

# **Atomic Layer Deposition of Metal and Transition Metal Nitride Thin Films and In Situ Mass Spectrometry Studies**

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**Academic Dissertation**

To be presented, with the permission of the Faculty of Science of the University of Helsinki,  
for public criticism in Auditorium A110 of the Department of Chemistry on December 14,  
2001, at 12 noon.

ISBN 952-91-4123-8 (print)  
ISBN 952-10-0221-2 (PDF)  
<http://ethesis.helsinki.fi>

Helsinki 2001  
Yliopistopaino

## ABSTRACT

The shrinking feature sizes of basic electronic components, like transistors, memory cells and metal wires, in integrated circuits sets high demands on both materials and thin film deposition methods. One of the major changes in the materials has been the adoption of copper interconnects. Due to the tendency of copper to react with silicon and insulators, use of a diffusion barrier is necessary. With the currently used deposition methods the future requirements for thin films, for example, strict conformality and low deposition temperature, can not be fulfilled at the same time. One of the most promising methods to be exploited in the near future is atomic layer deposition (ALD). In the present work the ALD method was used to deposit copper and molybdenum films, and some transition metal nitride films focusing on TiN.

Copper and molybdenum films were deposited from the corresponding chlorides using zinc as a reducing agent. The dissolution and outdiffusion of zinc caused problems with the controllability of the film growth. The deposition of copper was also studied from various copper precursors and reducing agents of different chemical nature. Altogether, the ALD of metals seemed quite complicated, and although metals could be deposited their properties were only modest.

The main problem with the existing TiN ALD processes is that usually the films have to be deposited at too high temperatures to obtain films with reasonably good properties. Fairly good properties can be achieved by using zinc as an additional reducing agent, but it is known to dissolve into silicon. In most of the previous ALD processes  $\text{NH}_3$  has been used as a nitrogen source and but it is not very effective at low temperatures. In order to be able to grow TiN films at temperatures tolerable in the future (below  $400\text{ }^\circ\text{C}$ ), the deposition of TiN films was studied from titanium halides by using two different approaches. Nitrogen sources more reactive than  $\text{NH}_3$ , namely dimethylhydrazine, *tert*-butylamine and allylamine, were used. Another approach was to deposit TiN films by using trimethylaluminium (TMA) as an additional reducing agent with  $\text{NH}_3$ . Each of the studied approaches produced films with better properties than those obtained with bare  $\text{NH}_3$  at low temperatures. The lowest resistivity (around  $150\text{ }:\text{ S cm}$ ) was obtained by using TMA as an additional reducing agent, but the carbon contamination was quite high (above 6 at.%). Somewhat higher resistivities were obtained with dimethylhydrazine and amines ( $200 - 500\text{ }:\text{ S cm}$ ), but with *tert*-butylamine the carbon contents were only minor (below 1 at.%).

In order to understand the reaction mechanisms involved in ALD, the growth of  $\text{Al}_2\text{O}_3$  and  $\text{Ti}(\text{Al})\text{N}$  were studied by means of *in situ* mass spectrometry. The results obtained gave information about the possible surface reactions, and it seems that through the *in situ* mass spectrometry the ALD reaction mechanisms can be identified.

## PREFACE

During the years that I have worked with this thesis, I have had the opportunity to work with a quite large number of people to whom I would like to express my deepest gratitude. I would also like to thank them not just for their work, but also for being there for support and company.

I am especially thankful to my supervisors Professor Markku Leskelä and Docent Mikko Ritala for their valuable ideas and guidance throughout my PhD studies. Without you this would not have been possible.

I am grateful to my co-workers and co-writers in the ALD laboratory Ms. Petra Alén, Mr. Antti Rahtu and Mr. Marko Vehkamäki, and also Dr. Per Mårtensson originally from University of Uppsala with whom I had the pleasure to work and to study the secrets of ALD. I am also grateful to Mr. Timo Sajavaara for carrying out the numerous TOF-ERDA measurements. In addition, I would like to give special thanks to Mr. Antti Niskanen for helping with XRD studies and computer problems that, unfortunately, sometimes occurred. I want to acknowledge the whole thin film group and also the other staff in the Laboratory of Inorganic Chemistry for sharing, for example, the refreshing coffee breaks and the mainly interesting discussions during them.

