly reduce outgassing. Another approach might be to investigate different spacer materials, in particular the ones that allow the gaseous products of outgassing to escape the system. Finally, different photoresist materials and also different lithography techniques might be investigated that possibly show no outgassing issues after development.

- **Trimming the resist by a plasma exposure:**
  The parameters of the plasma-assisted ALD processes, employed to deposit the spacers, were chosen such that the patterned resist film was not affected by the plasma species. A plasma exposure before or during the spacer deposition could however also be used deliberately to trim the patterned features. A trimming process might also induce outgassing of the resist as a result of ion bombardment. This can possibly reduce the outgassing and related deformations during later processing steps.

- **Etching by Ion Milling:**
  As stated, it was found that the ion milling process induced outgassing and this effect contributed to the deviation found between the actual etch rate and the etch rate obtained during process characterization. If the outgassing issues are solved it is expected that an accurate characterization of the etch rates can be achieved. However, a more accurate characterization of the etch rate might still be possible even if outgassing effects remain. If that can be achieved, the relatively thing PMMA A2 can be used for the realization of a D-SDDP process. Intermediate results showed that this particular resist is of great interest, since outgassing had less influence on the spacer profile because features were more mechanically strong due to smaller size. Furthermore, if the distance between spacers is to be further decreased, the A2 resist offers a better resolution for EBL than PMMA A4.

- **Resist Stripping**
  Results have indicated that the plasma stripping process resulted in a deformation of the spacer sidewalls, as a consequence the spacers deviated significantly from the desired vertical alignment. This deformation could be connected to an elevated processing temperature. Although the plasma stripping process successfully removed all resist material, the procedure that was applied in this work is considered non-preferential in a D-SDDP process. Therefore, the plasma stripping should be investigated in more detail so that the process could be adapted so that it has no influence on the spacer sidewall. Additionally, the resist removal using an acetone bath should be further explored. Preliminary results have indicated this technique can also successfully remove the resist, although the quality of the resist removal should be confirmed by additional experiments. If required, an increase of the acetone temperature could possibly enhance the
resist removal. Although the effect of the increased temperature should be monitored carefully. Another possibility is to combine this wet technique at room temperature with a very short plasma exposure to remove final remnants of PMMA.

In conclusion: the demonstration and exploration of the D-SDDP has delivered some great insights with respect to the issues encountered at all processing steps, and offers many possibilities for future research.

4.5 Outlook

When the issues described in section 4.4 can be solved or circumvented, the D-SDDP process might be taken to the next level: quadruple patterning. The concept of quadruple patterning is illustrated by figure 4.24. In this patterning technique, a second spacer material is deposited after a single SDDP process is executed. The spacer sidewalls of the first spacer material are now coated by a second spacer material and again an anisotropic etch step is performed after which the first spacer material is removed selectively. For the implementation of a quadruple patterning process, a proper choice of the two spacer materials is of key importance. It is necessary to select two materials that can be etched by a process that can obtain a good etch selectivity between the two.

In section 4.3.1 it was shown that a selectivity of approximately 1:3 can be obtained for $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ during an ion milling process. This already offers some possibilities for quadruple patterning. The selectivity can possibly be enhanced drastically in a RIE process used to etch the $\text{SiO}_2$. Therefore, if $\text{SiO}_2$ is used as the first spacer material and $\text{Al}_2\text{O}_3$ as the second, then the RIE process can be employed to remove the $\text{SiO}_2$ from between the $\text{Al}_2\text{O}_3$ spacers with a high selectivity, bringing a quadruple patterning process within reach. Unfortunately, samples containing $\text{Al}_2\text{O}_3$ are not allowed in the current RIE reactor, to prevent contamination. In the future a new RIE reactor will be installed in the TU/e cleanroom where these kind of experiments can be done.

Figure 4.24 A direct quadruple patterning process scheme using a photoresist (orange) directly applied on top of the target layer (light grey). The first spacer material (green) is deposited on top of the patterned photoresist. After an anisotropic etch and a resist removal step, the remaining spacer sidewalls are coated by a second spacer material (purple). The second spacer material is now etched, after which another etching process is used to selectively remove the first spacer material. The mask consisting of the spacer sidewalls of the second spacer material can now be used to etch down in a target layer.
Chapter 5

General Conclusions

This chapter will return on the project goals as formulated in section 1.6. The main project goal was formulated as follows:

The realization and the exploration of the Direct Spacer-Defined Double Patterning (D-SDDP) process using energy-enhanced atomic layer deposition (EE-ALD).

In order to attain this main goal, several sub-goals were defined that could be divided into two categories being 1) a comprehensive study of EE-ALD and 2) the integration of all D-SDDP processing steps. This chapter will first discuss the conclusions that can be drawn with respect to the sub-goals, after which the overall conclusions will be drawn.

5.1 A comprehensive study of two energy-enhanced ALD techniques

An essential step in the D-SDDP process is the deposition of the spacer material on top of a layer of patterned resist. This needs to be done in a controlled way, since the width of the resulting features of a D-SDDP process is determined by the spacer thickness. For this reason, the spacer layer has to be deposited at a relatively low temperature and with a control of the thickness on the sub-nanometer scale, which makes EE-ALD the method of choice. Three EE-ALD processes were successfully developed, each with a relatively high growth rate at room temperature (> 1 Å/cycle).

