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Atomic layer deposition of Pt and its combination with electron beam induced deposition for the fabrication of nanostructures

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Abstract

A novel direct local deposition approach was developed for the deposition of platinum nanostructures that combines the material quality and the thickness control of atomic layer deposition (ALD) with the patterning capability of electron beam induced deposition (EBID). ALD is a thin film deposition technique based on sequential self-limiting half-reactions, whereas EBID is a direct-write local deposition technique that relies on electron beam induced decomposition of a precursor. Due to its excellent electrical properties Pt is an interesting material for many nanopro-totyping applications such as adding electrical contacts to nanodevices. The approach chosen in this work consists of seed layer deposition by EBID followed by area-selective ALD growth.

The thermal ALD process of Pt from (CH\textsubscript{3})\textsubscript{2}CpPt(CH\textsubscript{3})\textsubscript{3} precursor and O\textsubscript{2} gas was extensively characterized by using in situ spectroscopic ellipsometry (SE). This process turned out to be suitable for the combinatorial EBID-ALD approach, since the thermal ALD growth could only be initiated on catalytic active Pt seed layers in case a low O\textsubscript{2} pressure was employed. In addition, a new plasma-assisted ALD process using (CH\textsubscript{3})\textsubscript{2}CpPt(CH\textsubscript{3})\textsubscript{3} precursor and O\textsubscript{2} plasma was developed which offered several merits compared to the thermal ALD process such as a reduced growth delay, the possibility to deposit high-purity Pt at low substrate temperatures, and the ability to deposit PtO\textsubscript{2}. A part of the work focused on obtaining a fundamental understanding of the reaction mechanisms of the ALD processes and of the mechanism of selective ALD growth on EBID seed layer material.

The thermal ALD growth was found to start selectively on an EBID seed layer of only a few nanometers thick, which demonstrates the feasibility of the combinatorial EBID-ALD approach for the deposition of local Pt structures. A method for thickness determination of microscale deposits was developed based on energy dispersive X-rays spectroscopy (EDX) which was used to characterize the dependence of the ALD growth on the seed layer properties. It was established that the deposits have a uniform thickness and a high purity value (>93%), whereas the method has the potential to achieve sub-10 nm lateral dimensions. Especially the high-purity of the Pt nanostructures that can be achieved with this novel approach is a major improvement compared to the 16 at.% purity that can be obtained by the EBID process of Pt to date.
Preface

The work described in this thesis is part of a collaboration between the research group "Plasma & Materials Processing" (PMP) at the Eindhoven University of Technology and FEI company. FEI company develops and produces focused electron and ion beam systems. The maturing of nanotechnology is of strategic importance for FEI and therefore the company contributes to nanotechnology research by demonstrating the capabilities of their equipment. For these reasons FEI is involved in research on focused ion and electron beam induced processing. The PMP research group has expertise in the field of (plasma-assisted) atomic layer deposition, and in plasma processing and thin film growth in general. The collaboration between PMP and FEI was initiated just before the start of this graduation project. The initial goal of this project was therefore to investigate the possibility of combining the benefits of ALD and the benefits of charged particle beam processing. To this end, a part of the experiments has been carried out at FEI company and a part has been performed at PMP. Based on the ideas developed during this project, a patent application was filed "Method for forming microscopic structures on a substrate" [1].
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Chapter 1

Introduction

Much of the progress in nanomanufacturing has been driven by the need for ever smaller structures in semiconductor industry. Since conventional nanomanufacturing techniques reach their limits, new fabrication methods capable of reproducibly processing material at the nanoscale are required to ensure the progress of nanomanufacturing. Consequently, there is much interest in the development of novel approaches for nanoscale fabrication.

The deposition of thin films is one of the essential steps of current nanomanufacturing technologies. As typical dimensions of electronic devices become smaller, there is an increasing interest for ultrathin films (1 - 100 nm) and therefore also a need for new thin film deposition technologies. This can for example be illustrated by the requirements for the fabrication of gate dielectrics in complementary metal-oxide-semiconductor (CMOS) transistors. For this application, the deposition of extremely thin and pinhole-free films with an ultimate control of thickness and material properties is required. A technique that recently gained increasing attention for its ability to deposit thin films with an excellent thickness control and conformality is atomic layer deposition (ALD). A unique feature of this technique is the use of sequential self-limiting surface reactions. Recently, Intel announced the application of ALD in their latest microprocessor [2].

Another potential application for ultrathin films and ALD in particular is the fabrication of future high-density dynamic random access memory (DRAM) trench capacitors. To produce these capacitors, ultrathin high-k dielectric and metallic layers need to be deposited inside high-aspect ratio structures. These thin layers must be deposited with a high conformality, i.e. the deposition must result in comparable film thickness throughout the trench structure1.

The lateral structuring of material using lithography techniques is another important step in nanomanufacturing. Photolithography is the dominant method for integrated circuit manufacturing currently capable of producing features with lateral dimensions in the order of a few tens of nanometers by using deep ultraviolet light. Further downscaling is considered by using extreme ultraviolet (EUV) light. However photolithography in general will eventually reach its technological limits.

An alternative lithography technique that gives access to even smaller length scales is electron beam lithography (EBL). Using this technique, sub-10 nanometer features can be fabricated [3]. A disadvantage is that the throughput is low due to the fact that every feature of the pattern needs to be defined individually by the electron beam. Since atoms are the building blocks of matter, single atom positioning using scanning tunneling microscopy (STM) yields the ultimate lithography resolution [4], but with the current low throughput this method it is not a serious candidate for lithography.

Electron beam induced deposition (EBID) is situated in between EBL and STM with respect to resolution. The smallest features that have been produced using this technique have an average

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1 Conformality is defined as the ratio of the film thicknesses at the top and bottom of a trench.
diameter of 0.72 nm at full width at half maximum (FWHM) [5]. It has a comparable throughput as e-beam lithography and is much faster than STM positioning. A major benefit of EBID as compared to multistep resist-based methods such as e-beam lithography is that the feature can be deposited directly. On the other hand, the technique suffers from incomplete precursor decomposition and has a limited control of the deposit thickness.

This thesis focuses on the development of a novel direct local deposition method for the fabrication of platinum nanostructures by combining atomic layer deposition and electron beam induced deposition. It combines the ultimate resolution of lithography with the thin film synthesis technique that enables ultimate control of film thickness, and has therefore the potential to yield an excellent control of the deposit dimensions. Moreover, the method is potentially able to fabricate high-purity nanoscale structures.

The basic principles of both ALD and EBID will be explained and some background information will be given in the next two subsections. The developed approach for the combination of ALD and EBID will be introduced in Sec. 1.3 together with the goal of the project and the outline of the thesis.

1.1 Ultrathin film synthesis by atomic layer deposition (ALD)

ALD is a vapor phase thin film deposition method in which the precursor and reactant gases are introduced into the reactor chamber in alternate pulses separated by pump or purge steps. It can be regarded as a special modification of chemical vapor deposition (CVD), a more widely used deposition technique that can be characterized by the thermally driven reaction or decomposition of one or more volatile precursors on a substrate.

At the atomic level the ALD process consists typically of two self-limiting surface reactions, referred to as half-reactions. A schematic representation of the deposition of a material containing two elements by ALD is depicted in Fig. 1.1. During the first step of the process, the substrate is exposed to the precursor which reacts with the surface groups on the substrate resulting typically in the deposition of one of the desired elements and the release of a volatile reaction product. New surface groups are formed that are not reactive to the precursor molecules which limits the adsorption of precursor molecules to one (sub)monolayer. Subsequently, the excessive amount of precursor and the formed reaction products are evacuated or purged from the chamber. The second half-cycle starts with the introduction of the reactant gas into the reactor after which the reactant species react with the surface groups of the adsorbed precursor. In this reaction, new surface groups are created, the second desired element is deposited and reaction products are formed. This half-reaction is also self-limiting, since it is completed when the reactant has reacted with all surface groups created during the preceding precursor adsorption half-reaction. The last step of the process is again a pump or purge step. After these four steps, together referred to as one ALD cycle, a (sub)monolayer of material is deposited and a new cycle can be started.

When sufficient amounts of precursor and reactant species are supplied to the surface, saturation of the self-limiting half-reactions is achieved. Consequently, the deposition rate of ALD is not proportional to the flux of precursor and reactant species to the surface, as is the case for chemical vapor deposition or physical vapor deposition (PVD). As a result, the same amount of material is deposited everywhere on the surface, even in high aspect ratio structures. High *conformality* on demanding topologies and good *uniformity* on large substrates are the features that make ALD an attractive thin film synthesis technique for many applications. Also due to the self-limiting nature of the surface reactions, the amount of material deposited in an ALD cycle, referred to as the growth-per-cycle (GPC), is constant with the number of cycles in the order of a (sub)monolayer of material. Because the number of cycles can be chosen in order to reach the projected film thickness, an *ultimate control of the thickness* on the atomic level is obtained, which is another key feature of ALD.
1.1 Ultrathin film synthesis by atomic layer deposition (ALD)

Figure 1.1: Schematic illustration of one ALD cycle for the deposition of a material containing two elements. An ALD cycle consists of the alternate exposure of precursor and reactant gases separated by pump or purge steps.

More information on ALD can be found in several review articles [6, 7, 8]. Two modifications of the ALD technique that are important for this work will be addressed below to serve as background information, that is plasma-assisted ALD and area-selective ALD.

Plasma-assisted ALD

Plasma-assisted ALD is a special ALD configuration in which the reactant step of the ALD cycle consists of the exposure of the surface to the reactive species of a plasma. These species, predominantly radicals, react with the surface groups formed during the preceding precursor exposure step. Due to the role of the reactive species from the gas phase in the surface reactions, the process is less dependent on the thermal energy supplied by substrate heating. Plasma-assisted ALD offers several potential merits in addition to the aforementioned key features of ALD [9]:

- Improved material properties such as higher film density and lower impurity levels.
- A shorter incubation period (nucleation delay) on growth-inhibiting surfaces.
- The possibility of depositing at lower substrate temperatures.
- The ability to deposit materials which are difficult to obtain with thermal ALD.
- Additional control of film composition by varying the plasma conditions.

These merits might open new application areas for ALD. Previously, plasma-assisted ALD has been extensively studied in the "plasma & materials processing" research group.

Area-selective ALD

In addition to the ultimate control of the growth in the height direction, there is also interest in controlling the lateral dimensions of the deposit by area-selective ALD. The major benefit of area-selective ALD lies in the ability to directly create patterns and thereby eliminating the need for post-deposition structuring steps (i.e. resist deposition, lithography and etching / lift-off), which can simplify the overall process significantly. Moreover, it is difficult to define small features using post-deposition structuring steps, and therefore, area-selective ALD might enable the fabrication of smaller features.

ALD film growth depends critically on the chemistry of the surface and consequently, it is possible to chemically tailor the surface properties to achieve area-selective deposition. One example of an approach is to mask designated areas of the surface to prevent ALD reactions in
those areas, resulting in ALD film nucleation only on the desired unmasked regions. Alternatively, an area-selective ALD approach can also rely on locally stimulating ALD nucleation on growth inhibiting substrates.

All the early area-selective ALD approaches were based on the use of self-assembled monolayers (SAMs) of long chain alkyl silanes serving as a masking layer [10, 11, 12]. These silane molecules chemically convert reactive surface sites on the substrate into non-reactive form after which selective ALD occurs on unprotected regions only. The patterning of the SAMs is based on photocatalytic lithography [11] or microcontact printing [10].

Unfortunately it is necessary to form defect-free SAMs, which is extremely difficult, in order to produce succesfull patterning. Alternatively, polymer films such as PMMA can be used to form ALD masking layers, which rely primarily on physical screening of active sites on the substrate surface [13]. Pattering of the polymer films can be done by conventional photolithography [13] or by using a heated AFM cantilever probe tip [14]. After the completion of the ALD process, the polymer mask layer can be removed, resulting in a direct patterned structure.

A drawback of all these area-selective ALD approaches is that they comprise many processing steps, i.e. coating the surface with a resist, pattern definition by lithography, resist development, ALD, and finally removal of the resist. Furthermore, in addition to the resolution of the lithography technique, the resolution is also limited by the properties of the resist.

1.2 Direct-write lithography by electron beam induced deposition (EBID)

Electron beam induced deposition is a direct write local deposition technique in which an electron beam stimulates the dissociation of precursor molecules on a substrate surface (See Fig. 1.2). EBID is a member of a family of charged particle beam induced processing techniques which further comprises ion beam induced deposition (IBID, also known as focused ion beam chemical vapor deposition or FIB-CVD) and electron beam induced etching (EBIE).

The basic principle of EBID relies on electron beam induced decomposition of adsorbed precursor molecules. Gas molecules are introduced in the electron beam system and adsorb on the surface of the substrate. Locally, as a result of the interaction of adsorbed precursor molecules with secondary electrons generated by the electron beam, the precursor molecules are dissociated into volatile and nonvolatile components. The nonvolatile components adhere to the substrate and form the deposit, whereas the volatile species are evacuated from the system. By scanning the electron beam over the surface, a two- or three-dimensional nanostructure can be defined.
Direct-write lithography by electron beam induced deposition (EBID)

EBID allows the deposition of structures of micro- or nanoscale dimensions, since an electron beam can be focused into a spot in the range from 100 nm down to sub-nanometer diameter. Control over the dimensions of the deposits is one of the major research areas of EBID studies reported in literature [15], which will be elucidated below. One of the most important advantages of EBID is that the pattern is written directly, without the use of a resist, which limits the number of process steps basically to only one and enables deposition on either flat or topographical surfaces. Deposition can be performed as long as it is possible to focus the electron beam on the selected area, resulting in the ability to fabricate three-dimensional structures. Its low throughput and low material purity, which will also be discussed in more detail below, can be mentioned as the most important drawbacks of the technique. However, EBID has the potential due to its low resolution to become an important nanoprototyping technique, especially if the problem of the low material purity can be solved, and/or the throughput can be enhanced.

A more detailed description of EBID can be found in recent review articles. Utke et al. reviewed the state of the art and level of understanding of electron and ion beam processing [16]. Van Dorp and Hagen compared experimental results reported in the literature with each other and with the existing models of EBID processes [15].

Some aspects of EBID will be addressed below to serve as a background for the introduction of the combinatorial EBID-ALD approach. First, the interaction between the electron beam and the sample will be described since this is important for the explanation of the results. Second, some key features of EBID will be addressed: the deposit dimensions and shape, the material quality, and its throughput.

1.2.1 Electron beam - sample interaction

As a beam of electrons (primary electrons or PEs) enters the sample, they interact with the electrical fields of the sample atoms. The electron - sample interaction can deflect the original direction of a electron along a new trajectory causing the electrons to spread laterally from the incident beam footprint. In addition to these elastic scattering events, inelastic collisions can occur, characterized by the transfer of a part of the PE energy to electrons in the solid.

So-called secondary electrons (SEs) are created due to inelastic collisions between PEs and outer shell electrons of semiconductors or conduction electrons of metals. Although they are generated along the entire path of the PEs, only those generated close to the substrate surface...
can escape and contribute to the deposition process. Some of the primary electrons are reflected as a result of elastic collision and leave the surface as backscattered electrons (BSEs). In general, electrons that leave the surface are called secondary electrons if their energy is smaller than 50 eV and backscattered electrons if their energy is larger than 50 eV.

As a consequence of all the collisions in the substrate material, there is an interaction volume in the solid below the irradiated spot. Both the PE energy and the substrate material determine the size and shape of the interaction volume. Figure 1.3(b) shows a Monte Carlo simulation of the interaction of an electron beam with a sample. SEs and BSEs can escape the substrate from this volume, meaning that there is a spatial distribution of emitted electrons around the irradiated area.

During the EBID process, a deposit forms on the substrate material in which also scattering events can occur. Figure 1.3(a) shows a schematic illustration of scattering events in a growing tip deposit. As can be seen, electrons can cross the interface between the vacuum and the target in many different ways.

1.2.2 Deposit dimensions and shape

Since the high resolution of EBID is the property that distinguishes the technique from other lithography approaches, improving its resolution is an important research area. High resolution can be achieved by focusing the electron beam to a very small spot and using a thin membrane as substrate to eliminate the contribution of backscattered electrons.

Several studies reported that the deposit diameter of tips with a certain height is always larger than the beam diameter [15]. An explanation for this lateral broadening was suggested by Silvis-Cividjian et al. [18]. At the start of the deposition, the deposit may be very small. As the deposit becomes thicker, SE emission from the deposit occurs. Consequently, precursor molecules adsorbed close to the deposit are dissociated by the SEs generated in the deposit resulting in lateral broadening. The width of the final deposit approximately equals the beam diameter plus twice the path length SEs can travel.

This explanation reveals an approach for the fabrication of deposits with small lateral dimensions, i.e., stopping the deposition before the onset of lateral broadening. Using this method, van Dorp et al. succeeded in depositing subnanometer scale dots with an average diameter of 0.72 nm at full width at half maximum (FWHM). For these small features, the deposited volume varies from dot to dot, suggesting that the number of precursor molecules involved in the deposition dominates the statistics, rather than the number of electrons [5]. A disadvantage of stopping the deposition process before lateral broadening occurs is that it is not possible to control the height of the deposits independently of the width, since the growth has to be stopped in its initial stage.

For larger scale deposits, the deposit shape is very important. A nonuniform height distribution was found in several studies [15]. Typically in these cases, the deposit is thicker along the edges than in the center. An explanation for this behavior can be found by modeling the EBID process in terms of precursor gas and electron flux [15]. Using such a model, EBID processes can be divided into two regimes, i.e., electron-limited and precursor-limited growth. For precursor-limited growth, the area exposed by the electron beam will become depleted of precursor molecules. Surface diffusion may then become the prevalent precursor supply mechanism instead of adsorption from the gas phase. If the precursor molecules that diffuse over the surface are dissociated before they reach the center of the irradiated area, a "bowl"-shape deposit forms with an ill-defined height. In general, there are enough parameters to improve the uniformity by moving from the precursor-limited regime to the electron-limited regime.

1.2.3 Material quality

EBID suffers in most cases from incomplete precursor dissociation and hence undesired atoms in the deposit material. The purity of the material is strongly dependent on the precursor. Typical
purity values are 8-9 at.% for gold from Me$_2$Au(acac), 60 at.% for Fe from Fe$_2$(CO)$_9$, and ∼16 at.% for Pt from MeCpPtMe$_3$ [19]. In general, the deposit composition is a derivative of the precursor species. However, the residual background vapor might also contribute to the contamination in the material [20].

In the case of metal-organic precursors, large amounts of carbon are deposited along with the metal and the deposit can be described as small metal grains embedded in a matrix of amorphous carbon [21]. Some reduction of the carbon contents can for example be obtained by using a higher beam current [15], but this does not solve the problem. The use of inorganic, carbon-free precursors such as WF$_6$ or Pt(PF$_3$)$_4$ has been considered in several studies [15]. A disadvantage of these precursors is that they contain Cl or F atoms, which can induce beam induced etching effects. Alternatively, reactive gases are added to the precursor vapor to improve the deposit purity. Also several post-deposition treatments are proposed [19]. These approaches work to some extent, resulting in purity levels in the range 30-80 at.%.

A higher purity has also been obtained by using IBID, which can be explained by the combination of several effects, such as the larger dissociation cross-section of ions, and the selective sputtering of light impurity atoms [22]. However, the use of a FIB causes other problems such as ion implantation and surface damage, whereas it is only suitable for dimensions larger than ∼20 nm.

To summarize, several methods to improve the deposit impurity have been proposed, but so far none of these make the deposition of high-purity structures possible.

1.2.4 Throughput and applications

As mentioned, the throughput of EBID is low as compared to several other lithography techniques. Therefore the applications of EBID are currently limited to applications where the feature dimensions have to be small, smaller than attainable with other techniques, and where the time it takes for deposition is less important. Presently, there are three industrial applications for which EBID is considered or already used: photomask repair of the 65 nm node and below, functionalization of high-aspect ratio atomic force microscopy (AFM) sensors, and circuit editing of multilevel architectures [16].

If the throughput of EBID can be improved in the future, application areas will be more diverse. One approach to enhance the throughput is to develop an electron beam system containing multiple electron beams. For example, Van Bruggen et al. designed a multibeam system in which 100 beams can write sub-10 nm EBID structures in parallel [23].

In addition to industrial applications, EBID can become an important technique for nanoprototyping in research environments. Various laboratory prototype nanoelectronic devices have already been fabricated using EBID [16].

1.3 Goal of the project: Combinatorial EBID-ALD

The main objective of this work is to develop a new local deposition method by combining electron beam processing and atomic layer deposition in such a way that the strengths of both techniques are amplified whereas some weaknesses are eliminated. The motivation for this lies in the fact that (sub)nanometer scale deposits can be fabricated by electron beam processing, however these deposits often possess a low material purity, whereas ALD yields high quality material and ultimate control of the thickness but without an intrinsic method to control the lateral growth dimensions. To our knowledge, the only combination of electron beam processing and atomic layer deposition reported in literature involves the use of electron beam lithography for defining the pattern in a lift-off method [24]. This approach yields high quality local deposits with ultimate thickness control and good uniformity, but includes many process steps. Our aim is to develop a direct local deposition method suitable for nanoprototyping applications.
ALD was invented by two research groups independent of each other: in the 1960s under the name ‘molecular layering’ by Aleskovskii et al. in former USSR, and in the 1970s by Suntola et al. in Finland who called it ‘molecular layer epitaxy’ [8]. The first commercialization in high volume production was its use in thin film electroluminescent (TFEL) flat panel displays [25] in the mid 1980s. Apart from this application, the technique developed slowly in the first years after its invention, as can be seen by the number of publications per year in Fig. 1.4(a). This was due to the fact that no real benefit could be achieved compared to other deposition techniques such as chemical vapor deposition (CVD) and molecular beam epitaxy (MBE) in combination with its low deposition rate. The driving forces for the interest in the last 8 years are the search for new high-k materials and the upcoming field of nanotechnology. Apparently, the merits of ALD such as the excellent conformality and the control of thickness and material quality have become more important than its most important drawback (i.e. the low deposition rate), due to the scaling down of device dimensions. As illustrated by the announcement of Intel and IBM regarding the use of ALD in the fabrication of the next generation integrated circuits [2], ALD has currently achieved industrial readiness.