I would like to thank my roommates Ms. Petra Alén, Mr. Petri Räisänen, Dr. Heini Saloniemi and Mr. Marko Vehkamäki for not only sharing the room, but also for conversations, laugh and great company.

I appreciate my dear friends Mrs. Suvi-Maarit Kario and Mrs. Aija Lindholm for being there for support and encouragement. We have had many valuable discussions saving the world or at least part of it and, of course, great time together. I am also grateful for my dear friend Ms. Riikka Pastila for times that we spent together especially during the first years at the University. I hope that we will continue to stay as friends for many years to come.

My “strange” neighbours are also acknowledged for all those parties and fun that we have had together and hopefully the party spirit will be high also in the future.

I am grateful to Haagan Terä for enjoyable time with volleyball. It has been a great pleasure to play in such a nice team.

I want to thank my parents, sisters and brother, and also Juhana’s parents, sister and brother, for their support. I am greatly indebted to Juhana’s sister, skilful Tuija, for being my personal tailor.

Last, but not least, I am grateful to my husband, Juhana, and our daughter, Mona, for all the love that I have been privileged to get from you. You have been wonderful and I would not change you for anything.

Academy of Finland, the Finnish Cultural Foundation, the Finnish National Technology Agency (TEKES) and the Foundation for Technology are acknowledged for the financial support.

## LIST OF PUBLICATIONS

This work is based on the following original publications which are referred in the text by their Roman numerals. In addition, some unpublished deposition studies of copper are discussed.

I. M. Juppo, M. Ritala, and M. Leskelä: Deposition of Copper Thin Films by an Alternate Supply of CuCl and Zn.

*J. Vac. Sci. Technol.*, A15 (1997) 2330.

II. M. Juppo, M. Vehkamäki, M. Ritala, and M. Leskelä: Deposition of Molybdenum Thin Films by an Alternate Supply of MoCl<sub>5</sub> and Zn.

*J. Vac. Sci. Technol.*, A16 (1998) 2845.

III. P. Mårtensson, M. Juppo, M. Ritala, M. Leskelä, and J.-O. Carlsson: Use of Atomic Layer Epitaxy for Fabrication of Si/TiN/Cu Structures.

*J. Vac. Sci. Technol.*, B17 (1999) 2122.

IV. M. Juppo, M. Ritala, and M. Leskelä: Use of 1,1-Dimethylhydrazine in the Atomic Layer Deposition of Transition Metal Nitride Thin Films.

*J. Electrochem. Soc.*, 147 (2000) 3377.

V. M. Juppo, P. Alén, M. Ritala, and M. Leskelä: Trimethylaluminium as a Reducing Agent in the Atomic Layer Deposition of Ti(Al)N Thin Films.

*Chem. Vap. Deposition*, 7 (2001) 211.

VI. M. Juppo, P. Alén, M. Ritala, T. Sajavaara, J. Keinonen, and M. Leskelä: Atomic Layer Deposition of Titanium Nitride Thin Films Using *Tert*-butylamine and Allylamine as Reductive Nitrogen Sources.

*Electrochem. Solid-State Lett.*, to be published 1 (2002).

VII. M. Juppo, A. Rahtu, M. Ritala, and M. Leskelä: In Situ Mass Spectrometry Study on Surface Reactions in Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub> Thin Films from Trimethylaluminium and Water.

*Langmuir*, 16 (2000) 4034.

VIII. M. Juppo, A. Rahtu, and M. Ritala: In Situ Mass Spectrometry Study on Surface Reactions in Atomic Layer Deposition of TiN and Ti(Al)N Thin Films.

*Chem. Mater.*, accepted.

The author has written the articles II, IV-VIII and done most of the experimental work to these articles and also to the article I. The experimental work includes thin film growth experiments, XRD, SEM, EDX, profilometry, four point probe measurements, TG analysis and also *in situ* mass spectrometry analysis. TOF-ERDA analysis were done in the Accelerator Laboratory at Department of Physics at the University of Helsinki. The article III was done in co-operation with Per Mårtensson (University of Uppsala, Sweden) and the author has deposited the studied diffusion barriers and carried out part of the SEM analysis.