Initial experiments using the O₃ generator, showed that for maximum ozone output the generator should be operated at a power of 150 W and that the optimal pressure during an O₃ exposure step in an ALD process is 250 mTorr. Only for Al₂O₃ a successful ozone ALD process could be developed at low temperature. The ozone ALD process for SiO₂ was not feasible at room temperature. The reason was the surface chemistry at 25 °C using the SAM.24 precursor that resulted in Si-H bonds after the precursor dosing step which were less reactive to ozone and prevented film growth.

The ozone-based ALD process developed for Al₂O₃ resulted in a process with a growth rate of 1.1 Å/cycle. For increasing substrate temperatures during deposition, the number of Al atoms deposited per cycle increased, indicating the thermal energy provided by the substrate heater influenced the surface chemistry. Furthermore, the film density increased with increasing substrate temperature as a result of a lower amount of -OH groups incorporated in the films. Carbon was incorporated as well, mainly in the form of formates and carbonates, especially at
the low deposition temperatures. The film composition does not necessarily provide drawbacks for the implementation of $\text{Al}_2\text{O}_3$ deposited by ozone ALD in the D-SDDP process (although this might become of importance for actual applications).

Plasma-assisted ALD processes could be successfully developed for both $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ at room temperature using an $\text{O}_2$ plasma. The integration of a plasma-assisted ALD process in a D-SDDP process proved to be less straightforward than was the case for ozone ALD. Results showed that, depending on the process parameters such as plasma power and pressure, the plasma species could affect the patterned resist layer. A relatively low power and high pressure during in the plasma-assisted ALD process resulted, however, in elimination of these effects.

The development of the plasma-assisted ALD processes for $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ resulted in processes with a growth rate at room temperature of 1.5 and 1.2 Å/cycle, respectively. Upon an increase of the substrate temperature, the number of Al and Si atoms deposited per cycle decreased, due to thermally activated dehydroxylation reactions. The film density increased with increasing substrate temperature, related predominately to a decrease in the incorporation of -OH groups into the films. Due to the increased reactivity of the species in the plasma, the plasma-assisted processes for both $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ resulted in an only limited amount of carbon incorporation, even at room temperature.

5.2 Integration of all D-SDDP processing steps

The D-SDDP process, starts with patterning of a resist layer. In the subsequent step, the spacer is deposited on top of this patterned resist by EE-ALD, after which an anisotropic etch is performed. After removal of the resist, the free standing spacer sidewalls remain.

It was shown that EBL could be successfully employed to create 100 nm grating patterns in two types of PMMA resist (both A2 and A4). Reproducibility issues were encountered, however, for the A4 resist, which could possibly be related to the fact that the resist had expired or to an ineffective resist baking step. When PMMA A2 was used, instead of A4, higher resolutions could be obtained because the resist layer obtained after spin-coating is thinner and thus results is less beam broadening.

The most significant challenge that was encountered regarding the PMMA resists, was outgassing, which occurred at a high vacuum when D-SDDP structures were studied by SEM at intermediate steps or when they were exposed to ions during the ion milling process. Outgassing resulted in deformation of the resist patterns, which, consequently affected the shape of the spacer sidewalls.

As mentioned in the previous section, both the ozone-based and plasma-assisted ALD processes could be used for the deposition of the spacers without affecting the resist. Due to the gas barrier properties of $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$, additional stress in the system was built up during outgassing which contributed to destructive effects.

For the anisotropic etch step, two methods were investigated; Ion Milling (IM) and RIE. The high vacuum and high ion energies promoted outgassing during the IM process, which consequently made it difficult to control the etch depth during processing. So far, this rendered the use of the PMMA A2 resist in a D-SDDP process unfeasible. It was shown that only for the $\text{SiO}_2$ spacer a RIE process could be successfully employed in D-SDDP, without significant outgassing issues. Furthermore, the RIE process offered good control of the etch depth during processing.

For the resist removal step it was shown that the plasma stripping process resulted in deformation of the spacer sidewalls. This effect is likely related to an significant increase in sample temperature during this processing step as a result of heat transfer between plasma and sur-

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face. These effects can be avoided, when an alternative acetone-based resist removal step is used. Preliminary results have shown that an acetone bath can also be used successfully for removing all remaining PMMA.

The combination and integration of all processing steps just described lead to very promising results, showing that vertically aligned free standing spacer sidewalls could be obtained after execution of a complete D-SDDP process. Future work will have to focus on the optimization of each individual processing step and on optimizing the shape of the resulting structures. Nevertheless, a successful realization of the D-SDDP was achieved. With respect to the main project goal, it can therefore be concluded that the exploration and realization of the Direct Spacer-Defined Double Patterning process using energy-enhanced atomic layer deposition was successful.