Focused electron beam induced processing (FEBIP) started with the realization that the formerly considered detrimental effect of electron irradiation induced contamination growth can be utilized as a lithography technique. Contamination growth occurs at surfaces exposed to the electron beam, due to the presence of hydrocarbons in the vacuum system. Cristy [26], and Baker and Morris [27] were the first to realize in the 1960s that such electron beam induced deposition processes can be used to deposit a polymer film, whereas Broers et al. demonstrated in 1976 that ‘contamination lithography’ can be exploited to write sub-100 nm features [28]. It took until the 1980s before researchers deliberately introduced precursor gases to deposit other materials [29, 30]. In the following years, the technique developed slowly (see Fig. 1.4(b)) while the use of several precursors was demonstrated. The application areas did not increase rapidly in these years. At the same time, focused ion beams (FIBs) became accepted as milling tools for photomask repair in the integrated circuit industry [16]. At some point, the unavoidable ion implantation and sample damage effects of FIBs started to affect the light transmission through the repaired masks. This increased the interest in FEBIP methods for photomask repair, and currently, electron beam induced etching and deposition are being developed for photomask applications [17]. Although the use of FEBIP methods is considered for a number of applications, the technique cannot be said to have achieved industrial readiness, like in the case of ALD. FEBIP is still in a very early stage of its development. If the problem with the low purity can be solved and/or the throughput can be improved, the major advantage of the technique, i.e. its high resolution, may at some point overshadow its most important drawback, the low throughput.

Figure 1.4: Number of (a) ALD and plasma-assisted ALD, and (b) FEBIP publications per year since 1975. The searches were performed using Web of Science [31]. See Ref. [32, 33, 34] for the search terms.
1.3 Goal of the project: Combinatorial EBID-ALD

Since the goal is to combine the patterning capability of electron beam processing with the material quality of ALD the obvious approach is to develop a two-step process; patterning by electron beam exposure followed by ALD growth. A number of ways can be suggested to use electron beam processing for patterning such as:

- Removal of material or surface groups by sputtering or electron beam induced etching.
- Seed layer creation by electron stimulated reduction of metal-oxides.
- Stimulation of ALD nucleation by local surface charging.
- Seed layer deposition by EBID.

Seed layer deposition by EBID has been chosen as the patterning method since EBID is an extensively studied technique and because of the expertise of FEI Company within this research area. The other methods might also be considered in the future to achieve similar goals.

The approach thus comprises two main steps, i.e. the pattern definition by means of EBID seed layer deposition and the selective building of the structure by ALD. The ALD process consists in turn of the alternate exposure of the surface to precursor and reactant pulses. See Fig. 1.5 for a schematic representation of the method. Selectivity of ALD growth is a necessary requirement for this approach to work, which means that the ALD growth is only allowed to occur on the EBID seed layer and not on the substrate material. Therefore, a fundamental understanding of ALD nucleation on substrate and seed layer surfaces is required for this study.

Although most direct-write processes comprise only one step, our two-step approach can be considered a direct-write local deposition method since the final deposit contains material deposited during both process steps. Moreover, ALD can be integrated in an electron beam system making it more easy to perform the ALD building step right after the patterning step.

The new method offers several potential merits that will be described in the next subsection.

![Schematic representation of the principle of local deposition of high-purity nanostructures. The principle is a combination of an electron beam pattering step and an ALD building step consisting of the alternating exposure of the surface to the ALD reactants.](image)
1.3.1 Merits of the combinatorial EBID-ALD approach

Ideally, the approach combines the advantages of both ALD and EBID, while eliminating several problems. An overview of the key features of the combinatorial EBID-ALD approach and their relation to the features of ALD and EBID is shown in Fig. 1.6.

By selective ALD growth on a relatively thin EBID seed layer, the material quality is expected to come close to ALD material quality, which potentially solves the impurity problem of EBID. In case the ALD process yields virtually pure films, and a thin seed layer is able to induce selective ALD growth, almost 100% pure deposits can be fabricated. The ability to deposit high-purity nanoscale structures is expected to open new application areas for direct-write lithography.

Besides single atom positioning by scanning probe microscopy, EBID yields the ultimate control of lateral deposition dimensions, but with no accurate thickness control. On the other hand, ALD gives a sub-nanometer control of the film thickness, due to its layer-by-layer growth character, and a good uniformity. By combining these features, the combinatorial EBID-ALD approach enables direct local deposition with an ultimate control of the deposit dimensions in both height and lateral direction. Such a control of the size and shape of material on the nanometer scale may offer scientists new nanoprotyping possibilities, needed for the study and fabrication of nanoscale devices. Since material and device properties can dramatically change when sizes become smaller, the technique may also be of interest for nanoscience research.

Another benefit is that a higher throughput may be achieved when a thin seed layer is able to induce ALD growth. In that case, a high writing speed can be obtained for the patterning step because only a small quantity of precursor needs to be converted to metal deposit to form the seed layer. This is in contrast to EBID, where the complete deposit is formed by precursor dissociation due to electron beam irradiation, and where the deposition time thus scales with the volume of the deposit. The building step can be carried out by parallel processing of (a number of) large patterned samples in order to increase the throughput significantly. The total deposition times is thus the sum of time needed for the patterning step which scales with the footprint area of the structure to be deposited and the time needed for the building step which scales with the thickness.

A last merit that can be mentioned is that it is very easy to switch between ALD processes, yielding the possibility to create multilayer or compound material local deposits. This property can be interesting for specific applications.

In summary, it is the ultimate deposit dimension control in combination with the material quality which makes this technique a potential revolutionary nanoprotyping method. The combinatorial EBID-ALD approach tackles one of the two most important drawbacks of EBID, i.e. the low material purity, and alleviates the other one, i.e. the low throughput. Since ALD can relatively easy be integrated in an electron beam system, the combinatorial EBID-ALD approach yields a two-step direct write deposition technique.

1.3.2 Project setting and outline of the report

Platinum was chosen as the material to demonstrate the capabilities of the combinatorial EBID-ALD approach due to the fact that the catalytic nature of the material plays an important role in its deposition mechanism, which was expected to promote the selectivity of ALD growth. Furthermore, Pt is an interesting material for many EBID applications due to its electrical properties.

To this end, ALD processes for the deposition of Pt needed to be implemented or developed. The project was started with the implementation of the thermal ALD process of platinum as developed by Aaltonen et al. [35]. Due to some problems with initiating the growth on regular substrates, it was decided to develop the plasma-assisted ALD process first to be able to deposit Pt seed layer films and then switch back to thermal ALD. The development of the plasma-assisted ALD process yielded many interesting results. Furthermore, it aided in obtaining insight into the reaction mechanism and in the development of the local deposition approach, since a plasma-
1.3 Goal of the project: Combinatorial EBID-ALD

<table>
<thead>
<tr>
<th>Features ALD</th>
<th>Key features combinatorial EBID – ALD approach</th>
<th>Features EBID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good material quality</td>
<td>ALD material quality</td>
<td>Low material purity</td>
</tr>
<tr>
<td>No control of growth in lateral direction</td>
<td>Ultimate control of dimensions in both lateral and height direction</td>
<td>(Sub)nanometer control of growth in lateral direction</td>
</tr>
<tr>
<td>Atomic layer thickness control</td>
<td></td>
<td>Limited control of growth in height direction</td>
</tr>
<tr>
<td>Competitive growth rate</td>
<td>Higher throughput than EBID</td>
<td>Low throughput</td>
</tr>
</tbody>
</table>

Figure 1.6: Overview of the key features of the combinatorial EBID-ALD approach compared to the features of ALD and EBID. The overview shows how the strengths (in green) of both ALD and EBID are combined, whereas some of their weaknesses (in red) are eliminated or alleviated. The arrows indicate which technique is responsible for the specific key features of the combinatorial approach.

Assisted ALD grown film initiates the thermal ALD growth in a similar way as a EBID seed layer. The implementation of the thermal ALD process and the development of new plasma-assisted ALD processes of Pt as studied by in situ spectroscopic ellipsometry are described in Chapter 2.

Understanding of the underlying reaction mechanism is essential for the development of new ALD processes. To avoid trial-and-error experiments, it is necessary to understand the surface reactions that take place at the surface of the growing film. Insight into the reaction mechanism also helps to comprehend the nucleation properties on different substrates, which is required for the development of the combinatorial EBID-ALD approach. Based on the results presented in Chapter 2 and on additional results obtained by spectroscopic ellipsometry and infrared spectroscopy, the reaction mechanisms of both thermal and plasma-assisted ALD are addressed in Chapter 3 as well as the nucleation behavior of the processes on different substrates. Furthermore, the regime for which selective growth on a Pt seed layer can be obtained is evaluated.

As mentioned, the main goal of the project is to develop a combinatorial EBID-ALD approach. Within this project, the objective was to establish the following aspects of the approach:

- Initiation of ALD growth on EBID seed layer material.
- Selectivity of the ALD growth.
- Purity of the deposits.
- Uniformity and thickness control.
These aspects are addressed in Chapter 4 and serve as proof-of-principle for the combinatorial EBID-ALD approach. In addition, the mechanism of selective ALD growth on EBID seed layer material is unraveled in Chapter 4.

One of the plans for the continuation of this project is to integrate ALD in an electron beam system. Preliminary experiments to investigate this possibility were already carried out during this study and some preliminary results are discussed in Chapter 5. A comparison of the list of studied aspects shown above and the merits presented in Sec. 1.3.1 reveals that two aspects of the approach, i.e. the lateral dimensions of the deposits and the throughput enhancement, were not experimentally investigated. However, these two issues are addressed briefly in Chapter 5 by discussing the improvement that can potentially be achieved.

The general conclusions are summarized and suggestions for future research are given in Chapter 6.
Chapter 2

Thermal and plasma-assisted ALD of Pt and PtO$_2$ films

2.1 Introduction

Platinum possesses high chemical stability in oxidative environments, excellent electrical properties, and a high work function (5.6 eV). As a catalytic active material it is able to lower the activation barrier of many chemical reactions. All of these properties together with the ability of ALD to deposit conformal films on demanding topologies, yield that Pt ALD has many potential application in catalysis and microelectronics. Some applications for Pt ALD reported in literature are: capacitor electrode material in dynamic random access memories (DRAMs) [35], seed layer for copper electroplating [37], catalyst for solid oxide fuel cells (SOFCs) [38] and for polymer electrolyte fuel cells (PEFCs) [39], gate metal in metal-oxide-semiconductor field effect transistors (MOSFETs) [35], and current collector in 3D-integrated solid-state thin film Li-ion batteries [40, 41].

Initially, Pt film deposition by thermal ALD has been studied using Pt(acac)$_2$ and H$_2$ gas reactants [42], and recently, combinations of Pt(acac)$_2$ and O$_3$ [43], and MeCpPtMe$_3$ and H$_2$ [39] gas have been considered. However, the thermal Pt process from MeCpPtMe$_3$ and O$_2$ gas as developed by Aaltonen et al. [35, 44] has become most the adopted [37, 45]. In this process, the catalytic activity of the film is essential for the dissociation of reactants for subsequent decomposition of the metal precursor ligands. The reaction mechanism consists of the combination of two elementary surface reactions, i.e. dissociative chemisorption of O$_2$ molecules and oxidative decomposition of MeCpPtMe$_3$ molecules by chemisorbed oxygen atoms. See Fig. 2.1 for schematic

![Chemisorption and Decomposition Diagram]

Figure 2.1: Reactions taking place on an as-deposited Pt surface during the ALD process. (a) Dissociative chemisorption of O$_2$ molecules. (b) Oxidative decomposition of MeCpPtMe$_3$ molecules by chemisorbed oxygen atoms. When an as-deposited Pt film is exposed to molecular O$_2$ gas, it catalyzes the dissociative chemisorption reaction in which the O$_2$ molecules are dissociated in oxygen atoms that chemisorb at the surface. Oxidative decomposition of the MeCpPtMe$_3$ molecules by chemisorbed oxygen atoms follows after the adsorption of the MeCpPtMe$_3$ precursor at the surface and involves the combustion of formed precursor ligands to CO$_2$ and H$_2$O reaction products [36].
representations of these two chemical reactions. The reaction mechanism and its effects on the growth and nucleation behavior will be addressed in more detail in the next chapter.

As a noble metal Pt shows chemical stability in oxidative environments, and therefore, it has been found difficult to deposit PtO$_2$ films. Therefore PtO$_2$ deposition is less investigated and only a few applications are reported in the literature. PtO$_2$ could however be of interest for many applications because of its optical properties [46] and because of the potential of locally reducing PtO$_2$ to Pt as a patterning method [47, 48]. To our knowledge PtO$_2$ ALD has only been achieved using Pt(acac)$_2$ and O$_3$ reactants for a very small temperature window (120 - 130$^\circ$C) [43].

An issue for thermal ALD of Pt is the initial growth delay on non catalytic active substrate materials, due to the inability of these substrates to form reactive oxidizing species, which is essential to initiate the growth. It is expected that the growth delay can be eliminated by using plasma-assisted ALD, since the plasma provides reactive plasma species from the gas phase to the surface. Furthermore, plasma-assisted ALD yields often the possibility to use lower substrate temperatures because the process is less dependent on the thermal energy provided by substrate heating. A low temperature Pt ALD process might lead to the possibility to deposit pure Pt films on substrate materials that are not able to withstand high substrate temperatures, for instance plastics for flexible electronics. To the best of our knowledge, no plasma-assisted ALD process for Pt deposition has been reported in the literature yet.

The goal of the work described in this chapter is twofold. First, the main objective was to find conditions suitable for the combinatorial EBID-ALD approach. More specifically, settings had to be found for which the Pt film growth occurs selectively, i.e. the growth is only allowed to take place on the surface of a seed layer and not on the substrate material itself. Furthermore, a new plasma-assisted ALD process was developed for the deposition of Pt by using MeCpPtMe$_3$ precursor and O$_2$ plasma, and additionally, settings were found for which PtO$_2$ films can be deposited. The second goal is thus to develop new plasma-assisted ALD processes and investigate their merits. The following research topics form the basis of this study:

- **Nucleation of Pt on different substrate materials.** Is it possible to obtain selective growth when using a Pt seed layer? Is the plasma-assisted ALD process less dependent on the starting surface because reactive plasma species are delivered from the gas phase?

- **Material properties.** Can Pt be deposited using plasma-assisted ALD? What are the material properties of films obtained using thermal or plasma-assisted ALD and how do these properties depend on the process parameters?

- **Temperature window of the processes.** Is it possible to use lower substrate temperatures for the deposition of Pt with a high purity?
2.2 Experimental details

In this part, the experimental details of thermal and plasma-assisted ALD are presented. The ALD setup is described in Sec. 2.2.1, whereas the thermal and plasma-assisted ALD cycles are discussed in Sec. 2.2.2. This part concludes with the description of the ex situ material characterization techniques in Sec. 2.2.3. The main in situ diagnostic technique, spectroscopic ellipsometry, will be presented in a separate section (Sec. 2.3).

2.2.1 ALD-I setup

A schematic representation of the ALD reactor is presented in Fig. 2.3. The reactor is designed for plasma-assisted ALD and was previously used to study plasma-assisted ALD of several materials [49, 50, 51]. It consists of a stainless steel deposition chamber connected to a plasma source, precursor and gas dosing systems and a pump system. The pump system is a combination of a turbo-molecular pump (250 l/s) and a rotary pump and is capable of pumping to a base pressure of $<10^{-5}$ mbar.

The inductively coupled plasma (ICP) source consists of a copper coil wrapped around a glass tube connected to a power supply which can generate a radio frequency plasma with a power up to 100 W. The glass tube is separated from the deposition chamber by a gate valve to prevent the deposition of a conductive film in the source. \(\text{H}_2\) and \(\text{O}_2\) gases can be fed into the ICP source to generate the plasma.

A substrate holder is present in the deposition chamber which can be heated resistively from room temperature to 400°C. The substrate temperature is controlled by a proportional-integral-
Table 2.1: Standard operating settings for Pt deposition by the thermal and plasma-assisted ALD process. The ranges in which the operating settings were varied in the experiments are also given.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Thermal ALD</th>
<th>Range studied</th>
<th>Plasma-assisted ALD</th>
<th>Range studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeCpPtMe₃ dosing</td>
<td>1 s</td>
<td>0 - 2 s</td>
<td>3 s</td>
<td>0 - 5 s</td>
</tr>
<tr>
<td>Wait time</td>
<td>3 s</td>
<td>-</td>
<td>3 s</td>
<td>-</td>
</tr>
<tr>
<td>Intermediate pump down time</td>
<td>3 s</td>
<td>-</td>
<td>3 s</td>
<td>-</td>
</tr>
<tr>
<td>O₂ gas exposure time</td>
<td>5 s</td>
<td>0 - 7 s</td>
<td>4 s</td>
<td>0 - 5 s</td>
</tr>
<tr>
<td>O₂ plasma exposure time</td>
<td>-</td>
<td>-</td>
<td>0.5 s</td>
<td>0 - 5 s</td>
</tr>
<tr>
<td>O₂ pressure</td>
<td>0.03 mbar</td>
<td>0 - 0.7 mbar</td>
<td>0.01 mbar</td>
<td>-</td>
</tr>
<tr>
<td>Intermediate cycle time</td>
<td>3 s</td>
<td>3 - 6 s</td>
<td>3 s</td>
<td>3 - 6 s</td>
</tr>
<tr>
<td>Deposition temperature</td>
<td>300 °C</td>
<td>150 - 300 °C</td>
<td>300 °C</td>
<td>100 - 300 °C</td>
</tr>
<tr>
<td>Wall temperature</td>
<td>75 °C</td>
<td>-</td>
<td>75 °C</td>
<td>-</td>
</tr>
<tr>
<td>Precursor bubbler temperature</td>
<td>70 °C</td>
<td>40 - 70 °C</td>
<td>70 °C</td>
<td>40 - 70 °C</td>
</tr>
<tr>
<td>Plasma power</td>
<td>-</td>
<td>-</td>
<td>100 W</td>
<td>-</td>
</tr>
</tbody>
</table>

derivative (PID) controller which uses the temperature determined by a thermocouple to regulate the power of the resistive substrate heater. The chamber walls, the gate valves and the precursor supply lines are also heated (\(\sim 75^\circ\) C) to prevent condensation of the precursor and to aid the removal of sticky reaction products.

Spectroscopic ellipsometry data can be obtained after the opening of the gate valves to the light source and the detector. These valves protect the windows to the SE equipment from deposition. The SE measurements were carried out using a J.A. Woollam, Inc M200U visible and near-infrared ellipsometer (0.7 - 5.0 eV).

To monitor the pressure, the system is equipped with two pressure gauges. A gas independent pressure gauge with a range from \(10^{-4}\) to \(10^3\) was used to set the working pressures of the gases. The vacuum quality was monitored using a Pfeiffer Cold cathode and Pirani combination pressure gauge with a range from \(5\times10^{-9}\) to \(10^3\) mbar. Both pressure gauges are connected to the chamber at vacuum port located in the wall of the reactor close to the substrate table.

For the deposition of Pt, the precursor MeCpPtMe₃ (methylcyclopentadienyl(trimethyl)platinum, Sigma Aldrich, 98% purity) was used. MeCpPtMe₃ is air-sensitive and a powder at room temperature, and in order to fill the precursor pot, it was liquidized by heating it to approximately 40°C in a glovebox with nitrogen environment. During ALD experiments, the precursor pot was heated to 70°C to obtain an adequate vapour pressure¹.

Crystalline silicon (c-Si) substrates with an toplayer of 400 nm SiO₂ were used as substrates in this work.

### 2.2.2 ALD cycle

We used the results of the thermal ALD study of Aaltonen et al. [35] as a starting point for our thermal ALD experiments. However some operating settings characteristic to our system are different from the settings reported by Aaltonen et al. The plasma-assisted ALD process can be regarded as a special modification of the thermal ALD process. Both processes are described in detail below. Standard operating settings of both the thermal and plasma-assisted ALD process can be found in Table 2.1. Most of these settings are based on the results of the experiments described in Sec. 2.4.
Figure 2.4: Schematic representation of the standard thermal ALD cycle for Pt deposition consisting of MeCpPtMe_3 precursor dosing and O_2 gas exposure separated by pump steps. The bottom valve is only closed during the MeCpPtMe_3 dosing and the subsequent wait time.

Thermal ALD

Figure 2.4 shows a schematic diagram of the standard thermal ALD cycle used for most thermal ALD experiments. The cycle consists of the alternating exposure of MeCpPtMe_3 precursor and O_2 gas. Since no plasma exposure is part of the process the top gate valve in between the deposition chamber and the plasma source is continuously closed and the O_2 gas is fed into the reactor through a connection in the reactor wall as is depicted in Fig. 2.3. The first step of the cycle is the MeCpPtMe_3 dosing. To maximize the usage of the rather expensive MeCpPtMe_3 precursor, the bottom gate valve in between the reaction chamber and the turbo pump is closed during the MeCpPtMe_3 precursor dosing, and the exposure time is prolonged by keeping the bottom valve closed for 3 seconds after dosing. Subsequently the bottom gate valve opens and the unreacted MeCpPtMe_3 molecules and the reaction by-products are evacuated from the chamber. After 3 seconds of pump down resulting in a pressure of approximately $2 \times 10^{-4}$ mbar, the O_2 exposure step starts by opening the valve to the O_2 supply line. Although 0.5 seconds O_2 exposure turned out to be sufficient to combust the MeCpPtMe_3 precursor ligands on the surface, an O_2 exposure time of 5 seconds was chosen as standard setting to ensure saturation of the oxidation half-reaction. The O_2 pressure during stabilized O_2 flow is equal to 0.03 mbar. The last step of the thermal ALD cycle is a second pump step for the removal of the reaction products formed during the O_2 dosing step.