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**LIST OF ABBREVIATIONS AND ACRONYMS USED**

acac	=	2,4-pentanedione (acetylacetonate)
AES	=	Auger Electron Spectrometry
AFM	=	Atomic Force Microscopy
ALCVD™	=	Atomic Layer Chemical Vapor Deposition
ALD	=	Atomic Layer Deposition
ALE	=	Atomic Layer Epitaxy
allylNH <sub>2</sub>	=	allylamine
Cp	=	cyclopentadienyl
CVD	=	Chemical Vapor Deposition
DEAH	=	diethylaluminiumhydride
DIBAH	=	di-isobutylaluminiumhydride
DMHy	=	1,1-dimethylhydrazine
EDX	=	Energy Dispersive X-ray (analysis)
Et	=	ethyl
FTIR	=	Fourier Transmission Infrared Spectroscopy
hfac	=	1,1,1,5,5,5-hexafluoro-2,4-heptanedione
IC	=	Integrated Circuit
ML	=	monolayer
MOCVD	=	Metal Organic Chemical Vapor Deposition
MP	=	Mechanical Pump
NMR	=	Nuclear Magnetic Resonance
NRB	=	Nuclear Resonance Broadening
PEALD	=	Plasma Enhanced Atomic Layer Deposition
Pr	=	propyl
PVD	=	Physical Vapor Deposition
QCM	=	Quartz Crystal Microbalance
RBS	=	Rutherford Backscattering Spectrometry
RC	=	Resistance x Capacitance
RDS	=	Reflectance Difference Spectroscopy
sccm	=	standard cubic centimeter per minute
SEM	=	Scanning Electron Microscopy
SPA	=	Surface Photo Absorption
<sup>t</sup> BuNH <sub>2</sub>	=	<i>tert</i> -butylamine
TBTDET	=	<i>tert</i> -butylimidotris(diethylamido)tantalum
TDMAT	=	tetrakis(dimethylamino)titanium
TEM	=	Transmission Electron Microscopy
TEMAT	=	tetrakis(ethylmethylamido)titanium
TFEL	=	Thin Film Electroluminescent
thd	=	2,2,6,6-tetramethyl-3,5-heptanedione
TMA	=	trimethylaluminium
TOF-ERDA	=	Time of Flight Elastic Recoil Detection Analysis
UHV	=	Ultra High Vacuum
XPS	=	X-ray Photoelectron Spectrometry
XRD	=	X-ray Diffraction
XRF	=	X-ray Fluorescence
XRR	=	X-ray Reflectance



## 1. INTRODUCTION

The requirements for microelectronic devices have increased throughout their whole history and this has put high demands on microelectronic manufacturing. Transistors and other microelectronic components have to become continuously smaller and faster, but not at the expense of reliability and price. The line width used today is already below 0.20  $\mu\text{m}$  and in the future it is predicted to be reduced below 0.10  $\mu\text{m}$ .<sup>1</sup> With the currently used materials and thin film fabrication techniques the future requirements can not be achieved and therefore an enormous effort has been spent on research and development of new materials and deposition methods.

Until quite recently aluminium and aluminium based alloys were the most commonly used interconnect materials. Nowadays, however, copper has replaced aluminium in many applications because of its lower resistivity and better electromigration resistance leading to higher performance of the electric circuits. Since copper is known to diffuse through silicon dioxide-based dielectrics weakening the properties of the device, eventually leading to its total destruction, a diffusion barrier is needed to encapsulate copper. The materials that exhibit the most promising barrier properties are transition metals, transition metal nitrides, metal silicides and metal-silicon-nitrides.<sup>2</sup> The most studied diffusion barrier material has so far been titanium nitride.