Suggestions for future work are to further minimize the distance between the spacer sidewalls and to realize a successful D-SDDP process on a smaller scale. Moreover, to scale down feature sizes even further and to control the pitch (i.e. the distance between two spacers), the application of two subsequent SDDP processes (quadruple patterning) can be investigated. Finally, when the whole D-SDDP process is optimized, it can be added to the process portfolio of the Nanolab @ TU/e cleanroom after which it can be used for the fabrication of nano-devices such as FinFETS or NAND-flash memory cells.
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Appendix A

Performance data Absolute Ozone Atlas generator

This appendix displays the performance data that was provided by the manufacturer of the Atlas ozone generator. Figure A.1 shows the ozone concentration and the ozone production of the generator as a function of the flow. As stated in chapter 2 the oxygen flow into the generator is 250 sccm, or 0.250 slp.

![Figure A.1](image-url)

As is seen from figure A.1, at the settings where the $O_3$ generator is operated during this thesis the $O_3$ concentration by weight is optimal. However the amount (g/h) of $O_3$ generated at this setting is relatively low.
Appendix B

Influence of pressure on the $O_3$ exposure saturation curve

This appendix discusses an initial experiment in the development of ozone ALD processes. The ALD process of $Al_2O_3$ is a well studied and exemplary process that demonstrates the merits of ALD [14]. Next to the availability, this will be an ideal process to start the development of $O_3$ ALD. An experiment was executed on the FlexAL mark 1 at a substrate temperature of $200^\circ C$. The first step in developing an ozone ALD process is to determine the saturation curves. As explained in section 1.5 an ALD process consists of four steps: the precursor dosing, the precursor purge, the reactant dosing and the reactant purge. The precursor and reactant dosing have to be long enough so that all surface sites have reacted. The purge steps have to be long enough to ensure no CVD like processes also occur. The thermal and plasma ALD process of $Al_2O_3$ on the FlexAl mark 1 were already developed. Since the same aluminum precursor will be used to develop the ozone process, namely TMA, the precursor dose time and the precursor purge time can be taken from these processes. The TMA dosing time is 20 ms, the purge step after the precursor exposure is set to 3 s. Since the $O_3$ exposure time is of most interest, this will be investigated, therefore the reactant purge step will be set to 7 s. This is a very long purge step to ensure the process is within saturation.

The saturation curve for the $O_3$ exposure step, made by varying the exposure time and looking at the growth per cycle (GPC), is displayed in figure B.1. The first saturation curve made, was based on a process where all four process steps were executed with a completely open butterfly valve. This butterfly valve between the reaction chamber and the pump, can be varied in angle between fully opened ($90^\circ$) and closed ($0^\circ$), to obtain certain process pressures. The red points in figure B.1 resemble this saturation curve with a fully opened butterfly valve. The GPC that was obtained, was relatively low compared to the thermal and plasma-assisted ALD processes of $Al_2O_3$ already developed on the FlexAl system. Also the required exposure time was very long, even though saturation was not even reached. Apparently there are relatively few $O_3$ molecules present to react with all surface sites. To increase the amount of $O_3$ molecules, the pressure can be increased by closing the butterfly valve. During the ozone exposure step the position of this valve was set in order to achieve a pressure of $250mTorr$ (maximum operating pressure). The curve in figure B.1 with the black points shows the obtained saturation curve under these conditions.

It is clear from figure B.1 that increasing the pressure to $250mTorr$, results in a faster saturation. In chapter 3 the $O_3$ ALD process will be developed further and more detailed information will be given. However it should be clear that future experiments were an ozone ALD process is used all had an $O_3$ exposure at a pressure of $250mTorr$.
Chapter B Influence of pressure on the $O_3$ exposure saturation curve

Figure B.1 Saturation curve of the $O_3$ exposure step in the ozone ALD process of $Al_2O_3$. The two curves resembling different operating pressures show different saturation behavior.
Appendix C

Result of inaccuracy in the ion milling process in D-SDDP using PMMA A2

In chapter 4 it became clear that the etch rates for the ion milling process determined by the etch characterization experiments differed from the actual etch rates in the D-SDDP process. This resulted in an inaccurate ion milling process, which consequentially lead to the systematic overetching during the D-SDDP process. When PMMA A2 was used this overetching caused the removal of all spacer material and hence PMMA A2 could not be used to realize a D-SDDP process. The SEM images displayed in figure C.1 proof that indeed all spacer material was removed. Figure C.1 (a) shows a side-view of a 100 nm grating after Al₂O₃ was deposited as spacer material by ozone ALD. Figure C.1 (b) shows a top-view of the same pattern after an anisotropic etch by the ion milling process and a 30 minute plasma strip. As observed in figure C.1 (a), the Al₂O₃ spacer and the silicon substrate can be clearly distinguished by a different contrast. Figure C.1 (b), displays that no spacer material was left, since no distinctive contrast can be observed. The contrast that is visible in this figure originates for height differences in the silicon substrate. Because of this result the PMMA A4 resist is the preferred resist for the realization of the D-SDDP process.
Figure C.1 SEM images of an attempt to realize the D-SDDP process using the PMMA A2 resist. (a) shows a pattern were spacer deposition was successful, (b) however shows that all spacer material is removed as a result of overetching during the ion milling process, since no distinctive differences in contrast can be observed.
Bibliography