Plasma-assisted ALD

The plasma-assisted ALD process consist of the alternating exposure of MeCpPtMe_3 precursor molecules and O_2 plasma instead of O_2 gas. Therefore the cycle is slightly different from the thermal ALD cycle and includes the switching of the top gate valve. The first part of the cycle consisting of MeCpPtMe_3 dosing, wait time and pump down is similar, although a longer MeCpPtMe_3 exposure time is necessary to saturate the precursor adsorption half-reaction since there is also growth on the reactor walls for plasma-assisted ALD as will be discussed later (Sec. 2.4.3). After the first pump step the top gate valve is opened and when the flow stabilizes after 3 seconds the plasma power is applied for a certain plasma exposure time (typically 0.5 s for Pt ALD). The O_2 flow is continued for 0.5 seconds after the plasma exposure. Subsequently, the second pump step starts during which the top valve closes. The O_2 gas pressure was set to 0.01 mbar for the plasma-assisted ALD experiments.

2.2.3 Ex situ film characterization

In addition to in situ thickness determination by spectroscopic ellipsometry, film thickness was measured ex situ by spectroscopic ellipsometry and by X-ray reflectometry (XRR) using a Bruker

---

1Initially, the precursor pot was heated to 40 °C. Evaluation of the pressure peak during MeCpPtMe_3 precursor dosing measured by the Baratron pressure gauge revealed a decrease in MeCpPtMe_3 dosing in consecutive cycles. In order to maintain constant precursor dosing, the precursor temperature was raised to 70 °C.
Figure 2.5: Schematic diagram of the standard plasma-assisted ALD cycle for Pt or PtO$_2$ deposition consisting of MeCpPtMe$_3$ precursor dosing and O$_2$ plasma exposure separated by pump steps. The bottom valve is only closed during the MeCpPtMe$_3$ dosing and the subsequent wait time. The top valve is open during the plasma exposure step. Pt or PtO$_2$ can be deposited depending on the plasma exposure time.

D8 Advance X-ray diffractometer. XRR was also used to determine the mass-density of the films. Surface roughness was determined by atomic force microscopy (AFM) using an NT-MDT Solver P47 SPM. The resistivity was obtained from the determined film thickness and sheet resistance measured by a Signatone four-point-probe (FPP) in combination with a Keithley 2400 Sourcemeter acting as current source and voltage meter. Film mass density and atomic composition were measured using 2 MeV He$^+$ Rutherford backscattering spectroscopy (RBS) and elastic recoil detection (ERD). X-ray diffraction (XRD) obtained with a Philips X’Pert MPD diffractometer equipped with a Cu K$_\alpha$ source (1.54 Å radiation) was used to study the microstructure. XRR, XRD, and RBS analysis were carried out at the Philips Materials Analysis Labs.

2.3 In situ spectroscopic ellipsometry

It was demonstrated in previous work that in situ spectroscopic ellipsometry (SE) is well-suited to study the deposition of thin films by (plasma-assisted) ALD [49, 51]. Therefore spectroscopic ellipsometry was used in this work to study the growth and optical properties of the deposited material in situ. The operating principle of SE is briefly explained in Fig. 2.6.

SE data can be acquired during temporary interruptions of the deposition process after opening of the gate valves to the detector and light source. Each SE measurement consisted of 200 data acquisitions to obtain a high signal-to-noise ratio which gives an acquisition time of about one minute. SE data analysis was performed using WVASE32 software. The dielectric functions of Pt and PtO$_2$ films were determined over the photon energy range from 0.75 to 5.0 eV using the J.A. Woollam, Inc M200U visible and near-infrared ellipsometer.

2.3.1 Optical model

Analysis of spectroscopic ellipsometry data requires an optical model defined by the optical constants and layer thickness of each layer in the sample. The WVASE32 software program calculates the $\Psi$- and $\Delta$- spectra from the optical model and tries to fit the experimentally measured $\Psi$- and $\Delta$- spectra by varying the model parameters while minimizing the mean-squared error (MSE) of the fit.

The dielectric function can also be determined directly by a method called direct numerical inversion [52], by fitting the optical constants at each photon energy (i.e. point-to-point fit) using an estimation of the film thickness. Subsequently, the determined dielectric function can be used to define the optical model.
2.3 In situ spectroscopic ellipsometry

Figure 2.6: In ellipsometry the change in polarized light upon light reflection on a sample is measured. Depending on the dielectric functions and thicknesses of the layers composing the sample, there is a polarization change due to different reflection coefficients for \( p \)- and \( s \)-polarized light on the sample. From the amplitude ratio \( \Psi \) and the phase difference \( \Delta \) between the \( p \)- and \( s \)-polarized light waves, material properties such as the dielectric functions of the layers and film thicknesses can be extracted. In general, most ellipsometry configurations are insensitive to source and background light fluctuations since it measures ratios, which results in a high accuracy and a good reproducibility. In spectroscopic ellipsometry, \( \Psi \), \( \Delta \)-values are measured as a function of the photon energy, and consequently, the photon energy dependence of the dielectric function can be determined. The incidence angle \( \Theta \) is chosen close to the Brewster angle (68° for silicon) in order to maximize the sensitivity.

The Si substrates with \( \sim 400 \) nm SiO\(_2\) were modeled by a semi-infinite c-Si layer, an one nanometer thick interface layer, and a top oxide layer of SiO\(_2\). Prior to the deposition, the starting surface was characterized by determining the SiO\(_2\) thickness of the substrate material. The deposited Pt or PtO\(_2\) film was modeled by adding a layer on top of the SiO\(_2\) layer that describes the optical properties of the deposited material. Two different parameterizations which will be described below, were used to model the various Pt-based materials.

Pt films

Following the literature on sputtered Pt films [53], we used the Drude-Lorentz parametrization to describe conductive Pt films. The Drude term accounts for the intraband absorption by conduction electrons and the Lorentz oscillators for the interband absorption by bound electrons. Choi et al. reported seven Lorentz oscillators to describe the dielectric function of sputtered Pt films in the photon energy range 0 - 10 eV. We found that one Drude and only three Lorentz oscillators are sufficient to model the dielectric function of Pt films in the smaller photon energy range 0.7 - 5 eV if the contribution of transitions greater than 5.0 eV are taken into account by a pole positioned at a high photon energy. The dielectric function is then given by:

\[
\epsilon = \epsilon_1 + i\epsilon_2 = \epsilon_\infty - \frac{\omega_{pu}^2}{\omega^2 - i\Gamma_D\omega} + \sum_{j=1}^{2} \frac{f_j\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j\omega} + \frac{A}{\omega_p^2 - \omega^2}
\]  

where the Drude term is described by the unscreened plasma energy \( h\omega_{pu} \) and the damping factor \( \Gamma_D \), and the Lorentz oscillators by the energy position \( h\omega_{0j} \), strength \( f_j \) and damping factor \( \gamma_j \). The pole is characterized by the position \( \omega_p \) and the magnitude \( A \).

Figure 2.7 shows the imaginary part of the dielectric function of a typical ALD grown Pt film. As can be seen in the graph, the dielectric function is modeled by one Drude term, a strong
Lorentz peak located at 0.9 eV, one Lorentz peak positioned at 1.2 eV, and a very broad Lorentz peak with a less defined position. The near-infrared extension that measures down to a photon energy of 0.75 eV enables the more accurate determination of the Drude term and the strong Lorentz oscillator positioned at 0.9 eV.

PtO$_2$ films

To model the dielectric function of transparent conductive oxides or amorphous materials the Tauc-Lorentz model can be used. In the Tauc-Lorentz model, the imaginary part of the dielectric function is modeled as the product of a unique bandgap and the Lorentz model and is given by:

$$\epsilon_2(E) = \begin{cases} 
\frac{A E_0 \Gamma (E-E_g)^2}{(E-E_g)^2 + \Gamma^2}, & E > E_g, \\
0, & E \leq E_g,
\end{cases}$$  \hspace{1cm} (2.2)

where $E_g$ is bandgap, $E_0$ the peak transition energy, $\Gamma$ the broadening, and $A$ the optical transition matrix element [54]. The real part of the dielectric function can be derived from the imaginary part by using Kramers-Kronig relations. We used this parametrization to model the dielectric function of PtO$_2$ films.

2.3.2 Growth rate determination

In situ spectroscopic ellipsometry measurements were carried out during several deposition runs to determine the process window of ALD growth. The growth rate as a function of operating settings such as MeCpPtMe$_3$ dosing and O$_2$ gas / plasma time was determined to investigate the self-limiting character of the ALD half-reactions. To this end SE measurements were done during temporary interruptions of the deposition process. After several SE measurements a growth rate was determined from the graph of the thickness as a function of the number of cycles by determining the slope of the curve. Hereafter, the operating setting in question was changed in order to measure the growth rate for a new setting. Typically, a SE measurement was carried out after every 10 cycles and the operating setting was changed after 5 SE measurements, i.e. 50 cycles.
2.4 Results

Table 2.2: Material properties of Pt films deposited by thermal and plasma-assisted ALD and of a PtO₂ film deposited by plasma-assisted ALD. The material properties were obtained by using in situ spectroscopic ellipsometry (SE), X-ray reflectrometry (XRR), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS), and four-point probe (FPP). The RBS mass density was calculated using the thickness determined with XRR. The growth of the thermal ALD film was started with 150 cycles plasma-assisted Pt ALD.

<table>
<thead>
<tr>
<th>ALD process</th>
<th>Thickness (nm)</th>
<th>Mass density (g cm⁻³)</th>
<th>Composition (at. %)</th>
<th>Electrical resistivity (µΩ cm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>SE XRR XRR RBS</td>
<td>Pt O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 s plasma</td>
<td>27.3±0.5</td>
<td>26.6±0.3</td>
<td>22±1</td>
<td>20.8±0.5 100 &lt;5 13±1</td>
<td>0.7±0.3</td>
</tr>
<tr>
<td>5 s plasma</td>
<td>~30 29.2</td>
<td>22 20.0</td>
<td>100 &lt;5 15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As is presented in Table 2.2 pure, low-resistivity, high-density Pt films were deposited using either plasma-assisted ALD with short plasma exposure (0.5 s) or thermal ALD. Semi-conductive PtO₂ films were obtained by using a longer plasma exposure step (5 s). The remaining material properties will be treated in Sec. 2.4.2. First, the ALD growth and nucleation results will be presented. And after that, the temperature dependences of the ALD processes will be discussed in Sec. 2.4.3.

2.4.1 ALD growth and nucleation

Initial growth

Figure 2.8 shows the thickness as a function of the number of cycles as measured by in situ SE for the growth initiation period on a thermal SiO₂ substrate for three different deposition runs. No growth of Pt was observed for the thermal ALD process. Even continuing the experiment for 1200 cycles did not result in an observable growth on the SiO₂ substrate.

The plasma-assisted ALD process resulted in immediate growth with a short nucleation period after which a linear increase of the film thickness with the number of cycles was obtained. Furthermore the graph shows that the growth continues linearly after switching from plasma-assisted ALD to thermal ALD yielding the possibility to start the thermal ALD growth by deposition of a Pt seed layer by plasma-assisted ALD. Both processes show a similar growth per cycle as reported by Aaltonen et al. [35]; 0.045 ± 0.04 nm/cycle for thermal ALD and 0.047 ± 0.04 nm/cycle for plasma-assisted ALD.

As can also be seen in the graph, the growth initiation for PtO₂ deposition by plasma-assisted ALD is similar to the initiation of plasma-assisted ALD of Pt. The growth is linear with the number of cycles (0.047 ± 0.04 nm/cycle) after a short nucleation period.

The difference in initial growth behavior between both plasma-assisted processes and the thermal ALD process suggests that the plasma-assisted processes do not rely on the ability of the surface to induce the dissociative chemisorption of O₂, due to the delivery of reactive species from the gas phase. Furthermore, the fact that the thermal ALD process starts on a plasma-assisted ALD grown seed layer and not on a SiO₂ substrate implies that the ability of the substrate material to catalyze the creation of more reactive oxidizing species is required for thermal ALD. Therefore, it can be said that the plasma-assisted ALD processes are less dependent on the starting surface than the thermal ALD process. The mechanism of growth initiation will be discussed in more detail in the Chapter 3.

The aforementioned observation that the thermal ALD growth does not start on a SiO₂ substrate is in contrast with the thermal ALD studies reported in literature [44, 37, 45]. However, we use a low O₂ pressure (0.03 mbar) in comparison with these studies. Using a higher O₂ pressure (≥ 0.08 mbar) in our reactor also resulted in growth on SiO₂ substrates as will be presented in
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Figure 2.8: Initial growth of Pt by thermal and plasma-assisted ALD (0.5 s plasma) and PtO$_2$ by plasma-assisted ALD (5 s plasma) on a 400 nm thermal SiO$_2$ substrate as measured by in situ spectroscopic ellipsometry. After 150 cycles plasma-assisted ALD of Pt the growth was continued with thermal ALD indicating the possibility to deposit on a plasma-assisted ALD deposited seed layer by thermal ALD. The SE measurements have a reduced accuracy for very thin films (1-2 nm).

Sec. 3.4.2.

From the observations that a catalytic active seed layer is required for the thermal ALD process to initiate the growth, whereas no growth occurs on a SiO$_2$ substrate even after 1200 cycles, it can be deduced that the settings for thermal ALD are probably suitable for the combinatorial EBID-ALD approach. At least, if the EBID seed layer material is also able to induce ALD growth. In Chapter 3, the regime in which selective growth can be obtained will be characterized further.

ALD growth window

Various process conditions, i.e., the MeCpPtMe$_3$ dosing time, the O$_2$ dosing time, and the plasma exposure time, were varied to determine the process window of ALD growth for both thermal and plasma-assisted ALD. The growth rate per cycle as a function of both reactant dosings reveals the self-limiting nature of the ALD half-reactions, which is the unique feature of ALD.

The growth rate as a function of the plasma exposure time was investigated for the plasma-assisted ALD process. In Fig. 2.9(a) the results are shown for a MeCpPtMe$_3$ dosing time of 3 s and a deposition temperature of 300°C. The growth rate per cycle was measured to be about 0.047 nm/cycle irrespective of the plasma exposure time.

Whether Pt or PtO$_2$ is deposited can be investigated by using in situ SE for measuring the dielectric function of the deposited film. In Fig. 2.9(b) the imaginary part ($\epsilon_2$) of the dielectric functions of two Pt based films are plotted as a function of the photon energy. A short plasma exposure (0.5 s) yielded a conductive material for which the Drude-Lorentz parameterization was used to model the dielectric function. This film shows a significant Drude term in the infrared accounting for the absorption by conduction electrons. For 5 s plasma exposure, a bandgap material was obtained which is the PtO$_2$ phase. The dielectric function of this film is parametrized with a single Tauc-Lorentz oscillator which gives a Tauc bandgap of 1.5 eV. The bandgap is close to the bandgap of amorphous sputtered PtO$_2$ reported in the literature (1.2-1.3 eV) [46]. This graph clearly illustrates that it can be examined in situ whether Pt or PtO$_2$ is deposited by using spectroscopic ellipsometry since the dielectric function is sensitive to the material composition.

As is indicated in Fig. 2.9(a), for plasma exposure times of >1 s the Tauc-Lorentz model could
only be used to fit the SE data which is a strong indication that PtO\textsubscript{2+x} films were deposited for these conditions. Based on these observations, it can be stated that the stoichiometry can be tuned to pure Pt or PtO\textsubscript{2} with the O\textsubscript{2} plasma exposure time parameter.

Subsequently, the growth per cycle as a function of MeCpPtMe\textsubscript{3} dosing was measured for both plasma-assisted ALD processes and for the thermal ALD process. In Fig. 2.10 the results are presented for films deposited at a substrate temperature of 300 °C. The MeCpPtMe\textsubscript{3} dose was varied while keeping either the O\textsubscript{2} dosing time constant to 5 s, or the plasma exposure time constant to 0.5 s for Pt or 5 s for PtO\textsubscript{2} deposition. The data sets are fitted with single exponential functions of the form $A(1 - e^{-bx})$, which corresponds to the assumption that the MeCpPtMe\textsubscript{3} molecules chemisorb saturatively on the surface of the film.

For the thermal ALD process, the growth rate becomes constant when the MeCpPtMe\textsubscript{3} dosing time is greater than 0.3 s, with a saturated value of 0.045 ± 0.004 nm/cycle. A maximum growth rate of 0.047 ± 0.004 nm per cycle was obtained with the Pt plasma-assisted ALD process using 3 s MeCpPtMe\textsubscript{3} dosing. The growth rate per cycle for PtO\textsubscript{2} deposition (5 s plasma exposure) saturates to 0.047 ± 0.004 nm for MeCpPtMe\textsubscript{3} dosing times longer than ~2 s. Apparently a longer MeCpPtMe\textsubscript{3} dosing time is required for both plasma-assisted ALD processes as compared to the thermal ALD process to reach saturation. This can be explained by the effect that for the plasma-assisted processes also film growth occurs on the cold reactor wall (~75 °C), as can be seen by visual inspection, due to larger temperature window of the plasma-assisted ALD processes (See Sec. 2.4.3). Because of the increased area on which growth occurs, a higher amount of precursor molecules is required to reach saturation of the MeCpPtMe\textsubscript{3} adsorption half-reaction. The faster saturation of the PtO\textsubscript{2} process as compared to the plasma-assisted Pt process might be related to the lower number of Pt atoms that are deposited per cycle for the PtO\textsubscript{2} process (See Sec. 2.4.2).

The O\textsubscript{2} dosing time was varied for the thermal ALD process from 0.5 to 7 s for a constant MeCpPtMe\textsubscript{3} dosing of 1 s and was found to have no significant effect on the growth rate, which indicates that a short O\textsubscript{2} exposure is sufficient to complete the oxidation half-reaction.
2.4.2 Material properties

An overview of the material properties of Pt obtained with thermal and plasma-assisted ALD and of PtO$_2$ deposited with plasma-assisted ALD can be found in Table 2.2. The material properties of both Pt films are very similar, i.e. high density ($\sim$21 g/cm$^3$), low-resistivity ($\sim$15 $\mu$Ωcm) and high purity ($\sim$100%). Both films are virtually pure Pt as determined by Rutherford backscattering spectroscopy (RBS), that is the O and C content are below the detection limit (<5%) of RBS. The resistivity of the Pt films as measured with the four-point-probe technique is only slightly higher than bulk resistivity (10.8 $\mu$Ωcm) and comparable to values reported in literature [35, 45]. RBS also revealed that the number of deposited Pt atoms per cycle is $(3.0 \pm 0.2) \times 10^{14}$ cm$^{-2}$ cycle$^{-1}$, which corresponds to 0.2 monolayer Pt growth per cycle.

The grazing incidence X-ray diffraction spectra in Fig. 2.11(a) of Pt films deposited by thermal and plasma-assisted ALD contain only diffraction lines that were assigned to Pt metal indicating that cubic phase Pt films were grown. No diffraction peaks related to oxides such as PtO or $\alpha$-PtO$_2$ were observed. The relatively high intensity of the (220) peak in the grazing incidence diffractogram reveals that the Pt crystallites have a preferred orientation with their (111) lattice planes parallel to the sample surface as also reported for the thermal ALD process in the literature [35, 37]. This orientation is thermodynamically favored because the close-packed (111) plane of fcc Pt has the lowest surface energy [55]. From the stronger diffraction peaks of the plasma-assisted ALD film, which is only three nanometers thicker than the thermal ALD film, it can be deduced that the crystallinity of this film is higher.

PtO$_2$ deposition by the plasma-assisted ALD process using 5 s plasma exposure led to slightly overstoichiometric platinum oxide (PtO$_{2.2}$) with a lower mass density ($\sim$9 g/cm$^3$) compared to the the mass densities of the $\alpha$-PtO$_2$ ($\sim$11.4 g/cm$^3$) and $\beta$-PtO$_2$ ($\sim$10.9 g/cm$^3$) phases [46]. The number of Pt atoms deposited per cycle ($(9.7 \pm 0.2) \times 10^{13}$ cm$^{-2}$ cycle$^{-1}$) is roughly a factor three lower than for the Pt processes. In agreement with the semiconducting nature indicated by the optical band gap, the resistivity of the PtO$_{2.2}$ film is very high and above the detection limit of the four-point-probe (>100,000 Ωcm). For the PtO$_2$ thermal ALD process using Pt(acac)$_2$ and O$_3$ precursors reported in the literature a lower resistivity value of 1.5 - 5 Ωcm was obtained, which might be related to the understoichiometric composition (PtO$_{1.6}$) of the material prepared with this process [43]. The diffraction pattern of the PtO$_{2.2}$ film shows a few broad peaks that can not
2.4 Results

Figure 2.11: (a) Grazing incidence X-ray diffraction (XRD) spectra of Pt films deposited by thermal (27 nm thick) and plasma-assisted ALD (~30 nm thick) and of a PtO$_2$ film (27 nm thick) deposited by plasma-assisted ALD. (b) Atomic force microscopy (AFM) image of a 27 nm thick Pt film deposited by thermal ALD on a Pt seed layer deposited with 150 cycles plasma-assisted ALD.

be identified as α- or β-PtO$_2$ phases meaning that the film is nano-crystalline or amorphous.