Microelectronics industry has until these days relied mainly on various physical (PVD) and chemical vapor deposition (CVD) techniques in the fabrication of thin films. These methods, however, suffer from many difficulties which could be overcome by using atomic layer deposition (ALD) technique. Atomic layer deposition, also known as atomic layer epitaxy (ALE) and atomic layer chemical vapor deposition (ALCVD<sup>TM</sup>), was developed in mid 70's and offers many advantages over the traditional deposition methods.<sup>3-6</sup> ALD relies on self-limiting surface reactions which provide accurate thickness control, excellent conformality and uniformity over large areas. These unique features make ALD one of the most promising deposition methods in the manufacturing of the future circuits where the feature sizes are continuously shrinking and the controllability of the film growth becomes increasingly important.

Although many materials have been deposited by ALD, the chemistry involved has been studied in detail only for a few precursors. It would be of both practical and theoretical importance, if the actual surface reactions taking place in all important processes were adequately understood. This would greatly help in designing and optimizing the processes and the future requirements would become easier to fulfill.

In this thesis ALD growth of some metals (Cu, Mo) and transition metal nitrides (mainly TiN) has been studied. Copper and transition metal nitrides are important in the high density integrated circuits as described above. Molybdenum, on the other hand, is a potential material for many thin film applications in different fields, for example, in electroluminescent displays. More insight into the reactions taking place during ALD growth is gained by means of *in situ* mass spectrometry. In this thesis this technique has been used to study the surface reactions taking place during the ALD of Al<sub>2</sub>O<sub>3</sub>, TiN and Ti(Al)N thin films.

As a background for the present study the main characteristics of the ALD method and *in situ* mass spectrometry characterization technique will be introduced. A brief review of metals and transition metal nitrides, particularly copper and titanium nitride deposited by ALD, is also given. After experimental details describing the film deposition and characterization techniques, the results achieved will be summarized.

## 2. PURPOSE OF THE PRESENT STUDY

The purpose of the present study was three-fold. One goal was to examine the suitability of ALD in depositing metal films. The main interest was on copper, since it is the most wanted and studied metal to be used in the microelectronics. Formerly, ALD has mainly been used to deposit different compounds, focusing on oxide, sulfide and nitride thin films, and the studies on metals have been sparse.<sup>6</sup> Considering the future interest on the conformally grown ALD films, it is important to explore the capability and suitability of ALD also in deposition of metals. In the case of copper, it would already be sufficient if a process for a thin conformal seed layer could be found. The deposition of copper could then be continued onto this seed layer by the currently dominating electrochemical methods or by CVD.

Due to the necessity of diffusion barriers in the adoption of copper interconnects the second goal of this study was to deposit diffusion barriers. Titanium nitrides were studied the most, since they have the longest history of nitride barriers. They have already been deposited by ALD, mainly from titanium halides and ammonia, but often the temperatures needed to achieve good quality films have been too high ( $> 400\text{ }^{\circ}\text{C}$ ) for the future purposes.<sup>7-9</sup> Good quality films have, however, been deposited at reasonably low temperatures by using zinc as an additional reducing agent.<sup>7,10</sup> Due to the tendency of zinc to dissolve into silicon, producing electrically active defect sites, its use in electronic applications is undesirable. Therefore, the possibility of reducing the deposition temperature to values tolerable in the future ( $\approx 400\text{ }^{\circ}\text{C}$ ) by using new chemical approaches was studied. In the first place, the aim was to explore new chemistry and therefore the processes were not entirely optimized, for example, in respect of saturation.

The third goal of this study was to find out what kind of reactions take place during an ALD process. In order to realize this, a quadrupole mass spectrometer was installed to an ALD reactor. This was a challenging task on itself, since there are many things that have to be taken into account in order to be able to study the reactions in a meaningful manner. The deposition of  $\text{Al}_2\text{O}_3$  from trimethylaluminium and water was studied first. Because it is one of the most studied ALD processes, it was a good process to begin with. This study and the results obtained later with the developed equipment<sup>11-14</sup> encouraged to study also the reactions occurring during the deposition of TiN and Ti(Al)N thin films from titanium tetrachloride, trimethylaluminium and ammonia.