The surface morphology of the films was examined by atomic force microscopy (AFM) giving the roughness values listed in Table 2.2. A typical AFM image of a film deposited by thermal ALD on a plasma-assisted ALD seed layer is shown in Fig. 2.11(b). Films with low RMS values (0.7 ± 0.3) were obtained for all processes, which were lower than the values for thermal ALD reported in literature (0.75 - 4 nm) [35, 37, 44, 45]. The low roughness values may indicate that the plasma-assisted ALD growth starts through layer-by-layer growth instead of island growth, since island growth is known to result in increased surface roughness [8].

2.4.3 Temperature windows of the ALD processes

Figure 2.12 illustrates that both plasma-assisted processes have wider temperature windows than their thermal ALD counterparts. The graph shows the dependence of the growth rate on the substrate temperature for the thermal ALD process, for the two plasma-assisted processes (0.5 and 5 s plasma) and for a modified plasma-assisted ALD process which will be discussed later in this section.

For PtO$_2$ deposition the growth rate increases with decreasing deposition temperature and shows a large temperature window (100$^\circ$C - 300$^\circ$C). Previously, PtO$_2$ ALD was only obtained using O$_3$ as a oxidizing agent for a small temperature window (120$^\circ$C - 130$^\circ$C) [43].

The temperature window of Pt deposition by thermal ALD ranges from 200$^\circ$C to 300$^\circ$C with low growth rates below 225$^\circ$C. No Pt was deposited for substrate temperatures of 150$^\circ$C and lower. The dissociative chemisorption of O$_2$ is believed to be the limiting factor here. Due to the delivery of reactive species from the gas phase, the plasma-assisted ALD process is not limited by this factor, which is illustrated by the higher growth rate at 200$^\circ$C. However a higher resistivity (~500 $\mu$Ωcm) indicates that the film deposited at 200$^\circ$C probably contained more impurities (O and/or C atoms). Exposure of this film to a H$_2$ plasma at 100$^\circ$C led to a lower resistivity of 61 $\mu$Ωcm as well as a decrease in thickness (from 9 to 6 nm). These observations suggest that a H$_2$ plasma is able to reduce a PtO$_2$ film to Pt. Apparently, the oxygen atoms were removed from the PtO$_2$ film by the interaction of the H$_2$ plasma with the film resulting in a decrease of the thickness.

The ability of a H$_2$ plasma to reduce a PtO$_2$ film to Pt can be illustrated by monitoring the
Figure 2.12: Growth rate per cycle for all four ALD processes as a function of substrate temperature by using spectroscopic ellipsometry. The plotted lines serve as a guides to the eye.

Figure 2.13: Pictures of the interior of the reactor chamber before and after H\textsubscript{2} plasma exposure. After the H\textsubscript{2} plasma exposure, a metallic Pt reactor wall condition is obtained.

condition of the reactor wall. Figure 2.13 shows a picture of the interior of the deposition chamber showing the substrate holder in the middle and the reactor wall on the background. It was found that the color of the reactor wall changes with the thickness of the film coated on the wall by plasma-assisted ALD, which indicates that a (partly) transparent film was deposited on the wall, most probably PtO\textsubscript{x}>0. After a H\textsubscript{2} plasma exposure, the PtO\textsubscript{2} was transformed into metallic Pt as can be seen in the other picture.

A similar change of the reactor wall can be observed as a result of H\textsubscript{2} gas exposure, which means that also a H\textsubscript{2} gas is reductive enough to transform PtO\textsubscript{2} into Pt as was also reported in literature [46]. The decomposition of the PtO\textsubscript{2} by the interaction with H\textsubscript{2} gas demonstrates the low stability of the PtO\textsubscript{2} phase relative to the metallic Pt state.

Low temperature plasma-assisted Pt ALD process

Two aspects mentioned above are relevant for the development of a new low temperature Pt ALD process:

1. PtO\textsubscript{2} deposition is possible by plasma-assisted ALD at a substrate temperature as low as 100 °C.

2. PtO\textsubscript{2} can be reduced to Pt by H\textsubscript{2} gas or H\textsubscript{2} plasma exposure at 100 °C.
2.5 Conclusions

A new plasma-assisted ALD process for the deposition of Pt using MeCpPtMe3 as precursor in combination with an O2 plasma was developed in addition to the already existing thermal ALD process. Furthermore, settings were found for which PtO2 films can be deposited. The processes were characterized and a comparison was made with the thermal ALD process of Pt. High-purity, low-resistivity Pt was obtained for short O2 plasma exposure while PtO2 was deposited for long plasma exposure times. The nucleation behavior was investigated by using in situ spectroscopic ellipsometry, which revealed that the plasma-assisted processes yields virtually immediate growth on SiO2 substrates. For both plasma-assisted ALD processes wider temperature windows were obtained as compared to their thermal ALD counterparts. It was found that by adding a H2 gas exposure step to the plasma-assisted Pt ALD process, pure Pt can be deposited at substrate temperatures as low as 100°C.

No growth was observed for thermal ALD on a SiO2 substrate but the growth could be started on a plasma-assisted ALD grown Pt seed layer. This observation reveals that a catalytic active seed layer is required to initiate the growth, and therefore the standard thermal ALD settings seem to be suitable for the combinatorial EBID-ALD method. When depositing on a thin plasma-assisted ALD seed layer, similar material properties were obtained for the thermal ALD process as achieved using plasma-assisted ALD, i.e. high purity, low resistivity, high density Pt films.

The above-mentioned merits offered by the plasma-assisted ALD process may open new ap-
plication areas for Pt ALD. For example, the fact that the growth immediately starts for the plasma-assisted process while a growth delay is observed for the thermal ALD process might be an important result for the catalysis industry, since this means that a significant amount of expensive Pt precursor can be saved. Although less investigated, ALD grown PtO$_2$ may also be an interesting material for many applications in catalysis and microelectronics. Furthermore, the ability to deposit pure Pt at relatively low substrate temperatures yields the possibility to deposit thin conformal Pt films on temperature-sensitive substrates.
Chapter 3

Reaction mechanisms of Pt ALD

3.1 Introduction

Fundamental insight into the reaction mechanisms of ALD processes is essential to comprehend the dependence of the nucleation behavior and material properties on the operating settings. Moreover, an understanding of the reaction mechanisms aids in the development of novel applications such as the combinatorial EBID-ALD method introduced in this work.

The Pt ALD process can be regarded as a model system for a class of transition metal ALD processes in which the catalytic activity of the as-deposited film is essential for the process. Insight into the mechanisms of Pt ALD can therefore also help in understanding other metal ALD processes. Previously, the reaction mechanisms of Ru and Pt ALD were studied by Aaltonen et al. [36], whereas no reaction mechanism studies of related plasma-assisted ALD processes have been reported yet.

Figure 3.1 shows a schematic representation of the reaction mechanism of Pt ALD as suggested by Aaltonen et al. [36]. The cycle starts with the MeCpPtMe₃ exposure step during which the MeCpPtMe₃ molecules adsorb at the surface and a part of the formed precursor ligands oxidatively decompose forming CO₂ and H₂O reaction products. The fact that these reaction products were detected during the MeCpPtMe₃ precursor half-reaction by quadrupole mass spectroscopy (QMS) [56], indicates that surface bound oxygen must be present at the Pt surface at the start of the MeCpPtMe₃ exposure step. Because of the limited availability of oxygen atoms at the Pt film some unreacted ligands remain at the surface during the subsequent pump step. In the second half-reaction O₂ gas is introduced in the reactor and oxygen atoms are created at the surface due to dissociative chemisorption of O₂. The oxygen atoms react with the unreacted ligands leading to the deposition of Pt atoms and again the formation of CO₂ and H₂O reaction products. O atoms reside at the surface during the subsequent pump step which leads to a similar surface as at the start of the cycle, i.e. a Pt film containing surface bound oxygen. In the study of Aaltonen et al. it was suggested that the surface bound oxygen might partially diffuse into the subsurface region [36] which increases the amount of O atoms that can be adsorbed.

Because of the catalytic nature of as-deposited films, a distinction must be made between the reaction mechanisms on the as-deposited Pt film and on the substrate surface. Since most substrate materials are not able to catalyze the dissociative chemisorption of O₂, the Pt thermal ALD process can show a significant growth delay on particular substrates.

Because the interaction of O₂ with the Pt surface plays an essential role in the reaction mechanism of Pt ALD, it might be insightful to use the results of ultra high vacuum (UHV) studies of the exposure of Pt to oxidizing species as background information. Although care needs to be taken when comparing the results from UHV studies of well-defined extremely flat Pt surfaces with ALD performed at high vacuum conditions, these UHV studies can still be very useful for
unraveling the ALD mechanisms. The interactions between O$_2$ and a Pt(111) surface have been extensively investigated in the literature\(^1\). In short it has been found that O$_2$ is molecularly chemisorbed at low surface temperatures (<100 K) \([57]\), while molecular desorption and dissociation into atomic species begin to occur at substrate temperatures above 150 K \([58]\). When the surface is initially saturated with O$_2$, dissociative chemisorption generates an atomic oxygen coverage of 0.25 monolayers (ML) \([59, 60]\), where 1 ML is equal to the density of Pt atoms on the film surface. A higher O coverage can be obtained by using more reactive oxidizing species such as NO$_2$, O$_3$, or O$_2$ plasma \([61]\). Increasing the oxygen coverage above about 0.75 mL results in the formation of subsurface oxygen and the growth of PtO$_2$ particles \([58, 61]\).

In this chapter, some specific results presented in the previous chapter are explained in more detail in light of the reaction mechanism of thermal Pt ALD as proposed by Aaltonen \textit{et al.} The insight in this mechanism is also extended by considering the results of a Fourier transform infrared transmission spectroscopy (FTIR) study. Furthermore, some additional results obtained by using \textit{in situ} spectroscopic ellipsometry are presented, and also the mechanism of plasma-assisted Pt and PtO$_2$ ALD is addressed. Additionally, the nucleation behavior of both thermal and plasma-assisted ALD is discussed and the selective growth regime for the combinatorial EBID-ALD approach is explored. Literature results of UHV studies on the interaction of oxidizing species with a Pt surface are discussed accordingly to explain the observations. Due to the similarities of ruthenium ALD with Pt ALD, some results of Ru ALD studies are described for comparison.

### 3.2 Reaction mechanism of thermal Pt ALD

#### 3.2.1 Gas phase reaction products

A Fourier transform infrared transmission spectroscopy (FTIR) study was carried out in a project related to this work with the objective to measure the gas phase reaction products of the thermal ALD process \([62]\). See Ref. \([62]\) for details on the measurement procedure. Here, the main results of the FTIR study are summarized and the interpretation is extended by combining it with results obtained using \textit{in situ} spectroscopic ellipsometry and by considering literature studies.

Transmission infrared spectra obtained during the two half-reactions of the thermal ALD process are plotted in Fig. 3.2. The absorption bands in the region around 2360 cm$^{-1}$ reveal the formation of CO$_2$ during both the MeCpPtMe$_3$ and O$_2$ half-reactions. Also the formation of H$_2$O can be observed from the absorbance peaks around 1600 cm$^{-1}$ and 3700 cm$^{-1}$ in the spectrum recorded during the O$_2$ exposure step. These observations suggest that the ligand

\(^1\)The Pt crystallites of ALD grown films have a preferred orientation with their (111) lattice planes parallel to the sample surface (Sec. 2.4.2).
3.2 Reaction mechanism of thermal Pt ALD

Figure 3.2: Infrared absorbance spectra recorded during the MeCpPtMe$_3$ and O$_2$ exposure half-reactions [62]. Spectra of the individual reaction products and of the MeCpPtMe$_3$ precursor are displayed as a reference.

An oxidation reaction occurs during both the MeCpPtMe$_3$ and the O$_2$ exposure half-reactions, which implies that oxygen atoms created by the dissociative chemisorption of O$_2$ reside at the Pt surface after O$_2$ dosing. So far, these observations are in line with the reaction mechanism proposed by Aaltonen et al., and therefore serve as additional proof for that study.

Furthermore, the spectrum recorded during the MeCpPtMe$_3$ half-reaction shows a peak at 2909 cm$^{-1}$ related to the absorption of MeCpPtMe$_3$ molecules which suggests that the precursor dosing has reached saturation. In addition, some peaks caused by the presence of CH$_4$ molecules can be seen in the MeCpPtMe$_3$ half-reaction spectrum. From this observation, it can be concluded that also CH$_4$ molecules are produced during the MeCpPtMe$_3$ half-reaction. This was not reported before, and therefore extends the insight into the Pt ALD reaction mechanism.

A calibration was carried out to quantify the amount of CO$_2$ molecules by measuring the integrated infrared absorbance of the CO$_2$ band as a function of the CO$_2$ pressure. A similar calibration has been performed in a previous study to quantify the amount of CH$_4$ molecules released into the reactor by the surface reactions [63].

By using the CO$_2$ calibration data, it was deduced that roughly 6.5% of the total amount of CO$_2$ reaction product molecules are formed during the MeCpPtMe$_3$ half-reaction, which suggests that approximately 15 times more carbon atoms from adsorbed MeCpPtMe$_3$ molecules are oxidized during the O$_2$ pulse. This observation is in agreement with the study of Aaltonen et al. in which the detection of a relatively small amount of CO$_2$ during the MeCpPtMe$_3$ step was reported [56]. Furthermore, by quantifying the amount of created CH$_4$ molecules it has been established that during the MeCpPtMe$_3$ exposure step the amount of released CH$_4$ is roughly equivalent to the amount of formed CO$_2$ molecules.

Every MeCpPtMe$_3$ precursor molecule consists of 9 C atoms and 16 H atoms (See Fig. 3.3). From the quantification of CO$_2$ and CH$_4$ reaction products, it can be deduced that roughly one C atom is liberated as reaction product during the adsorption of a MeCpPtMe$_3$ precursor molecule on the Pt film. The other eight C atoms stay at the surface and are oxidized during the O$_2$ half-reaction. By taking into account that the Pt atom in the MeCpPtMe$_3$ precursor molecule is bonded to three CH$_3$ groups and one CpCH$_3$ group it can be suggested that one CH$_3$ is group is split off during the MeCpPtMe$_3$ adsorption. This CH$_3$ group can react to CH$_4$ by ligand exchange or become oxidized by the reaction with oxygen atoms adsorbed at the Pt surface. The virtually
equal amounts of CH$_4$ and CO$_2$ formed during the MeCpPtMe$_3$ adsorption reaction indicate that half of the MeCpPtMe$_3$ molecules adsorb by ligand exchange and the other half by oxidation of the -CH$_3$ ligand.

Based on this picture, the reaction mechanism of thermal Pt ALD can be summarized as:

$$2NaCpPtMe_3(g) + 3O(ads) \rightarrow 2NaCpPtMe_2(ads) + CH_4(g) + CO_2(g) + H_2O(g) \quad (3.1)$$

$$2NaCpPtMe_2(ads) + 24O_2(g) \xrightarrow{Pt} 2Pt(s) + 3O(ads) + 16CO_2(g) + 13H_2O(g) \quad (3.2)$$

where Eq. 3.1 describes the MeCpPtMe$_3$ adsorption half-reaction and Eq. 3.2 the O$_2$ exposure half-reaction. In Eq. 3.2, the Pt surface is essential of the dissociative chemisorption of O$_2$ molecules. According to Eq. 3.1 two MeCpPtMe$_3$ molecules react with the surface liberating one CH$_4$ molecule, and one CO$_2$ molecule and leaving 2 MeCpPtMe$_2$ on the surface. In Eq. 3.2, surface bound oxygen species created by dissociative chemisorption of O$_2$ oxidize these two ligands leading to the formation of CO$_2$ and H$_2$O reaction products. Three O atoms reside at the surface and thereby provide again the initial surface while two Pt atoms are deposited.

Information on the surface groups formed during the O$_2$ exposure step cannot be deduced directly from the measured data. However, the fact that CH$_4$ is released during the MeCpPtMe$_3$ exposure step might be an indication that hydrogen atoms are present at the surface of the film after O$_2$ gas exposure.

The surface chemistry of thermal ALD of Pt may show similarities to the plasma-assisted ALD reaction mechanism of for example Al$_2$O$_3$ due to the role of oxygen atoms as oxidizing species. These oxygen atoms might play a similar role as the oxygen radicals in an O$_2$ plasma of plasma-assisted ALD. For Al$_2$O$_3$ deposition, it has been reported that -OH surface groups are formed in combustion like reactions between -CH$_3$ surface groups and O$_2$ plasma species (most notably O atoms) in which CO$_2$ and H$_2$O reaction products are formed. During the TMA (Al(CH$_3$)$_3$) precursor half-reaction TMA molecules react with formed -OH surface groups liberating CH$_4$ reaction products and leaving -CH$_3$ ligands on the surface [64]. The combination of similar precursor ligands, i.e. -CH$_3$, and O atoms might lead also for Pt ALD to the formation of -OH surface groups as a result of ligand combustion. Also the combustion of cyclopentadienyl (Cp) ligands by oxygen radicals can lead to the creation of -OH groups as has been suggested by Elam et al. [65].

In case of the presence of -OH surface groups at the Pt surface, MeCpPtMe$_3$ might partly adsorb at the surface at these groups. The reaction of a -CH$_3$ ligand of the MeCpPtMe$_3$ precursor with a -OH group results then in the adsorption of the MeCpPtMe$_3$ molecule and the formation of a CH$_4$ molecule.

Alternatively, CH$_4$ may be created in a concurrent reaction between H$_2$O reaction product molecules and surplus MeCpPtMe$_3$ or by a reaction of a -CH$_3$ group with a H atom originating from one of the other groups of the MeCpPtMe$_3$ molecule.
3.2 Reaction mechanism of thermal Pt ALD

3.2.2 Influence of the amount of surface bound oxygen

As reported in the previous chapter, Rutherford backscattering spectroscopy revealed that approximately 0.2 monolayer (ML) Pt is deposited per cycle. Since during MeCpPtMe₃ adsorption 1.5 O atoms are consumed per adsorbed MeCpPtMe₃ molecule according to Eq. 3.1, a surface coverage of 0.3 ML of adsorbed oxygen atoms is required for this reaction to occur. The 0.3 ML coverage is roughly equal to the O coverage that can be obtained by dissociative chemisorption of O₂ molecules at a Pt(111) surface (0.25 ML) [59, 60], and much less than the required critical O coverage for the incorporation of O atoms in the subsurface (0.75 ML) [61]. Therefore it can be concluded that the amount of O atoms chemisorbed at the surface is sufficient for MeCpPtMe₃ adsorption reaction and that the involvement of subsurface oxygen is not required for the standard thermal ALD process.

The pressure of the O₂ gas during the O₂ half-reaction might have an influence on the growth rate of the thermal Pt ALD process. A dependence of the growth rate on the O₂ gas pressure was reported for Ru ALD by Parsons et al. who measured the growth rate as a function of O₂ pressure and found an increase for O₂ pressures above 2 mbar [66]. This observation was explained by an increase of the amount of subsurface oxygen atoms with O₂ pressure, which leads to more pronounced precursor oxidation already during the precursor adsorption half-reaction and thus to the adsorption of more precursor molecules.

A growth rate of 0.085 nm/cycle was measured when an O₂ pressure of 0.7 mbar was employed instead of the standard 0.03 mbar. However this result was only obtained after a PtO₂ deposition run, which means that PtO₂ was present at the reactor wall. For a metallic Pt reactor wall condition, the growth rate was measured to be not dependent on the O₂ pressure: Growth rates of about 0.045-0.050 nm/cycle were measured when varying the O₂ pressure from 0.01 up to 5 mbar as will be presented in Sec. 3.4.2.

The high growth rate obtained for an O₂ pressure of 0.7 mbar and a wall coated with PtO₂ thus seems to be related to the condition of the reactor wall. Since PtO₂ does not support the adsorption of oxygen atoms at the surface, the surface loss of O₂ at a PtO₂ reactor wall is low, and consequently, more O₂ molecules are able to interact with the sample. This might result in the formation of subsurface oxygen which could be the explanation for the observed high growth rate.

The dependence of the growth rate on the O₂ pressure indicates that oxygen diffusion into the subsurface region can play a role in the reaction mechanism as was suggested by Aaltonen et al. [36]. However, this seems only be the case for very specific conditions (for example by using a high O₂ pressures in combination with PtO₂ on the reactor wall). Apparently, it is difficult to create subsurface oxygen for a Pt surface. Therefore it can be said that subsurface oxygen usually does not play a role for the standard Pt ALD process. This statement is in agreement with the observation of a constant growth rate per cycle as a function of O₂ pressure (for a Pt reactor wall condition) and with the fact that other thermal ALD studies [44, 37, 45] report a similar growth rate (0.045 - 0.50), while using higher oxygen pressures than the standard condition in this work.

The amount of oxygen atoms that resides at the surface after the O₂ exposure half-reaction might also have an influence on the growth rate of the process. For ruthenium plasma-assisted ALD using a NH₃ plasma, a growth rate of only 0.038 nm/cycle was obtained by Kwon et al. [67], which is much lower than the growth for conventional Ru ALD using O₂ (0.15 nm/cycle). The difference in growth rate between these processes was attributed in that study to the presence of surface bound oxygen during the precursor adsorption reaction of the conventional ALD process. Due to the (partly) oxidation of precursor ligands during the precursor exposure step by surface bound oxygen, more precursor molecules can be adsorbed as compared to the situation when no adsorbed oxygen is present at the surface. This implies that the presence of adsorbed oxygen atoms at the Pt surface after the O₂ step can have a significant influence on the growth rate of the process. The effect of the surface bound oxygen was verified by Kwon et al. by removing the
surface bound oxygen with an additional hydrogen plasma exposure step. In that case, a similar growth rate was obtained as the plasma-assisted ALD process [67].