### **3. BACKGROUND**

#### **3.1. Atomic Layer Deposition**

##### **3.1.1. Basic Principle**

ALD is a CVD related chemical thin film deposition method, which relies on sequential saturative surface reactions.<sup>5,6,15,16</sup> The feature that makes ALD a unique deposition method compared to CVD is that the gaseous precursors are alternately introduced onto the substrates. Between the reactant pulses the reactor is either purged with an inert carrier gas as in flow-type reactors or evacuated. The flow-type reactor is the most commonly preferred reactor type especially in production scale use, since both reactant exposure and purge sequence are more rapidly completed and therefore these reactors are more cost effective. Usually the flow-type reactors operate at pressures from about 1 to 20 mbar. Together with narrow flow channels this ensures high precursor utilization since a precursor molecule is forced to make multiple hits while being transported through the reactor.<sup>6</sup>

Under properly adjusted experimental conditions, i.e., deposition temperature, reactant dose and length of precursor and purge pulses, a chemisorbed monolayer of the first reactant is left on the surface after the purge sequence. This reacts subsequently with the incoming reactant pulse forming one layer of the desired material and gaseous reaction byproducts, if compounds are used as precursors. Hence, in an ideal case, the surface reactions are self-controlled and no detrimental gas phase reactions take place. As a result, the film thickness can be accurately controlled by the number of deposition cycles.

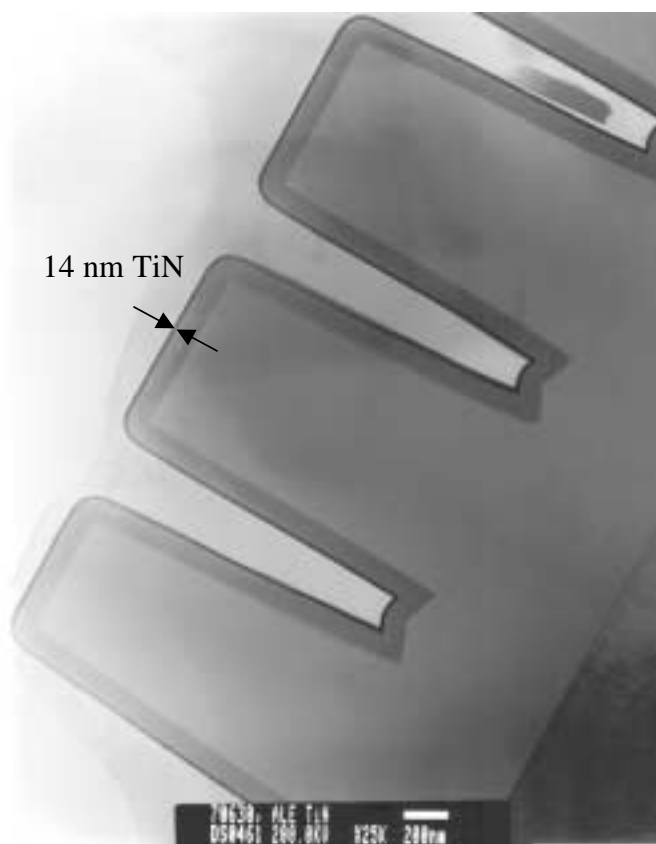
##### **3.1.2. Advantages of ALD Compared to Some Other Deposition Methods**

The requirements for the thin film deposition method to be exploited in the future manufacturing of microelectronic circuits are very demanding. Good quality films should be deposited at reasonably low temperatures tolerated by the other materials used in circuits, and the conformality of the films even on very deep trenches should be excellent.

Gaseous thin film deposition methods are traditionally divided into two main categories, i.e., to physical (PVD) and chemical vapor deposition (CVD) -techniques. These, however, tend to suffer from various difficulties. Films can be grown at quite low temperatures using the PVD techniques, but the conformality of the deposited films is poor. Films with better conformality are obtained by various CVD techniques, but usually the needed deposition temperatures are too high for the future

microelectronic purposes. Further, good conformality and good quality of the films are difficult to achieve at the same time.