Adding a H\textsubscript{2} plasma exposure step of 5 s to our thermal Pt ALD process resulted in a growth rate of only 0.020 nm/cycle. Growth rates of about 0.045 nm/cycle were measured for the standard thermal ALD process, which is 2.3 times more. This observation suggests that due to the presence of surface bound oxygen, 2.3 times as much MeCpPtMe\textsubscript{3} molecules are adsorbed during the precursor exposure step. Apparently, the surface bound oxygen atoms play an important role for the adsorption of MeCpPtMe\textsubscript{3} molecules.

These observations suggest that there are two different MeCpPtMe\textsubscript{3} molecule adsorption mechanisms. When surface bound oxygen is present at the surface, it may play a role in the adsorption mechanism in such a way that it enhances the adsorption of MeCpPtMe\textsubscript{3} molecules. In case no O atoms are present at the surface during the MeCpPtMe\textsubscript{3} half-reaction, the MeCpPtMe\textsubscript{3} adsorption occurs differently and only a relatively small amount of precursor molecules is adsorbed.

Taken together, it can be hypothesized that the amount of surface bound oxygen that is generated by dissociative chemisorption of O\textsubscript{2} molecules determines the growth rate of the thermal ALD process.

### 3.3 Reaction mechanism of plasma-assisted ALD

During the O\textsubscript{2} exposure half-reaction of the thermal ALD process, a maximum atomic oxygen coverage of only 0.25 ML can be achieved through the dissociative chemisorption of O\textsubscript{2} [59, 60]. Since this is approximately equal to the amount of oxygen that is consumed during the MeCpPtMe\textsubscript{3} adsorption reaction, PtO\textsubscript{2} cannot be deposited with the thermal ALD process.

As can be seen in Fig. 3.4, a higher coverage of adsorbed O atoms can be obtained by using a more reactive oxidizing agent as molecular O\textsubscript{2} gas. When a Pt(111) surface is exposed to a plasma-generated oxygen atom beam, an O coverage of up to 2.8 monolayers can be generated [61]. A toplayer of Pt oxide starts to form when the atomic oxygen coverage is increased above 1 ML [61].

**Figure 3.4:** Atomic oxygen coverage on Pt(111) as a function of the atomic oxygen beam exposure as measured by Weaver et al [61].
3.3 Reaction mechanism of plasma-assisted ALD

3.3.1 Pt oxidation by O₂ plasma exposure

Due to the delivery of reactive oxygen radicals to the Pt surface, it can be expected that a higher O coverage can be obtained during an O₂ plasma step of a plasma-assisted ALD process than for the O₂ gas exposure step of the thermal ALD process. The atomic O coverage is expected to increase with the plasma exposure time which means that the required coverage for PtO₂ formation can be achieved during a long plasma exposure step.

In the previous chapter, it was shown that a short plasma exposure time (0.5 s) results in pure Pt films, whereas longer plasma exposure yields PtO₂ films. From the fact that Pt is obtained for 0.5 s plasma exposure, it can be deduced that the atomic O coverage acquired in 0.5 s plasma is not sufficient for PtO₂ formation. In a similar way as for the thermal ALD process, the adsorbed O atoms are consumed during the MeCpPtMe₃ adsorption half-reaction. Although the Pt surface is slightly oxidized during the O₂ plasma exposure half-reaction, a pure Pt film is obtained, since the the surface is reduced by the MeCpPtMe₃ molecules during the precursor adsorption half-reaction. For 5 s plasma exposure, a higher adsorbed oxygen coverage is obtained resulting in the formation of PtO₂.

3.3.2 PtO₂ decomposition

An interesting phenomenon was observed while changing the O₂ plasma exposure time from 5 s to 0.5 during a deposition by the plasma-assisted ALD process. As is illustrated in Fig. 3.5, a decrease of the thickness of the film and a change of the dielectric function of the material was measured by using in situ SE. Initially, PtO₂ was deposited due to the use of a long plasma exposure time (5 s) indicated by the fact that the Tauc-Lorentz model could be used to correctly model the dielectric function of the deposited film. After changing the plasma exposure time, the Tauc-Lorentz model did not fit the data correctly and the Drude-Lorentz model was used, which suggests that the film transformed into a metallic Pt film as a result of the use of a short plasma exposure time (0.5 s). The deposition of Pt for 0.5 s plasma exposure is consistent with the results...
presented in the previous chapter, however, it is remarkable that the entire film transforms into Pt instead of the deposition of a Pt film on top of the as-deposited PtO\textsubscript{2} film. Apparently, the thin Pt film deposited on the PtO\textsubscript{2} is able to induce a reaction in which the oxygen diffuses out of the film transforming it into metallic Pt.

A similar phenomenon was reported in literature for an attempt to deposit amorphous PtO\textsubscript{2} onto evaporated gold by Maya et al [46]. The gold characterized by a (111) preferred orientation caused the decomposition of PtO\textsubscript{2} into metallic Pt. This can be explained by a higher free energy for crystallization of metallic Pt compared to the free energy of PtO\textsubscript{2} formation [46]. The decomposition of PtO\textsubscript{2} to Pt is a temperature activated process. For example, the \(\alpha\)-PtO\textsubscript{2} phase begins to being reduced at 300\(^\circ\)C in vacuum [68].

As was stated above, whether Pt or PtO\textsubscript{2} is deposited by plasma-assisted ALD depends on the exposure of the surface to O radicals, but also the thermal activated decomposition of PtO\textsubscript{2} into Pt may play a role. It appears to be a balance between the oxidation of the Pt by the O\textsubscript{2} plasma, the reduction of the surface of the deposited film by MeCpPtMe\textsubscript{3} molecules, and the decomposition of the PtO\textsubscript{2} toplayer into Pt.

### 3.3.3 Growth per cycle for the plasma-assisted ALD processes

For PtO\textsubscript{2} deposition by plasma-assisted ALD a growth rate of 0.045 nm/cycle was obtained which is comparable to both Pt ALD processes. Since a monolayer of PtO\textsubscript{2} is thicker than a monolayer Pt, this implies that less MeCpPtMe\textsubscript{3} molecules are adsorbed per cycle for the PtO\textsubscript{2} process, which is in agreement with the lower number of Pt atoms deposited per cycle as determined by RBS (see Sec 2.4.2).

During the plasma-assisted ALD process of Pt, a Pt layer will form on the substrate, which is able to catalyze dissociation of O\textsubscript{2} molecules. In addition to the oxidation of the surface ligands by plasma radicals, a second oxidation reaction pathway might be initiated in which O atoms formed on the Pt surface instead of the plasma radicals react with the MeCpPtMe\textsubscript{3} surface ligands. Oxidation reactions in which plasma radicals play a role can only take place during the plasma exposure step, while the oxidation by surface bound oxygen may also occur during the MeCpPtMe\textsubscript{3} dosing step since some oxygen resides at the surface.

Possibly, the MeCpPtMe\textsubscript{3} adsorption half-reaction occurs in a similar was as for the thermal ALD process (See Eq. 3.1) by the splitting off some ligands by either ligand exchange or ligand oxidation. The observation that the growth rates of thermal and plasma-assisted ALD are comparable indicates that also for the plasma-assisted ALD process, surface bound oxygen plays a role in the MeCpPtMe\textsubscript{3} adsorption reaction.

### 3.4 Nucleation and selective growth

In the previous chapter it was suggested that whether the growth of thermal ALD starts on a non catalytic surface depends on the O\textsubscript{2} pressure. No growth was observed for the standard pressure (0.03 mbar), whereas growth was obtained for O\textsubscript{2} pressures of 0.08 mbar and higher. The plasma-assisted ALD process yields immediate growth with a short incubation period. The initial growth for both processes will be discussed in more detail in this section. Additionally, the regime for which selective growth on a Pt seed layer can be obtained will be explored further which is useful for the development of the combinatorial EBID-ALD method.
3.4 Nucleation and selective growth

3.4.1 Initial growth of thermal ALD

A SEM image of the surface Al₂O₃ substrate after 1000 cycles thermal ALD is depicted in Fig. 3.6(a). The presence of small islands can be clearly observed in this image. Apparently, the growth starts for thermal ALD by the formation of small Pt islands. In general, island growth as a growth mode occurs for substrates that are not very reactive with the ALD reactants [69]. For the thermal ALD process, it can be expected that the MeCpPtMe₃ precursor adsorbs at the surface, but the limiting factor for the growth initiation is the oxidative decomposition reaction. A non catalytic surface cannot induce the dissociative chemisorption of O₂ and therefore, the growth initiation relies on the reaction between adsorbed MeCpPtMe₃ molecules and O₂ molecules.

Figure 3.6(b) shows the thickness of films deposited by 400 cycles thermal ALD on SiO₂ substrates as a function of the O₂ pressure. The thickness values were determined by using ex situ spectroscopic ellipsometry. In general, the growth for a complete deposition is on average lower per cycle as the "growth per cycle", due to the contribution of the initial growth delay.

The graph shows that growth on a SiO₂ substrate was obtained for O₂ pressures of 0.08 mbar and higher and increases with the O₂ pressure. The pressure dependence of the growth initiation on a SiO₂ substrate is probably related to a relatively low reaction cross section for the reaction between adsorbed MeCpPtMe₃ molecules and O₂ molecules. The flux of O₂ molecules to the surface increases with O₂ pressure, which leads at some point to growth initiation.

In summary, the reaction mechanism on non catalytic substrates (Fig. 3.7) is different from the reaction on an as-deposited Pt film. For low O₂ pressures (<0.08 mbar), the MeCpPtMe₃ surface ligands are not oxidized because a non catalytic surface is not able to induce the dissociative chemisorption of O₂, whereas the reaction probability for the reaction between adsorbed MeCpPtMe₃ molecules and O₂ gas molecules is low. According to Fig. 3.7, the surface after the O₂ gas exposure step is similar to the surface after MeCpPtMe₃ exposure, which means that there is no growth.
Figure 3.7: Schematic representation of the thermal and plasma-assisted ALD reaction mechanisms on a non catalytic surface for low O\textsubscript{2} pressures (<0.08 mbar). For the thermal ALD process there are no species present that are able to oxidize the adsorbed MeCpPtMe\textsubscript{3} precursor molecules, whereas for the plasma-assisted ALD process reactive O radicals are delivered to the surface by the plasma.

3.4.2 Selective growth regime

For the combinatorial EBID-ALD approach it is important that growth occurs selectively, i.e. the growth is only allowed to take place on a Pt seed layer and not on the substrate material itself. In the previous chapter, it was shown that for the standard thermal ALD process, no growth was observed on a SiO\textsubscript{2} substrate even after 1200 cycles. However, as discussed above thermal ALD growth can be initiated by using a higher O\textsubscript{2} pressure. The selectivity of the ALD growth will be explored in this section as a function of the O\textsubscript{2} pressure.

Figure 3.8 presents the growth per 400 cycles for deposition on an as-deposited Pt film and for deposition on a SiO\textsubscript{2} substrate (i.e., the graph of Fig. 3.6) by the thermal ALD process. For growth on an as-deposited Pt surface, the graph shows a threshold O\textsubscript{2} pressure at approximately 2×10\textsuperscript{−3} mbar. Above this pressure, the growth rate per cycle is constant at 0.045±0.005 nm/cycle as a function of O\textsubscript{2} pressure. On an as-deposited Pt film, the reactivity of the oxygen species is enhanced due to the creation O atoms that are more reactive than O\textsubscript{2} molecules. An as-deposited Pt film thus catalyzes thermal ALD growth and can therefore be used as a seed layer to initiate the process.

As is indicated in the graph, selective growth can be obtained in between the threshold O\textsubscript{2} pressure (2×10\textsuperscript{−3} mbar) and the pressure for which the growth starts on SiO\textsubscript{2} (0.08 mbar). However, even a thermal ALD process consisting of 1200 cycles did not result in growth on a SiO\textsubscript{2} substrate implying that the selectivity is guaranteed for this standard pressure. On other substrates that are more reactive to the ALD reactants (for example Al\textsubscript{2}O\textsubscript{3}), it might be safer to use a lower O\textsubscript{2} pressure.

3.4.3 Initial growth of plasma-assisted ALD

In the case of plasma-assisted ALD, O\textsubscript{2} plasma species are delivered to the surface during the plasma exposure step (See Fig. 3.7). In an inductively coupled O\textsubscript{2} plasma, O radicals are the dominant reactive species [70] and play an important role in the reactions that take place at the surface of the film. The O radicals are able to oxidize the MeCpPtMe\textsubscript{3} surface ligands and, consequently, plasma-assisted ALD is not dependent on the ability of the surface to catalyze O\textsubscript{2} dissociation. Pt films can therefore be deposited by plasma-assisted ALD on non catalytic surfaces. Furthermore, the delivery of reactive species from the gas phase results in a short nucleation period.
3.5 Conclusions

The reaction mechanisms of both thermal and plasma-assisted ALD were addressed in this chapter on the basis of infrared spectroscopy and spectroscopic ellipsometry results as well as reports in the literature. In agreement with the reaction mechanism proposed by Aaltonen et al. [56] it was found that the precursor ligands are mainly oxidatively decomposed during the O$_2$ half-reaction. Due to surface bound oxygen that resides on the surface after the O$_2$ exposure, ligand oxidation also occurs during the MeCpPtMe$_3$ half-reaction, however a concurrent ligand exchange reaction also takes place as revealed by the detection of CH$_4$ molecules.

Based on the quantification of reaction products it can be stated that the involvement of sub-surface oxygen is not required for the standard thermal ALD process. The surface bound oxygen that resides at the surface after the O$_2$ half-reaction appears to play an important role in the MeCpPtMe$_3$ adsorption reaction and determines the growth rate of the process.

Whether Pt or PtO$_2$ is deposited for plasma-assisted ALD depends on a balance between oxidation by the O$_2$ plasma, the reduction by MeCpPtMe$_3$ molecules, and the decomposition of PtO$_2$ into Pt. The oxidation of precursor ligands during plasma-assisted ALD can occur either by gas phase oxygen atoms generated in the plasma or by surface bound oxygen created by dissociative chemisorption of O$_2$ on the as-deposited Pt surface.

The availability of reactive species that are able to oxidize MeCpPtMe$_3$ surface ligands is a necessary requirement for the growth of Pt by ALD. Growth can be initiated by depositing on a catalytic active seed layer, by using plasma-assisted ALD, or by using a high O$_2$ pressure. Selective

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**Figure 3.8:** Growth per 400 cycles thermal ALD as a function of O$_2$ pressure on an as-deposited Pt film and on a SiO$_2$ substrate as a function of O$_2$ pressure. The growth per 400 cycles is in general somewhat lower than calculated from the growth per cycle due to the initial growth delay. The selective growth regime, i.e. the O$_2$ pressure regime for which thermal ALD yields growth on a Pt seed layer and not on a SiO$_2$ substrate, is indicated in the graph.

The low roughness values reported in the previous chapter suggest that smooth films are obtained when the growth is started with plasma-assisted ALD. This low roughness is probably due to a high nucleation density promoting layer-by-layer growth in an early stage of the ALD process.
growth on a Pt seed layer can be obtained with the thermal ALD process for O$_2$ pressures in the range from $2 \times 10^{-3}$ mbar to 0.08 mbar.
Chapter 4

Local deposition of high-purity Pt nanostructures by combinatorial EBID-ALD

4.1 Introduction

The deposition of nanoscale platinum structures is relevant for various nanoprototyping applications. Due to the low resistivity of platinum, Pt EBID has been considered for the fabrication of electrical connections in nanodevices [19]. Currently, the low purity values that are typically obtained limit the application of EBID in nanodevices [15].

EBID suffers generally from incomplete decomposition of the precursor, which leads to a low purity. When using a metalorganic precursor, Pt EBID results typically in a purity of only 16 at.%, with the deposit predominantly containing further carbon impurities\(^1\)[19]. During the EBID process, Pt aggregates in crystallites with an average diameter of 2 nm [21, 77]. The deposits can thus be described as a polycrystalline material consisting of small Pt grains embedded in a matrix of amorphous carbon. Due to this morphology, the conductivity properties are considered to be determined by the tunneling of electrons between the metallic grains [77]. Typical resistivity values of as-deposited Pt EBID material are in the order of \(10^6-10^7 \mu\Omega\text{cm}\) [19, 77], while the bulk resistivity of Pt is as low as \(10.5 \mu\Omega\text{cm}\) [76].

The low conductivity may cause problems when the material is used for nanowiring applications. Therefore, a number of methods for improving the purity of EBID deposits have been reported in the literature of which several examples are listed in Table 4.1. As can be seen in this table, none of these methods is able to achieve purity and resistivity values approaching the Pt bulk properties. Moreover, most purity improvement methods are accompanied by processes that may jeopardize the functionality of the material and the shape of the structure that is created. For example, post-deposition treatments lead to the formation of voids within the deposits due the volume loss of carbon, and ion beam induced deposition (IBID) suffers from sample damage and ion implantation. The highest purity value listed in Table 4.1 is 81 at.% achieved by using an inorganic precursor [72]. However note that these precursors are aggressive and can damage electron optical equipment and harm device functionality [15].

On the other hand, atomic layer deposition (ALD) enables the deposition of high-purity films. As was reported in Chapter 2, virtually pure Pt (C,O<5 at.%) can be obtained by both thermal ALD and plasma-assisted ALD. In this chapter, the combinatorial EBID-ALD approach introduced in Chapter 1, will be applied for the fabrication of local Pt structures. The approach has the potential to fabricate nanoscale deposits with ALD material quality and thereby approaches Pt bulk material quality.

An essential requirement for the selected approach to work is that the ALD growth occurs

\(^1\)The deposit may also contain O atoms originating from residual background gas or from the precursor.
Table 4.1: Overview of several methods for improving the purity of Pt material deposited by EBID or IBID and the corresponding composition and resistivity values. In addition, the composition and resistivity values of Pt films deposited by ALD and of bulk Pt are shown for comparison. A dash means “not reported” and a cross “not applicable”.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Purity improvement method</th>
<th>Composition</th>
<th>Resistivity ($\mu\Omega \text{cm}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtCpMe$_3$</td>
<td>EBID Anneal</td>
<td>-</td>
<td>-</td>
<td>0.5$x10^4$</td>
</tr>
<tr>
<td>MeCpPtMe$_3$</td>
<td>EBID Anneal in O$_2$</td>
<td>70</td>
<td>15</td>
<td>1.4$x10^4$</td>
</tr>
<tr>
<td>Pt(PF$_3$)$_4$</td>
<td>EBID Inorganic precursor</td>
<td>81</td>
<td>17</td>
<td>30 - 650</td>
</tr>
<tr>
<td>Pt(PF$_3$)$_4$</td>
<td>EBID Inorganic + anneal</td>
<td>-</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>MeCpPtMe$_3$</td>
<td>EBID Exposure to atomic H flow</td>
<td>-</td>
<td>65</td>
<td>2.2$x10^4$</td>
</tr>
<tr>
<td>MeCpPtMe$_3$</td>
<td>EBID Larger dissociation cross-section</td>
<td>&lt;27</td>
<td>&gt;65</td>
<td>1.5$x10^4$</td>
</tr>
<tr>
<td>Bulk</td>
<td>-</td>
<td>100</td>
<td>10.6</td>
<td>[76]</td>
</tr>
<tr>
<td>MeCpPtMe$_3$</td>
<td>ALD (film deposition)</td>
<td>100</td>
<td>&lt;5</td>
<td>13 ± 1</td>
</tr>
</tbody>
</table>

selectively, meaning that growth only starts on the EBID seed layer material and not on the substrate material itself. The selectivity of thermal ALD of Pt is illustrated in Fig. 2.8: growth was only obtained on a plasma-assisted ALD grown Pt seed layer, whereas no growth was observed on a SiO$_2$ substrate. These nucleation properties are related to the reaction mechanism of thermal ALD as discussed in the previous chapter. Briefly, a Pt surface catalyzes the dissociative chemisorption of O$_2$ molecules. This reaction leads to the creation of O atoms that are able to oxidize the precursor ligands, while the O$_2$ gas itself does not react with the ligands at low O$_2$ pressures. As a consequence, thermal ALD growth of Pt is only initiated on those areas where reactive O atoms are created, i.e. at the surface of a seed layer.

Whether thermal ALD initiates is thus related to the ability of the starting surface to catalyze the dissociative chemisorption of O$_2$. It is clear that thermal ALD starts on a plasma-assisted ALD prepared Pt seed layer, since this deposition technique yields smooth, virtually pure Pt films with a preferred (111) crystallographic orientation, capable of inducing the dissociative chemisorption of O$_2$ according to literature [58]. In the case of an EBID seed layer, it is less certain whether the EBID material has the ability to initiate the growth, since the material is far from pure and does only show crystallinity on very small length scales. Therefore, it is interesting to unravel the mechanism of ALD growth on EBID material.

The main objective of this chapter is to demonstrate the feasibility of the introduced combinatorial EBID-ALD approach for the direct local deposition of high-purity nanostructures and thereby establish the proof-of-principle. To this end, several experiments were carried out to test some of the key features of the method, i.e. the selectivity of ALD growth, the material purity, and the uniformity of the deposit. In addition, some experiments were performed to obtain more understanding of the mechanism of (area-selective) ALD growth on EBID seed layer material.

In order to study these aspects, an accurate diagnostic technique was required to determine the properties of the deposits. Energy dispersive X-ray spectroscopy (EDX) was used as the main diagnostic technique to characterize the deposits, since it can probe micrometer-scale areas, while it gives insight into both the deposit composition as well as the thickness. In general, EDX is primarily used for the determination of material composition, but in the case of pure-element films, it can also yield thickness information as will be demonstrated in this chapter. The ability to measure the thickness of the deposit enables the exploration of several aspects of the combinatorial EBID-ALD approach such as the nucleation behavior and the deposit uniformity. In case ALD is integrated in an electron beam system, EDX can be applied as an in situ diagnostic technique in a similar way as spectroscopic ellipsometry is used in the ALD reactor on a larger scale.

First, the EDX data analysis procedure and the experimental details will be described in Secs. 4.2 and 4.3, respectively. The results and discussion part is divided over two sections. In
Figure 4.1: (a) When an electron beam is focused into a sample, X-rays are formed due to the interaction between the high-energy electrons and the sample atoms. (a) A X-ray spectrum showing the intensity of the X-rays as a function of the X-ray photon energy contains a continuum radiation contribution as well as X-ray peaks characteristic for the elements in the sample. The continuum radiation, which is called Bremsstrahlung, is formed as a result of the deceleration of beam electrons in the Coulombic field of the sample atoms. (b) An electron beam is able to excite an inner shell electron of a sample atom, ejecting it from the shell and thereby creating an excited atom. Subsequently, the atom relaxes to its ground state through a transition of an outer shell electron to the inner shell vacancy while the difference in energy between the two shells is released by emitting a X-ray photon. The energy of this photon is characteristic for the sample atom and allows the elements present in the sample to be identified [78].

Sec. 4.4, the proof-of-principle results will be presented, whereas in Sec. 4.5 the mechanism of area-selective ALD growth on EBID seed layer material will be discussed. The conclusions of this part of the work are summarized in Sec. 4.6.

4.2 Energy dispersive X-ray spectroscopy

In Chapter 2 en 3, in situ spectroscopic ellipsometry was applied as the main diagnostic technique to study the growth and properties of thin films deposited by ALD. Due to the small dimensions of the deposits fabricated by the local deposition method treated in this chapter, another diagnostic technique was required. Energy dispersive X-ray spectroscopy (EDX) is the most commonly used technique to study EBID deposits, since it is based on X-ray formation upon electron beam irradiation, and can therefore be applied as an in situ diagnostic technique in electron beam systems. It is able to probe microscale features, and similar to spectroscopic ellipsometry it yields information on both the material composition and the thickness. For these reasons, EDX was applied as the main diagnostic technique for the experiments described in this chapter. The basic principle of EDX is explained in Fig. 4.1.

4.2.1 Data acquisition

EDX measurements were carried out in the same electron beam system as used for EBID seed layer deposition. This system is described in detail in the next section (Sec. 4.3). For each studied deposit, an EDX spectrum was obtained by scanning the electron beam over a part of the deposit. Typically, an area of 1×1 µm² in the middle of a 5×5 µm² deposit was selected for analysis.

The electron beam acceleration voltage determines the dimensions of the interaction volume that is probed by the electron beam, since the electron energy determines the penetration depth. For composition measurements, a low electron beam acceleration voltage has to be used to eliminate the contribution of the substrate in the EDX spectrum. On the other hand, the thickness of
4.2.2 Material composition determination

EDX enables the measurement of the chemical composition of a sample. Quantitative X-ray analysis is based on the fact that characteristic X-rays intensities scale with the abundance of the element in the sample. In general, quantification relies on the use of standards, i.e. reference samples with known composition. The ratio of characteristic X-ray intensity for a given element measured from the sample to that measured from the standard is roughly equal to the ratio of mass fractions in these specimens. This assumption is called Castaing’s ‘first approximation to quantitative analysis’ and is given by [78]:

\[ k_i = \frac{I_i}{I_{i(0)}} = \frac{C_i}{C_{i(0)}} \]  

(4.1)

where \( C_i \) and \( C_{i(0)} \) are the mass concentrations of the element \( i \) in the sample and in the standard respectively. The ratio of the characteristic X-ray intensity of the sample \( I_i \) and standard \( I_{i(0)} \) after continuum background subtraction is generally referred to as the ‘\( k \)-ratio’, and is the basic experimental parameter for quantitative EDX measurements.

For most measurements, Castaing’s approach is not accurate enough and the \( k \)-ratio has to be multiplied with the \( ZAF \) correction factors; \( Z \) for the atomic number effect, \( A \) for the X-ray absorption effect, and \( F \) to correct for X-ray fluorescence [78].

Alternatively, the use of standard samples can be eliminated in a method referred to as ‘standardless analysis’. For this method, the standard intensity that forms the denominator of the \( k \)-ratio is provided by calculation from a model of the X-ray generation rather than direct measurement. To quantify the composition of a sample, only accurate values of the beam energy, and the X-ray take-off angle are required in addition to the measured EDX spectrum.

4.2.3 Thickness determination

When the deposit thickness is less than the electron penetration depth in the material under investigation, the beam penetrates through the deposit into the substrate, generating X-rays in both deposit and substrate. Relative intensities of characteristic X-rays originating from the deposit and substrate elements change with the thickness of the deposit, which forms the basis for thickness measurements. To illustrate this, Fig. 4.2(a) presents EDX spectra of Pt films of different thicknesses deposited on SiO\textsubscript{2} substrates. As can be seen in this graph, the intensity of
4.2 Energy dispersive X-ray spectroscopy

Figure 4.2: (a) Energy dispersive X-ray spectroscopy (EDX) spectra of Pt films deposited by ALD on Si substrates with a toplayer of 400 nm thermal SiO$_2$. (b) Calibration curves for thickness determination by EDX (5 kV electron beam acceleration voltage). The thicknesses of the Pt films are determined by spectroscopic ellipsometry (0-40 nm) or estimated based on the number of ALD cycles used for deposition (40-70 nm), which gives a larger error as indicated in the graph. The graphs are fitted with semi-empirical analytical functions defined in Eq. 4.4 and 4.5.

Determination of both composition and thickness by EDX can be fairly complicated\(^2\). However, ALD of Pt yields virtually pure films as presented in Chapter 2, which leads to the ideal case of determination of the thickness of a pure-element film. The fact that the EBID seed layer on which the ALD growth is initiated contains high amounts of carbon impurities does not affect the accuracy of the thickness determination method, since the seed layer is relatively thin compared to the total deposit and the carbon is removed during the first ALD cycles as will be discussed later in Sec. 4.5.1.

Thin film thickness determination by EDX has been studied by several research groups [79, 80, 81]. In general, such studies characterize the films through the parameter $k$-ratio. A slightly different approach was chosen in the present study to circumvent the requirement of bulk sample usage, i.e. the integrated characteristic Pt X-ray intensity emerging from the film is scaled with the sum of the integrated intensities of the characteristic Si and Pt peaks:

$$K_F = \frac{Pt}{Pt + Si}$$

(4.2)

A similar ratio is defined for the signal emerging from the substrate Si atoms:

$$K_S = \frac{Si}{Pt + Si}$$

(4.3)

where $Pt$ is the integrated intensity of the 2.05 eV $M_\alpha$ Pt peak, and $Si$ the integrated intensity of the 1.74 eV $K_\alpha$ peak. Both values are corrected for the contribution of the continuum background radiation.

Calibration curves of both ratios as a function of the deposit thickness were determined. Following the literature, semi-empirical analytical functions were fitted to the calibration curves

\(^2\)Specific software programs can be used to determine both thickness and composition, but with a higher uncertainty in the thickness value compared to the method described here.
of the form [81]:

\[ K_F = \frac{Pt}{Si + Pt} = 1 - e^{-(Ax+Bz^2)} \]  

(4.4)

\[ K_S = \frac{Si}{Si + Pt} = e^{-(Cx+Dz^2)} \]  

(4.5)

where \( A, B, C, \) and \( D \) are the fit parameters. The form of this analytical function corresponds with the interaction of the electron beam with the sample. The parameters \( A \) and \( C \) can be associated with attenuation of the electrons in the film, whereas parameters \( B \) and \( D \) take backscattering effects into account. Details on the calibration procedure can be found in Appendix A. A typical calibration curve is depicted in Fig. 4.2(b). Based on this curve, it can stated be that thickness determination by this method can be done with an accuracy of 1-2 nm in the thickness range from 0 to 30 nm. As is discussed in more detail in Appendix A, the thickness of thicker films can be determined accurately by using a higher electron beam acceleration voltage.

### 4.3 Experimental details

#### 4.3.1 Experimental setup

EBID and EDX experiments were carried out in a FEI Nova 600 DualBeam system in which a focused ion beam (FIB) and a scanning electron microscope (SEM) are integrated in one machine. A schematic overview of the system is depicted in Fig. 4.3. The electron beam column consists of a Schottky field emission electron (FEG) gun, several lenses for beam focusing and coils for scanning the beam over the sample.

The system is equipped with several electron and ion detectors for its imaging possibilities. Depending on the detector and the selected operating mode, generated secondary electrons (SEs), backscattered electrons (BSEs) or secondary ions (SIs) can be used for imaging.

The device is a high vacuum system with a turbo molecular pump that is able to pump the system to a base pressure in the order of \( 10^{-6} \) mbar.

A computer-controlled, 5-axis stage offers repeatable and precise sample positioning. The electron beam column is perpendicular to the sample stage at zero tilt angle, whereas the ion beam is mounted under a 52° angle with respect to the electron beam column. For ion beam usage, the sample stage can be tilted to 52° in order to use the ion beam perpendicular to the sample.

For the delivery of precursor gases to the sample, the system is equipped with five gas injection systems (GISs). Each GIS consists of a temperature controlled precursor reservoir and a needle for localized precursor delivery. The needles can be inserted during gas-assisted charged particle beam processing.

An EDAX EDX detector enables the detection of X-rays for compositional analysis and deposit thickness determination as discussed in the previous section. The X-rays are collected under a take-off angle of 35°.

#### 4.3.2 Seed layer deposition by EBID

The seed layers were deposited by EBID on two different substrate materials: crystalline Si (c-Si) with 400 nm thermal SiO\(_2\), and c-Si with 50 nm Al\(_2\)O\(_3\). The Al\(_2\)O\(_3\) substrates were fabricated by depositing 50 nm Al\(_2\)O\(_3\) by ALD on one side of a c-Si wafer.

For EBID, the SEM was operated at an electron beam acceleration voltage of 20 kV, which ensures that most of the electrons penetrate through the oxide toplayer of the substrate necessary.
4.3 Experimental details

Electron column
Ion column
Substrate stage
Gas injection system
Turbo pump
LN2
EDX detector
Electron detector

Figure 4.3: Schematic overview of the dualbeam system showing the relevant parts for this work, i.e. the electron and ion beam columns, the substrate stage, the gas injection system (GIS), the EDX detector and an electron detector.

to eliminate charging effects. An electron beam current of either 0.62 nA or 1.1 nA was used in the experiments. Since the beam current can deviate significantly from the preset value, the electron beam current was measured prior to the depositions in a Faraday cup. An electron beam current of 0.62 nA yields a beam spot of approximately 7 nm full width half maximum (FWHM).

In contrast to ALD, no substrate heating was applied and as a result the EBID experiments were carried out at room temperature.

The MeCpPtMe$_3$ precursor was supplied to the sample using the standard GIS system. To obtain an adequate precursor flux, the precursor reservoir was heated to 44°C. During EBID, the GIS needle was inserted and the end of needle was located at approximately 100 µm above the substrate, which gives a flux of approximately 10$^{17}$-10$^{18}$ molecules/cm$^2$/s impinging on the substrate. The base pressure in the reactor chamber was lower than 1×10$^{-5}$ mbar prior to deposition and 2×10$^{-5}$ mbar during deposition, whereas locally higher pressures were obtained above the substrate due to the localized precursor injection.

Before the start of each deposition, a pattern was defined using the patterning tool of the Nova software. The patterning software divides the pattern in pixels and steers the electron beam over the pattern in a serpentine way. The electron beam exposes each pixel for a predefined dwell time after which it steps to the next pixel. After finishing one raster scan, the electron beam is stepped back to the first pixel of the pattern. This process is repeated for a predefined number of passes. The diameter of the focused electron beam dictates together with the adjustable value of the beam overlap the size of a pixels and the pitch, which is the distance between two pixels.

The thickness of an EBID deposit can be calculated from the EBID settings using:

$$t = \frac{YIT}{A} = \frac{YInNT_d}{A}$$

(4.6)

where $Y$ [µm$^3$/nC] is the EBID yield (i.e. the deposited volume per unit of charge), $I$ [nA] the electron beam current, $T$ [s] the deposition time, and $A$ [µm$^2$] the area of the defined pattern. As given, the deposition time $T$ can be calculated from the number of pixels $n$, the number of passes $N$ and the dwell time $T_d$ [s]. The thickness linearly scales with the ‘dwell time’ and ‘the number of passes’ preset values.
To be able to calculate the thicknesses of the deposited EBID seed layers, the yields $Y$ of EBID corresponding to the used electron beam currents were determined. This was done by depositing cuboids and subsequently determining their volume revealing $Y = 3 \times 10^{-3} \mu m^3/nC$ for $I=1.1$ nA, $V=20$ kV and $Y = 9 \times 10^{-4} \mu m^3/nC$ for $I=0.55$ nA, $V=20$ kV. Seed layer thickness values reported in this chapter are estimated using Eq. 4.6 and the yield values determined. The validity of this seed layer thickness estimation method was confirmed with atomic force microscopy (AFM).

Typically, a set of similar samples containing the same EBID seed layer pattern was fabricated during each deposition run. Before deposition, the FIB was used to fabricate a reference structure (a frame of $300 \times 300$ µm) such that it was easy to locate the deposits during analysis even when the sample was removed from and put back in the system. The deposition started with inserting the GIS needle, opening the precursor valve and starting the patterning software. After deposition, the system was vented and the samples were removed, without checking with SEM whether the deposition was successful. This was done to prevent additional deposition due to dissociation of precursor molecules still present on the substrate surface by the electrons used for SEM imaging. However, EBID can be carried out reproducibly and therefore it can be expected that the seed layer patterns deposited with the same conditions are very similar. One of the samples of each set was preserved in its after-EBID state as a reference sample to be able to study the EBID seed layer properties characteristic for the whole set afterwards.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard setting</th>
<th>Range studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam voltage</td>
<td>20 kV</td>
<td>-</td>
</tr>
<tr>
<td>Beam current</td>
<td>0.62 nA</td>
<td>0.45-1.1 nA</td>
</tr>
<tr>
<td>Dwell time</td>
<td>varied</td>
<td>10-100 µs</td>
</tr>
<tr>
<td>Pitch $x,y$</td>
<td>16.56 nm</td>
<td>-</td>
</tr>
<tr>
<td>Number of passes</td>
<td>varied</td>
<td>1-30</td>
</tr>
<tr>
<td>Scan type</td>
<td>Serpentine</td>
<td>-</td>
</tr>
<tr>
<td>MeCpPtMe$_3$ temperature</td>
<td>40 °C</td>
<td>-</td>
</tr>
</tbody>
</table>

The pattern and the EBID settings for seed layer deposition were varied depending on the intended measurement. Standard EBID operating settings are given in Table 4.2. A large number of sample sets were processed, but due to several constraints and issues, only three sets yielded interesting and reliable results that will be discussed in this chapter. See Table 4.3 for an overview. The first set of samples was primarily used to demonstrate the growth and selectivity of ALD, whereas the second set revealed information about the nucleation of ALD growth on EBID material. Samples of the third set were selected for purity and uniformity investigation.

<table>
<thead>
<tr>
<th>Sample set</th>
<th>Substrate</th>
<th>Beam current during EBID</th>
<th>Seed layer thickness range</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>c-Si with 400 nm SiO$_2$</td>
<td>1.1 nA</td>
<td>0.15 - 48 nm</td>
</tr>
<tr>
<td>2</td>
<td>c-Si with 400 nm SiO$_2$</td>
<td>0.55 nA</td>
<td>0.02 - 7.3 nm</td>
</tr>
<tr>
<td>3</td>
<td>c-Si with 50 nm Al$_2$O$_3$</td>
<td>0.45 nA</td>
<td>0.01 - 5.6 nm</td>
</tr>
</tbody>
</table>
4.3 Experimental details

4.3.3 ALD growth and selectivity

For these experiments, the defined EBID pattern consisted of a 3 by 3 matrix of square seed layers of different thicknesses with footprint areas of 5 by 5 \( \mu \)m each (see Fig. 4.4(a) for a SEM image of the reference sample). By varying the dwell time, the seed layer thickness was varied. Since the dwell time setting is restricted to values of 100 \( \mu \)s and smaller, also the number of passes was varied to be able to deposit also relatively thick seed layers. In general, increasing the number of passes has the same effect as prolonging the dwell time. Typical deposition times per seed layer vary from 1 second to 5 minutes.

After seed layer deposition by EBID, the samples were taken out of the dualbeam system and transferred to the ALD reactor while being stored in air in the meantime. Subsequently, the samples were loaded simultaneously (except for the reference sample) in the ALD reactor and heated to a substrate temperature of 300°C. When the substrate temperature was reached, the thermal ALD process of Pt was started for a certain number of cycles. Details of the ALD reactor and of the standard thermal ALD cycle are described in Sec. 2.2. Briefly, the thermal ALD cycle consists of the alternating exposure of the sample to MeCpPtMe3 precursor (1 s+3 s wait time), and \( \text{O}_2 \) gas (5 s) separated by pump steps (3s). Since the number of ALD cycles was varied for the different samples, the ALD deposition was stopped several times to remove one of the samples after which the deposition was continued. Finally, the samples were again exposed to air and transferred back to the dualbeam system for SEM and EDX analysis.

In addition to the EBID samples, one plasma-assisted ALD prepared Pt film and one clean SiO\(_2\) substrate were inserted in the ALD reactor. Since the thermal ALD growth starts immediately on the Pt film, this film can be used to determine the Pt growth in absence of a growth delay, referred to as the ‘nominal thickness’. The nominal thickness was measured using spectroscopic ellipsometry for every ALD run on an EBID seed layer sample. By comparing the growth on an EBID seed layer to the nominal thickness, the growth delay on the EBID material can be quantified. The SiO\(_2\) substrate surface is in principle similar to the areas of the EBID samples where no seed layer is deposited. Spectroscopic ellipsometry analysis of this substrate reveals information on the selectivity of the ALD growth. If no Pt is deposited by ALD on this film, it can be assumed that no Pt is coated on the SiO\(_2\) areas of the EBID samples.

The procedure of halting the ALD deposition to remove one of the sample turned out to be harmful for the remainder of the samples. Except for the sample that was removed first, a Pt film was deposited by ALD on the entire sample areas, which indicates that the selectivity of ALD growth was lost due to the venting of the ALD reactor to atmosphere\(^4\). As a consequence, only the first removed sample (500 cycles ALD) was useful for extensive analysis and this sample is the one that is described in the results section.

A special post-EBID treatment was performed on one of the samples before ALD. The sample was loaded into the ALD reactor and exposed to 5 minutes \( \text{O}_2 \) plasma and to 5 minutes \( \text{H}_2 \) plasma. This treatment was done to remove the carbon from the EBID material before the ALD process was started.

The selectivity of ALD growth was evaluated by zooming in on the area in between the deposits to see whether there was evidence of growth initiation. The ALD growth on the EBID seed layers was studied by measuring the deposit thickness using EDX.

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\(^4\)This effect can be explained by the combination of the high pressure of atmospheric gas and the presence of adsorbed MeCpPtMe3 molecules at the surface. As discussed in Sec. 3.4, the reaction between \( \text{O}_2 \) gas and adsorbed MeCpPtMe3 molecules has a low cross section, but the reaction probability increases with \( \text{O}_2 \) pressure.
4.3.4 Nucleation

To study the ALD nucleation on EBID material, a second set of samples was prepared. In this case, also a matrix of seed layers with different thicknesses was deposited, but the seed layer thickness was varied in a lower thickness range to be able to study the growth delay on very thin seed layers.

The transfer of samples and the ALD depositions were carried out in a similar manner as described in the previous subsection, but with the difference that the samples were loaded individually to prevent unselective Pt deposition. Again, the number of ALD cycles was varied.

Spectroscopic ellipsometry analysis of the Pt reference films that were lying next to EBID samples during the ALD depositions revealed that these films were thinner than expected and that thus the growth rate was lower than normal. This effect is probably related to the reactor wall condition. Prior to these depositions, TiO$_2$ experiments were performed which led to the deposition of TiO$_2$ on the reactor wall. Apparently, the presence of TiO$_2$ on the reactor wall instead of Pt results in lower growth rates$^5$.

The thickest sample (700 cycles ALD, nominal thickness = 27.6 nm) was selected for extensive analysis. The nucleation was studied by taking detailed SEM images of the deposits. Furthermore, the thicknesses of the deposits were determined by EDX.

4.3.5 Purity

For material purity investigation, the thickest deposit (39 nm) from sample set 3 was selected. Evaluation of the material composition was done by using the standardless analysis option offered by the EDAX Genesis software. A small electron beam acceleration voltage of 4 kV was chosen for the measurement. According to Monte-Carlo simulations [83], only a few electrons penetrate through the ~40 nm thick deposit for an electron beam acceleration voltage of 4 kV, whereas 4 keV electrons are still able to induce characteristic X-rays creation by Pt atoms (Pt M$_\alpha$, 2.05 eV). As a consequence, the measurement predominantly probes the ALD grown material, while the contribution of the substrate material is negligible.

The purity investigation was carried based on the Pt M$_\alpha$, C K$_\alpha$, and the O K$_\alpha$ lines. However, it was found that two Pt N lines (0.244 and 0.258 keV) [84] are situated close to the C K$_\alpha$ line (0.277 keV). Because the resolution of the EDAX EDX detector is 40 eV, these Pt N lines cannot be distinguished from the C K$_\alpha$ line and the peaks overlap. Therefore, to determine the carbon contents a correction had to be done.

Since the ratio of the number of counts in the Pt M$_\alpha$ and the Pt N peaks is a constant for a given electron beam acceleration voltage, this ratio can be used to correct for the Pt N contribution in the "Pt N-C K$_\alpha$" peak. To this end, the ratio of Pt M$_\alpha$ and the Pt N peaks was determined for a clean, pure Pt sample, and this ratio was subsequently used to subtract the number of Pt N counts from the counts in the "Pt N-C K$_\alpha$" peak. This gave the number of C K$_\alpha$ counts which was used to determine the carbon contents.

4.3.6 Uniformity

The sample used for purity investigation was also selected for these measurements. The thickness uniformity of the deposits was evaluated by measuring the thickness using EDX at several positions along a line that transects a square deposit (See Fig. 4.5). From the determined thickness values, the nonuniformity of the deposit can be calculated using the following equation [85]:

\[
\text{nonuniformity} = \frac{d_{\text{max}} - d_{\text{min}}}{2d_{\text{average}}} \tag{4.7}
\]

\hspace{1cm} Although the influence of the reactor wall condition on the ALD process has not been studied in detail, it is hypothesized that the lower growth rate obtained for a TiO$_2$ reactor wall condition is related to the ability of TiO$_2$ to induce Pt growth at lower temperatures [82] resulting in growth on the wall and thus a higher consumption of MeCpPtMe$_3$ precursor. This means that less precursor is available to react with the heated samples.
where \(d_{\text{max}}, d_{\text{min}}, \) and \(d_{\text{average}}\) are the maximum, minimum, and average thickness, respectively. Measurements close to the edge of the deposit can give a higher uncertainty in case the interaction volume extends outside the deposit.

### 4.3.7 Monotoring of the seed layer transformation

To simulate the transformation of the EBID seed layer material during the first ALD cycles, the effects of exposing an EBID deposit to \(O_2\) gas at 300°C were monitored in the dualbeam system by using *in situ* EDX. The same \(O_2\) dosing system and substrate heating were used as for the ALD experiments in the dualbeam system described in Chapter 5 (See Sec. 5.1). An EBID deposit of approximately 30 nm thick was deposited and an EDX spectrum (4 keV electrons) of the deposit was recorded. Subsequently, the substrate was heated to 300°C and then exposed to \(O_2\) gas for 10 s after which a second spectrum was collected.

### 4.4 Proof of principle results

In this section, the proof-of-principle experiments are presented in which some of the key features of the combinatorial EBID-ALD approach will be established, i.e., the selectivity, the purity, and the uniformity.

#### 4.4.1 ALD growth

Figure 4.4(b) shows a SEM picture of a sample from set 1 after 500 cycles ALD. As a reference, Fig. 4.4(a) presents a SEM image of a similar sample on which no ALD was carried out. The difference in contrast between the seed layers in Fig. 4.4(a) and the ALD deposits in Fig. 4.4(b), arises from the difference in electron emission of the materials. The deposits prepared by ALD appear brighter than the EBID seed layers due to a high (average) atomic number yielding a high backscatter yield\(^6\). This observation already indicates that material can selectively be deposited on an EBID seed layer by ALD. Moreover, it suggests that the ALD grown material has a higher purity as compared to the EBID seed layer material.

ALD growth was initiated on all seed layers except for the thinnest one (A, 0.15 nm) which shows that an EBID seed layer of 0.3 nm (B) is already sufficiently thick to initiate ALD growth. The thicknesses of the individual deposits on the sample depicted in Fig. 4.4(b) were measured using EDX, the results are shown in Fig. 4.4(d) and the total thickness is plotted as a function of the seed layer thickness in Fig. 4.4(e). For the medium-thick seed layers (D,E,F) a total thickness of 27\(\pm\)2 nm was measured, which is slightly thicker as expected based on the standard growth per cycle of the thermal ALD process, indicating that for these seed layers no significant growth delay occurred. The total thickness also contains the contribution of Pt from the EBID seed layer, but this only becomes a significant contribution for relatively thick seed layers as illustrated by the thickness increase with seed layer thickness for deposits G to I. This contribution is small for the other seed layers due to the low purity of the EBID material (~16 at% Pt)\(^7\). From the observation that the deposits A to C are thinner than deposits D to F, it can be concluded that a growth delay occurs on thin EBID seed layers, which will be discussed in more detail in Sec. 4.5.2.

#### 4.4.2 Selectivity

As is elucidated in the introduction, the selectivity of ALD growth forms the basis of the combinatorial EBID-ALD approach. The selectivity was examined also by using the sample corresponding

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\(^6\)In principle, the difference in brightness can also be caused by a difference in deposit thickness. However, by comparing Fig. 4.4(c) and Fig. 4.4(d) it can be seen that EBID seed layer I is thicker than ALD deposit I, which indicates that the difference in (average) atomic number is more important than the difference in thickness.

\(^7\)Note, that the carbon is removed from the EBID seed layer material during the first ALD cycles due to the exposure to \(O_2\) gas at a substrate temperature of 300°C; an effect that will be discussed in Sec. 4.5.1.
Figure 4.4: SEM images of (a) the reference sample of set 1 showing nine 5×5 µm seed layers deposited by EBID, and (b) a similar sample on which 500 thermal ALD cycles are performed. (c) Overview of the seed layer thicknesses as estimated using the EBID yield and the deposition time. The value of the seed layer thickness of deposit H was confirmed by AFM. (d) Overview of the total thicknesses of the ALD deposits as determined by EDX. (e) Graph of the total thickness as a function of the seed layer thickness. (f) SEM image of deposit E showing a halo deposit around the defined square pattern.
4.4 Proof of principle results

High magnification SEM investigation of the area in between the deposits (i.e., in between the EBID defined patterns) shows no evidence of growth initiation. Also other SiO$_2$ substrates that were exposed to the thermal ALD process for up to 1000 cycles resemble clean substrate surfaces$^8$. EDX spectra of these surfaces only contain peaks related to the elements present in the substrate material and no contribution of Pt. From these observations it can be concluded that the ALD growth occurs selectively on SiO$_2$ substrates for the standard O$_2$ pressure (0.03 mbar), which is consistent with the results presented in Fig. 3.6(b).

As can be seen in Fig. 4.4(b), and in more detail in Fig. 4.4(f), the deposition is not always entirely localized to the defined pattern. A circular halo is present around the square deposits E to I. The radius of the halo appears to be correlated to the seed layer thickness and thus to the electron dose used for EBID, and varies from 0.7 µm (E) to 2.5 µm (I). The halo consists of small islands in case of deposit E (Fig. 4.4(f)) and forms a continuous film around deposits G to I.

An explanation for this circular deposition is the generation of secondary electrons by escaping backscattered electrons. Monte-Carlo simulations carried out for a 20 kV electron beam show a distribution of secondaries emitted around the center of the beam that radially extents 4 µm. The secondary electrons generated during the EBID of the square pattern are thus able to dissociate the MeCpPtMe$_3$ precursor molecules adsorbed up to 4 µm distance to the square pattern. However, a certain seed layer thickness is required to initiate ALD growth, whereas the thickness of the halo EBID seed layer decreases with the distance from the square pattern. As a result, the radius of the halo is smaller than the range of secondary electrons, but increases with the electron dose (from E to I).

Such halo deposits can be eliminated by using a lower electron beam acceleration voltage (See. 5.2(b) for an example), since the range of secondary electrons is smaller for lower primary electron energy.

4.4.3 Purity

The material composition was investigated by EDX. A relatively thick deposit (39 nm) was selected for this measurement prepared by EBID seed layer deposition (5.6 nm thick) and 1000 cycles ALD on an Al$_2$O$_3$ substrate. Quantification using the Genesis EDX software, and correction for the overlapping Pt N and C Kα peaks resulted in 93 at.% Pt, 5 at.% O, and 3 at.% C. Since Pt does not readily oxidize, the 5 at.% O probably originates from the substrate material or is caused by a thin layer of surface bound oxygen at the surface of the deposit. Note, that for 4 keV electrons, EDX is sensitive to the surface area.

The measurement indicates that high-purity material is obtained with a purity higher than the values reported in literature (See Table 4.1). From this measurement, it can be stated that the combinatorial EBID-ALD approach enables the local deposition of high-purity structures.

4.4.4 Thickness uniformity

In Fig. 4.5 the thickness uniformity of a deposit fabricated by EBID and 1000 cycles ALD is plotted. The nonuniformity as defined in Eq. 4.7, was determined to be 3% when the two measurements close to the edge of the deposit were excluded. Although this value already reveals a good uniformity, the actual nonuniformity value might be lower since it is possibly predominantly determined by the accuracy of the EDX thickness determination method (∼1 nm accuracy), as can be deduced from the straight line that can be drawn through the error bars of the data points.

Details about the (non)uniformity of deposits fabricated using EBID have hardly been reported. As stated in the introductory chapter, a “bowl” shaped deposit can be obtained in case of limited precursor diffusion across the surface. For most EBID processes, there are enough parameters to improve the uniformity, by moving away from the precursor-limited regime towards the substrate.

$^8$This is in contrast to the SEM inspection of an Al$_2$O$_3$ substrate as shown in Fig. 3.6(a). Apparently, an Al$_2$O$_3$ substrate is more reactive to the ALD reactants than a SiO$_2$ substrate
4.5 Mechanism of ALD growth on EBID material

Here, the mechanism of ALD growth on EBID material will be addressed based on SEM images and EDX measurements. The first part deals with the transformation of the EBID seed layer material during the ALD process, and in the second part the ALD nucleation on EBID seed layer material is discussed.

4.5.1 Transformation of the EBID seed layer material during ALD

The ALD process shows similarities to one of the purity improvements methods listed in Table 4.1; the post-deposition-treatment consisting of annealing at 300°C in O₂ atmosphere [19]. Botman et al. reported a purity enhancement from 16 at.% to 70 at.% as well as a deposit volume decrease as a result of the removal of carbon atoms from the EBID material via a thermally activated reduction mechanism [19].

During the thermal ALD process, the substrate is heated to 300°C and is exposed every cycle to O₂ gas for 5 s (See Sec. 2.2.2). It can be expected that the carbon is (partly) removed from the EBID seed layer during the first ALD cycles in a similar reaction as described by Botman et
4.5 Mechanism of ALD growth on EBID material

Figure 4.6: Comparison of EDX spectra of an EBID deposit before and after a carbon removal treatment consisting of 10 s O\textsubscript{2} at a substrate temperature of 300 °C. As a result of the treatment, the carbon is (partly) removed from the deposit as indicated by the decrease of the "Pt N-C Kα" peak intensity.

Taking into account that our EBID seed layers are very thin compared to the 400 nm thick deposit of Botman et al., which most likely facilitates a more effective removal of carbon, it might be the case that most of the carbon is removed during the first ALD cycles.

In order to investigate the carbon removal from the Pt EBID material, the material composition of a 30 nm thick EBID deposit was monitored by EDX during the exposure to O\textsubscript{2} at 300 °C. See Fig. 4.6 for the results. A decrease of the carbon peak intensity indicates that a significant amount of carbon was removed from the material already during 10 s O\textsubscript{2} exposure. The graph shows a constant intensity of the Pt Mα peak as well as an increase of the peaks related to substrate elements. Due to the carbon removal, more electrons are able to penetrate through the deposit and cause X-ray formation in the substrate which leads to an increased intensity of the substrate element peaks.

Longer exposure to O\textsubscript{2} did not result in a further decrease of the C Kα peak intensity. The deposit is relatively thin, and therefore quantitative determination of the composition cannot be performed accurately. As a result, it can not be determined whether the carbon is completely removed from the material. However, this measurement clearly illustrates that a significant portion of the carbon is removed already during 10 s O\textsubscript{2} exposure and thus also during the first cycles of the ALD process. See Fig. 4.7 for a schematic illustration of the carbon removal process.

In order to retain the lateral shape of the structure, the removal of carbon needs to take place in such a way that the Pt grains stay within the area of the defined pattern (See Fig. 4.7(c)). As mentioned in the experimental section, for one sample a plasma treatment was added to the process after EBID with the purpose to remove the carbon from the EBID material before the ALD process was started. As a result, the shape of the deposit was completely lost probably due to the lateral spread of Pt grains during the too aggressive carbon removal. Therefore it can be stated that the removal of carbon has to occur in a mild way.

In addition to the carbon removal, the average grain size may also change during the first ALD cycles. Botman et al. reported that platinum grains of 25±4 nm are present in the deposits after the annealing in O\textsubscript{2} atmosphere [19]. An increase of grain size may affect the nucleation properties.
Local deposition of high-purity Pt nanostructures by combinatorial EBID-ALD

Figure 4.7: (a) Schematic illustration of the morphology of an EBID seed layer showing Pt grains embedded in a matrix of amorphous carbon. (b) During the carbon removal process, the amorphous carbon that functions as a matrix to keep the Pt grains together disappears. (c) Eventually, Pt grains located on the substrate surface form the actual seed layer.

4.5.2 ALD nucleation on EBID seed layer material

A scanning electron microscopy study of the thickest sample (700 cycles ALD) from the second set was performed to obtain insight into the initial stage of ALD growth on EBID seed layer material. Figure 4.8(c) presents SEM images taken by zooming in on several deposits. The differences between the images arise from the variation in EBID seed layer thickness. The SEM images suggest that ALD growth starts through island growth.

In general, island growth formation takes place on substrates that are rather unreactive to the ALD reactants. In many of these cases growth starts at defects, and can be characterized by a lower growth per cycle (GPC) in the beginning of the growth [69]. As was discussed in the previous chapter, MeCpPtMe3 molecules adsorb at the surface of the substrate, but the O2 gas is not reactive to non-catalytic surfaces. If the carbon is removed completely from the seed layer material, the surface of the seed layer resembles the substrate surface except for the presence of Pt grains (See Fig. 4.7(c)). Apparently, the growth starts on these grains, which suggests that the small Pt grains are able to catalyze the dissociative chemisorption reaction.

In case the dissociative chemisorption of O2 can take place at the surfaces of the grains, oxygen atoms are created that are able to oxidize adsorbed MeCpPtMe3 molecules. The reactions that play a role in Pt ALD film growth may occur similarly on the surface of the grains. It can be hypothesized that the grains are coated with a submonolayer thick Pt layer every cycle leading to a linear increase of the radius with the number of ALD cycles (See Fig. 4.9(a)). Note that the islands observed in the SEM images are not of similar size, suggesting that there is a size distribution of the Pt grains in the EBID material.

No Pt grains can be observed using SEM by zooming in on the seed layers on the reference sample. Apparently, the grains only become visible when the carbon is removed from the seed layer and the grains have increased in size significantly due to coating by ALD.

As can be seen in the SEM images, the island density increases with the seed layer thickness which is related to the density of Pt grains present at the surface after carbon removal. A thicker seed layer contains more Pt grains per unit area which results in a higher island density.

As the size of the islands increases every cycle, at some point, the islands start to touch each other, and the growth mode changes from island growth (Fig. 4.9(a)) to island coalescence (Fig. 4.9(b)). Finally, as the island coalescence stage proceeds and the deposit surface becomes more continuous, the growth mode evolves gradually to layer-by-layer growth. Although the growth delay involves both the island growth and the island coalescence stages, it can be said that the number of cycles that are required for the islands to touch each other is a measure for the growth delay. Taking into account that the island sizes increase linearly with the number of cycles, it can be assumed that the growth delay is dependent on the density of the Pt grains present at the surface after carbon removal and thus on the seed layer thickness.

The dependence of the growth delay on the seed layer thickness is graphically illustrated by the graph of the total thickness versus the seed layer thickness (Fig. 4.8(d)). For thin seed layers (< 2 nm), the island density is low as illustrated by the SEM images, and consequently, it takes many ALD cycles before the islands touch each other, which results in a significant growth delay. Due to this growth delay, the total thickness considerably deviates from the nominal thickness in
Figure 4.8: Results related to ALD nucleation on EBID material obtained by SEM and EDX on one sample. 700 ALD cycles were performed. (a) Schematic overview of the seed layer thicknesses as estimated based on the yield and the deposition time. (b) SEM image of the sample. The total thicknesses of deposits K to P as measured by EDX are given. (c) SEM images taken by zooming in on the deposits. (d) Graph of the total thickness as a function of the seed layer thickness as determined by EDX. The line is a guide to the eye. The insets show schematic illustrations of the seed layer after the carbon removal. For thin seed layers, the growth starts with coating of Pt grains dispersed on the substrate, whereas the Pt grains already touch each other after carbon removal for thick seed layers.
Local deposition of high-purity Pt nanostructures by combinatorial EBID-ALD

Figure 4.9: Schematic illustrations of the three phases of the ALD process that starts through island growth due to grain coating: (a) Island growth or grain coating, (b) Island coalescence. (c) Layer-by-layer growth.

- Island growth
- Island coalescence
- Layer-by-layer growth

The island coalescence stage starts when the individual islands start to touch each other. During the island coalescence stage, the surface of the deposit becomes more continuous, and gradually, the growth changes to layer-by-layer growth.

From the the saturation of the graph, it can be deduced that for seed layers thicker than 2 nm, the grains already touch each other after the carbon removal process (See the inset of Fig. 4.8(d)). However, the saturation of the thickness does not indicate that no growth delay occurs for thick seed layers. Although the grains may touch each other, it takes a number of cycles to obtain the continuous surface that is required for the onset of layer-layer-layer growth. Or in other words, the volume in between the grains has to be filled. In the case of thick seed layers, the growth initiation thus only involves the island coalescence stage (Fig. 4.9(b)). This stage may also take many cycles indicated by the observation that the 'saturation total thickness' (~24.5 nm) is lower than the nominal thickness (27.6 nm). Taken together, it can be said that a seed layer thickness of at least 2 nm is thus required to obtain a minimal growth delay.

The SEM images of deposits M and N show a smooth surface which is consistent with the picture that the ALD growth on these seed layers has entered the layer-by-layer growth stage. The total thickness of deposit M (19 nm) is much less than the nominal Pt thickness (27.6 nm), which suggests that island coalescence only occurred after a few hundred ALD cycles.

Figure 4.10 presents a comparison between samples from different EBID seed layer deposition runs (See Table 4.3). On all three samples, the growth already starts on subnanometer thickness seed layers. However, there is a difference in the seed layer thickness required to obtain a minimal growth delay. Apparently, depending on the conditions during EBID, there is a difference in the capability of the EBID material to induce the ALD growth. This effect might be related to the electron beam current used during EBID, which is not held constant as can be seen in Table 4.3. The purity of Pt EBID deposits is dependent on the beam current. A higher beam beam current yields deposits with a higher purity [74] which in turn can result in a higher grain density and thus a shorter nucleation period. The graph is consistent with this picture; the required seed layer thickness to obtain a minimal growth delay is only 1 nm for the sample from set 1 (1.1 nA), 2 nm for the sample from set 2 (0.55 nA), and approximately 3 nm for the sample from set 3 (0.45 nA). The growth delay thus appears to decrease with increasing beam current used for EBID.

4.6 Conclusions

In this chapter, the combinatorial EBID-ALD approach introduced in Chapter 1 was successfully applied to the local deposition of high-purity platinum structures, and thereby the feasibility of the method was demonstrated. Several experiments were carried out to test some of the key features of the method and thereby establish proof-of-principle. Additionally, insight was obtained into the mechanism of area-selective ALD growth on EBID seed layer material.

In order to study the ALD growth on the EBID seed layers a method had to be developed for the determination of the deposit thickness. Due to the high purity of the obtained material,
it was possible to determine thicknesses by energy dispersive X-ray spectroscopy (EDX) with an accuracy of 1-2 nm.

ALD growth was found to initiate on EBID seed layers using the thermal ALD process of Pt. The selectivity of the growth was confirmed by EDX and SEM measurements. A purity value of 93 at.% was measured using EDX, which establishes that high-purity Pt structures can be fabricated using the method. Furthermore EDX thickness measurements revealed that the deposits show a good thickness uniformity (nonuniformity < 3%).

ALD growth already starts on subnanometer thick seed layers, but shows a growth delay on extremely thin seed layers. A seed layer thickness of a few nanometers thick is required to minimize the growth delay. In addition to the seed layer thickness, also the seed layer purity determines the ALD nucleation properties.

The mechanism of ALD growth on EBID material consists of two processes. During the first ALD cycles, the carbon is removed from the seed layer material due to the exposure to O$_2$ gas at 300°C. The ALD growth starts as island growth by coating Pt grains originating from the seed layer material. From the observations it can be concluded that the small Pt grains are able to catalyze the dissociative chemisorption of O$_2$ which is required to initiate the ALD process.
Local deposition of high-purity Pt nanostructures by combinatorial EBID-ALD
Chapter 5

Integration of ALD in an electron beam system and additional considerations

From the results presented in the previous chapter, it can be concluded that the combinatorial EBID-ALD approach is definitely an interesting method for the fabrication of high-purity nanostructures. However, still a number of issues remain uninvestigated and therefore some additional considerations will be discussed in this chapter.

It was mentioned several times that the ALD method can be integrated in an electron beam system which changes the approach into a complete in situ method and enables in situ thickness measurement using EDX. Preliminary experiments were carried out during this project to investigate this possibility. Some considerations and first results will be presented in Sec 5.1.

The merits of the combinatorial EBID-ALD approach were presented in the introductory chapter (See Sec. 1.3.1 and Fig. 1.6). Two merits were established in the previous chapter, i.e. the material purity and the thickness uniformity. Both the throughput enhancement and the lateral resolution of the combinatorial EBID-ALD approach will be discussed in more detail in Sec. 5.2.

5.1 ALD in an electron beam system

In this section, the results of preliminary experiments that were carried to integrate ALD in an electron beam system are presented and some issues are discussed. First, the modifications of a Nova 600 Dualbeam system required to make ALD possible are discussed.

5.1.1 Modifications of the dualbeam system

Since the electron and ion beams play no role in the ALD deposition process, the electron and ion sources can be secured from the ALD gas reactants by closure of the valves in between the main chamber and the pressure-sensitive parts of the columns. Because the vacuum requirements for ALD are similar to those used for EBID, switching from EBID to ALD is possible without breaking the vacuum or changing the vacuum conditions.

For the MeCpPtMe₃ dosing, the standard Pt GIS system was used in retracted configuration and set to a temperature of 44°C. This GIS is the same GIS as used for the EBID experiments. Initially, O₂ gas was delivered to the substrate by injection of O₂ in the chamber through a vacuum port in the wall of the reactor. The O₂ dosage was controlled by a combination of a leak valve to regulate the flow and an automatic gas valve. However, it turned out that an O₂ pressure of only 1×10⁻³ mbar could be obtained in the system, due to the safety levels of the dualbeam software which initiate chamber venting when the pressure rises above the safety level. This safety level
value is below the pressure required to initiate ALD growth on a Pt seed layer (See Fig. 3.8), and therefore no ALD growth could be obtained in the system. Subsequently, it was decided to switch to local O$_2$ gas injection by using another GIS. The O$_2$ gas was delivered to this GIS through a side entrance on the needle. In this way, the chamber pressure stays below the safety level, while locally a high enough O$_2$ pressure can be achieved at the surface of the substrate.

Because a reasonable growth rate can only be obtained by thermal ALD for substrate temperatures above 225°C (See Fig. 2.12), it was necessary to heat the substrate. To this end, a substrate heater (a modified ESEM 500°C stage) was mounted on the sample stage.

A major difference between the two systems is the reactor wall temperature. In the ALD system, the reactor wall was heated to ∼75°C to prevent condensation of the precursor and to aid the removal of sticky reaction products, whereas the chamber wall cannot be heated in the dualbeam system. Due to the local MeCpPtMe$_3$ precursor injection, condensation losses of the precursor are no issue in the dualbeam system. However, the absence of wall heating can lead to relatively high residual gas concentrations of molecules such as H$_2$O that can interfere with ALD film growth. In order to diminish the effects of this dissimilarity, a cryocan containing liquid N$_2$ was added to the system that acts as a cold finger on which molecules condense. This should lead to a significant reduction of the amount of residual gases.

5.1.2 Results

As was discussed in Sec. 3.4.1, the O$_2$ pressure determines whether the ALD growth occurs selectively. The local O$_2$ pressure at the surface of the substrate was varied by changing the distance of the O$_2$ delivery needle to the substrate. In this way, operating settings were found for which selective growth on Pt seed layers could be obtained.

Figure 5.1 shows SEM pictures of a plasma-assisted ALD grown Pt film before and after 10 cycles ALD performed in the dualbeam system. SEM image (b) clearly shows a spot deposition which indicates that the growth was initiated locally close to the needle where the O$_2$ pressure was high enough. The thickness of the deposit was determined on three positions along the spot.

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The cycle consisted of 5 s O$_2$ exposure, 30 s pump, 5 s MeCpPtMe$_3$ exposure, and 60 s pump. The pump steps were chosen rather long to ensure that the excess amount of precursor and the reaction products were evacuated.
5.1 ALD in an electron beam system

Figure 5.2: SEM images of deposits prepared by EBID seed layer deposition and 10 cycles ALD both carried out in the dualbeam system. EBID was performed using an electron beam acceleration of (a) 20 kV, and (b) 5 kV. The thicknesses of the deposits as measured by \textit{in situ} EDX are given in the images.

Subsequently, seed layers of various thickness (in the range 0-6 nm) were deposited by EBID on an Al$_2$O$_3$ substrate on which 10 cycles "ALD" was performed using the same operating settings as for the experiment described above. A SEM image of the sample after the depositions is depicted in Fig. 5.2(a). The image shows that for these conditions selective growth is obtained which suggest that selective growth can also be achieved for CVD-like conditions. In principle, this result is not remarkable since the reaction mechanism of Pt CVD from MeCpPtMe$_3$ precursor and O$_2$ gas also relies on the catalytic activity of the as-deposited film to dissociate O$_2$ for the decomposition of MeCpPtMe$_3$ ligands [86]. Thickness measurements by \textit{in situ} EDX revealed that the local O$_2$ pressure and the seed layer thickness determine together the thickness of the deposits. In general, the thickness decreases with increasing lateral distance to the O$_2$ GIS needle.

SEM investigation of the surface in between the deposits showed the presence of Pt islands, which implies that the growth did not occur entirely selectively. However, it can be expected that the selectivity can be improved by increasing the distance from the O$_2$ delivery needle to the surface.

Figure 5.2(b) confirms that when a lower electron beam acceleration voltage (5 kV instead of 20 kV) is used for EBID, no halo deposit is obtained around the defined pattern as was suggested in Sec. 4.4.2.
5.2 Additional merits of the combinatorial EBID-ALD approach

5.2.1 Throughput enhancement

One of the merits of the combinatorial EBID-ALD approach lies in the reduction of the time needed for deposition. The deposition time for EBID is proportional to the volume of the deposit, while the deposition time for ALD scales with the thickness of the layer. By deposition of a thin seed layer pattern using EBID, and then building up the pattern by ALD, a shorter deposition time may be obtained compared to depositing the whole structure by EBID. The time consuming EBID process is limited to the deposition of a very thin seed layer, while the bulk of the material is deposited by ALD.

The total deposition time is given by:

\[ T_{\text{Comb.}} = T_{\text{EBID}} + T_{\text{ALD}} = \frac{A t_{\text{SL}} Y I}{Y} + \frac{t_{\text{cycle}} G}{G} \]  \hspace{1cm} (5.1)

where \( A \) \([\mu m^2]\) is the area of the pattern, \( t_{\text{SL}} \) \([\mu m]\) the seed layer thickness, \( Y \) \([\mu m^3/nC]\) the EBID yield (i.e. the deposited volume per unit of charge), \( I \) the electron beam current \([nA]\), \( t \) \([\mu m]\) the thickness of the deposit, \( T_{\text{cycle}} \) \([s]\) the ALD cycle time, and \( G \) \([\mu m/cycle]\) the growth per cycle of the ALD process.

Whether the combinatorial EBID-ALD approach is faster than EBID depends on the footprint area of the deposit. For the case that the seed layer thickness required to initiate the growth is much smaller than the total thickness of the deposit (\( t_{\text{SL}} << t \)), a certain area \( A_0 \) can be derived from Eq. 5.1 above which ALD is faster than EBID (\( T_{\text{Comb.}} < T_{\text{EBID}} \)):

\[ A_0 = \frac{Y IT_{\text{cycle}}}{G} \] \hspace{1cm} (5.2)

This area value is not dependent on the thickness of the deposit, since the deposition time of both the ALD building step and EBID scale with the thickness. Inserting the EBID yield for a current of 1.1 nA \( Y = 3 \times 10^{-3} \mu m^3/nC \) (Sec. 4.3.2), an ALD cycle time of 5 s \(^2\) and a growth per cycle of 0.045 nm/cycle gives \( A_0 = 4 \times 10^2 \mu m^2 \). This reveals that when a structure with a footprint area larger than \( 4 \times 10^2 \mu m^2 \) has to be fabricated, the combinatorial EBID-ALD approach is faster than EBID. Above this value, the difference in deposition time increases quickly. For example, a deposit with a footprint area of \( 4 \times 10^3 \mu m^2 \) and a thickness of 10 nm takes 3.4 hours with EBID and only 39 minutes with the combinatorial EBID-ALD approach for an one nm thick EBID seed layer.

5.2.2 Resolution and deposit shape

The lateral resolution that can be achieved with the combinatorial EBID-ALD approach is predominantly determined by the dimensions of the seed layer. The resolution that can be achieved by EBID ranges down to subnanometer length scale. Furthermore, it is required that the seed layer is able to induce ALD growth. From the SEM images in Fig 4.8, it was concluded that the thermal ALD growth of Pt starts on EBID seed layer material at the Pt grains, which suggests that the Pt grains of only a few nanometer size are able to initiate ALD. Therefore, it can be safely stated that the combinatorial EBID-ALD approach has the potential to fabricate nanostructures with sub-10-nanometer scale lateral resolution.

There might be a limit to the attainable lateral resolution when even smaller structures need to be deposited. As was discussed in Sec. 3.4, the ability of a surface to induce dissociative chemisorption of \( O_2 \) determines whether thermal ALD growth can be initiated. For small seed
layers, size effects that limit the reactivity of the seed layer toward the O_2 dissociation reaction may play a role.

Since the ALD growth involves the coating of the seed layers, it can be expected that the deposit also broadens laterally. Therefore, the approach is not particularly suitable for the fabrication of high-aspect-ratio deposits such as pillars. On the other hand, the approach enables the fabrication of well-defined dots by the coating of small Pt grains.
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Chapter 6

General conclusions and outlook

6.1 Conclusions

The primary goal of this project was to develop a new local deposition method that enables the deposition of high-purity platinum nanostructures by combining atomic layer deposition and electron beam induced deposition. The selected approach consisted of two main steps: seed layer deposition by EBID and building the structure by ALD. This approach combines the lateral resolution of EBID with the material quality and thickness control of ALD, while a higher throughput can be achieved as compared to EBID. Or in other words it can be said that the strengths of both techniques are amplified whereas some of their weaknesses are eliminated or alleviated.

The first part of the work dealt with the implementation and development of ALD processes for the deposition of Pt. Suitable conditions for selective deposition on a Pt seed layer were found for the thermal ALD process from MeCpPtMe$_3$ precursor and O$_2$ gas. A new plasma-assisted ALD process was developed using MeCpPtMe$_3$ precursor and O$_2$ plasma to be able to deposit a Pt seed layer required to characterize the thermal ALD process. The plasma-assisted ALD process yielded virtually immediate growth and settings were found for which also PtO$_2$ can be deposited. Furthermore, it was established that by adding a H$_2$ gas exposure step to the plasma-assisted ALD process, high-purity Pt can be deposited at substrate temperatures as low as 100 °C.

Secondly, the reaction mechanisms of Pt ALD were studied to obtain more insight into the ALD processes and the parameters that are important for the combinatorial EBID-ALD approach. It was found that the creation of reactive species that are able to oxidize MeCpPtMe$_3$ surface ligands is required to initiate growth of Pt by ALD, which is in case of a Pt seed layer governed by dissociative chemisorption of O$_2$ molecules. Moreover, quantitative insight into the reaction mechanism of thermal ALD was obtained and this was connected to the amount of surface bound oxygen that is generated by the dissociative chemisorption reaction of O$_2$ on Pt.

A method for the determination of the thickness of microscale deposits was developed based on energy dispersive X-ray spectroscopy. Deposit thicknesses can be determined with an accuracy of 1-2 nm using this method.

Finally, the combinatorial EBID-ALD approach using the thermal ALD process was successfully applied for the fabrication of Pt structures with microscale lateral dimensions and nanoscale thickness. Selective growth was obtained on EBID seed layers of only a few nanometers thick. It has been established that the deposits are of high-purity material (>93 at.%) and show a uniform thickness (nonuniformity 3%). SEM imaging revealed that ALD growth on EBID seed layer material starts after the removal of carbon by the coating of the Pt grains from the EBID material.

In addition, preliminary experiments were carried out to investigate the possibility of integrat-
ing ALD in an electron beam system. Selective growth was obtained in the system with relatively high growth rates.

6.2 Recommendations

6.2.1 Combinatorial EBID-ALD proof-of-principle experiments

Since the electrical resistivity is the most important material property for electrical connection applications, determination of the resistivity is an important measurement to demonstrate the feasibility of the approach for these applications.

Furthermore, the deposition of structures with nanoscale lateral dimensions still has to be explored. For the deposition of nanoscale seed layers, the electron beam has to be tuned in such a way that a strongly focused electron beam with a diameter of only a few nanometers interacts with the adsorbed MeCpPtMe₃ molecules.

6.2.2 Optimization of the EBID seed layer properties

In Sec. 4.5.2, it was reported that the nucleation properties depend on the EBID conditions. This motivates to think about the seed layer properties required for ALD growth initiation. Ideally, a high nucleation density of small Pt grains is obtained after the removal of carbon from the seed layer material to minimize the number of cycles required to obtain island coalescence. In this case, the transition from island growth to layer-by-layer growth takes place in an early stage of the ALD process, which results in low a surface roughness.

To satisfy these conditions, the EBID process can be tuned, but also a post-EBID treatment can be developed to remove the carbon from the EBID seed layer material before the ALD process starts. Optimization of the EBID process involves for example a study of the grain size dependence on the operating conditions.

6.2.3 ALD in an electron beam system

Apart from the fact that the overall process is much easier when ALD is integrated in an electron beam system as compared to the approach that involves the transfer of samples between two setups, it also opens new possibilities to characterize the ALD growth on an EBID seed layer. For example, EDX (Sec. 4.2) can then be used as an in situ diagnostic technique as was already illustrated in Sec. 5.1. By measuring the thickness during temporary interruptions of the deposition process, insight into several aspects of the growth process can be obtained, such as the nucleation delay and the process window of ALD growth. The use of EDX as an in situ tool enables for example the measurement of the deposit thickness as a function of the number of cycles (similar to Fig. 2.8) for different seed layer thicknesses and properties, which can reveal more insight into the nucleation properties of ALD on EBID material.

It was found that selective growth can also be obtained for CVD-like conditions, which yields high growth rates in the order of 1-2 nm/cycle. Characterization of the area-selective CVD process is required to exploit this process for applications where a high growth rate is needed.

The dependence of the growth on the local O₂ pressure disrupts the ability of ALD to achieve a excellent uniformity. Therefore an alternative method for the O₂ dosing has to be found for which a uniform flux of O₂ molecules to the substrate surface can be obtained.

¹Preliminary experiments were carried out to measure the resistivity, but due to several constraints did not lead to reliable results.
6.2 Recommendations

Figure 6.1: A polyethylene naphthalate (PEN) substrate on which Pt is deposited by using the "low temperature" plasma-assisted ALD process. A part of the substrate was covered with another sample showing no deposition.

6.2.4 Plasma-assisted ALD of Pt

As summarized in the conclusions, the plasma-assisted ALD processes offer several merits over the thermal ALD process. More research is required to demonstrate the potential of these merits for new application areas for Pt ALD.

The plasma-assisted ALD process of Pt was found to start with only a short nucleation delay (Sec. 2.4.1). Further characterization of its initial growth by surface sensitive techniques such as X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering spectroscopy (LEIS) may reveal the initial growth mode, which can be used to further optimize the process and thereby reduce the amount of required MeCpPtMe$_3$ precursor.

In preliminary experiments the possibility of deposition on a polymer substrate (i.e. PEN foil) at 100°C was explored, see Fig. 6.1. The deposition of high-purity conductive Pt on plastic substrates by ALD could be of interest for specific applications. A poor nucleation of Pt on PEN was found, which could be improved by the deposition of an Al$_2$O$_3$ adhesion layer. The process has to be optimized further for these class of substrates before this possibility can be exploited for applications.

The conditions for which PtO$_2$ can be deposited were found during the characterization of the plasma-assisted ALD process of Pt. The material has not been extensively characterized, however it may be an interesting material for several applications [43]. Therefore, an exploration of the material properties of ALD grown PtO$_2$ and its applicability is required.
Acknowledgments

First of all I would like to thank my supervisor and graduation docent Erwin Kessels for convincing me slightly more than a year ago to choose for the graduation project described in this report. Although I initially did not intend to do my graduation work at PMP, I certainly do not regret this decision since I really enjoyed this graduation project. Furthermore, I want to thank him for many discussions and suggestions.

Secondly, I want to thank Hans Mulders for supervision during the experiments carried out at FEI and for reading the drafts of this report. I also want to express my appreciation for the fact that he invested much of his time in this project.

Special thanks go to my third supervisor Harm Knoops. Although we were interested in Pt ALD for different reasons, I think that it can be said that our cooperation turned out to be fruitful for both our projects. Bas Dielissen is thanked for his contribution to the infrared spectroscopy measurements.

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Janneke, Ries and Herman are thanked for the technical assistance at PMP, and Erik and Noémi for fruitful discussions about ALD reaction mechanisms.
General conclusions and outlook
Bibliography


[32] Search terms used: "focused electron beam induced processing", "electron beam induced deposition", "electron beam induced selective deposition", "electron beam induced chemical vapor deposition", "electron beam induced etching", "electron beam induced selective etching", "electron beam induced surface reaction", "electron beam induced resist", "electron
beam induced selective etching and deposition”, ”electron beam assisted deposition”, ”electron beam assisted chemical vapor deposition”, ”electron beam assisted etching”, ”electron beam stimulated deposition”, ”electron beam stimulated etching”, ”electron beam stimulated chemical vapor deposition”, ”electron beam chemical vapor deposition”, ”electron beam writing”, ”environmental electron beam deposition”, ”electron beam direct write lithography”, and ”contamination lithography”.

[33] Search terms used: ”atomic layer deposition”, ”atomic layer epitaxy”, and ”atomic layer chemical vapor deposition”.

[34] Search terms used: ”plasma assisted atomic layer deposition”, ”plasma enhanced atomic layer deposition”, ”radical enhanced atomic layer deposition”, ”direct plasma atomic layer deposition”, and ”remote plasma atomic layer deposition”.


Appendix A

Calibration of EDX for thickness determination

The method of thickness determination by EDX was presented in Sec. 4.2.3. Here, the calibration procedure is discussed and the calibration curves are evaluated.

![Graphs](a) (b)

**Figure A.1:** Integrated X-ray intensity ratios as a function of Pt film thickness on SiO$_2$ substrates (400 nm thermal SiO$_2$ on c-Si) for (a) 5 kV (b) 10 kV electron beam acceleration voltage. The Pt thickness values are determined by using spectroscopic ellipsometry (0-40 nm) or estimated based on the number of ALD cycles used for deposition (40-70 nm). The graphs are fitted with semi-empirical analytical functions defined in Eqs. 4.4 and 4.5.

Calibration curves for thickness determination were obtained by measuring the ratios defined in Eqs. 4.4 and 4.5 for several ALD grown Pt films. The films of various thicknesses in the range 0-70 nm were deposited on c-Si substrates with 400 nm thermal SiO$_2$ by (plasma-assisted) ALD. The thicknesses of these films were determined by spectroscopic ellipsometry (SE).

Due to the strong light absorption of Pt, films become opaque for thicknesses above approximately 40 nm, and consequently, light does not reach the SiO$_2$ - Pt interface. Therefore, using SE for thickness determination only works in the 0-40 nm thickness range. For films thicker than 40 nm, the thickness was estimated based on the number of ALD cycles performed for the deposition of the film using the growth rate of the ALD process. As can be seen in the calibration curves Fig. A.1, this results in a higher uncertainty in the thickness value.

EDX spectra were measured for 5 and 10 kV electron beam acceleration voltage. The beam current was set to 1.6 nA and the electron beam was scanned over an area of 1×1 µm$^2$. The acquisition time was set to 200 seconds, which yields (depending on the film thickness) a number of counts per peak in the order of 3000 leading to an error in the integrated intensity below 1%.

The calibration curves for 5 and 10 kV electron acceleration voltage are presented in Fig. A.1.
The curves were fitted using the analytical functions Eqs. 4.2 and 4.3 and the fitting parameters are given in Table A.1.

In the calibration graph determined using 5 keV electrons, both the Pt/(Si+Pt) and the Si/(Si+Pt) ratio vary strongly with the Pt thickness in the 0-30 nm thickness range, indicating that the thickness can be determined very accurately in this range. Above 30 nm, the number of electrons that penetrate through the Pt film decreases significantly, and less X-rays are generated in the substrate as shown by the saturation behavior of both ratios. However, the 10 kV calibration graph continues changing with Pt thickness, also for the 30-70 nm range, since 10 keV electrons are able to penetrate through thicker films. Therefore, using the 10 kV calibration curve yields more accurate thickness values for films with a thickness in the 30-70 nm range.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Electron energy (keV)</th>
<th>A (10^{-3} nm^{-1})</th>
<th>B (10^{-4} nm^{-2})</th>
<th>C (10^{-3} nm^{-1})</th>
<th>D (10^{-4} nm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>5</td>
<td>20 ± 2</td>
<td>7.7 ± 0.9</td>
<td>23 ± 2</td>
<td>6.3 ± 0.8</td>
</tr>
<tr>
<td>SiO2</td>
<td>10</td>
<td>2.1 ± 0.4</td>
<td>1.5 ± 0.1</td>
<td>3.0 ± 0.9</td>
<td>1.3 ± 0.2</td>
</tr>
<tr>
<td>Al2O3</td>
<td>5</td>
<td>4.9 ± 0.7</td>
<td>8.4 ± 0.5</td>
<td>76 ± 7</td>
<td>5 ± 2</td>
</tr>
<tr>
<td>Al2O3</td>
<td>10</td>
<td>(9 ± 9)×10^{-3}</td>
<td>2.0 ± 0.3</td>
<td>7 ± 2</td>
<td>1.1 ± 0.5</td>
</tr>
</tbody>
</table>

Figure A.2 presents the calibration curves determined for the Al2O3 substrates (50 nm Al2O3 on c-Si) which show similar trends. In this case, the integrated characteristic Pt and Si X-ray intensities are scaled with the sum of the integrated intensities of the characteristic Si, Al and Pt peaks instead of with only the Si and Pt peaks.