Hence, in order to fulfill the future requirements, either the traditional methods and processes should be developed further or entirely new approaches should be found. ALD is one of the most promising deposition techniques to fulfill these requirements. The self-limiting manner of ALD reactions guarantees that the films are conformally deposited even onto the substrates with very high aspect ratios (Fig. 1).<sup>17</sup> Practice has shown that usually the deposition temperatures needed for depositing high quality thin films are lower than in the CVD methods.<sup>4,5</sup> Quite often the processing temperature windows are wide which enables easy multilayer processing. As a distinction from the CVD methods, no strict precursor flux homogeneity is required in ALD because of the self-limiting growth mechanism. The flux has only to be large enough to fully saturate the surface with the given reactant. This enables, for example, the utilization of low vapor pressure solids, which are difficult to be delivered at constant rates.



*Figure 1.* Cross sectional image of an ALD deposited TiN film.

Perhaps the most severe disadvantage of ALD is that it is rather slow. On the other hand, the films are uniformly deposited over large batches,<sup>17-19</sup> which is a clear advantage in the sense of productivity. The slowness of the method will not be a very serious problem in the future taking also into account that the device dimensions will continue to shrink and very thin films are needed.

### 3.2. ALD of Metals

ALD of metals has been sparse and gained only limited success as compared to the different compound materials. The metals, other than copper, deposited so far by ALD using different precursors and reducing agents are listed in Table I. The summary of ALD deposited copper films is presented later in Table II.

*Table I.* An overview of the metals deposited by ALD.

<b>Metal deposited by ALD</b>	<b>Metal precursor</b>	<b>Reducing agent</b>	<b>Reference</b>
W	WF <sub>6</sub>	Si <sub>2</sub> H <sub>6</sub>	20
Ti	TiCl <sub>4</sub>	H (RF plasma 13.56 MHz, 300-1200 W)	21
Ta	TaCl <sub>5</sub>	-“-	21
Ni	Ni(acac) <sub>2</sub>	2 step process: NiO by O <sub>3</sub> , reduced afterwards by H <sub>2</sub>	22

An effective ALD metal process would be of great importance in many applications. ALD of metals is, however, a chemically challenging task and involves many difficult aspects that have to be taken into account. In addition to an effective reducing agent, a suitable metal precursor has to be found. The metal precursor has to be stable against decomposition, chemisorb/adsorb evenly on the surface, and also easily reduced. Etching of the previously deposited film is not allowed, and therefore metal precursors that form lower oxidation state compounds etching the metal film can not be used. Because ALD relies on self-limiting growth mechanism the precursors that react by a disproportionation mechanism forming both lower and higher oxidation state products are not good choices for ALD. The adsorption mechanism of metal precursor is also an unresolved question, especially if the surface contains no functional groups.

### 3.2.1. Copper

It seems evident that copper will increasingly replace aluminium as an interconnect material in integrated circuits. Due to the lower resistivity of Cu as compared to Al (1.7 vs 2.7  $\mu\Omega\text{cm}$ ) the performance of the circuit increases since resistance times capacitance (RC) delays become smaller. The better electromigration resistance of copper enables the use of higher current densities.<sup>23,24</sup> This capability can be attributed to the higher atomic weight (63.55 vs 26.98 u) and melting point (1083 vs 660 °C) of copper compared to aluminium.

Currently, copper films are deposited by electroplating and they grow in a unique superfilling manner with a high growth rate. However, a continuous seed layer is needed to ensure that a continuous void-free Cu film is formed in high aspect ratio features and also to conduct current from the contact to the deposition areas.<sup>24,25</sup>

With CVD, copper films have mainly been deposited from different Cu(I)- and Cu(II)-  $\beta$ -diketonates.<sup>26</sup> The deposition of copper from Cu(I)- $\beta$ -diketonates takes place through disproportionation reaction and an additional reducing agent is not necessarily needed. However, utilization of a reducing agent is necessary when Cu(II)- $\beta$ -diketonates are used as precursors. Reasonably good films have been deposited by various CVD methods, although the conformality has to be improved. The films usually contain seams, defects, or microvoids at the center of the holes and trenches. This results from surface reactions that tend to deplete the precursor from the gas phase. Therefore, the bottom of the narrow via will receive fewer precursor molecules than the top of the via. Recently, however, quite promising results on improving the conformality have been achieved with so called superfilling CVD of copper by using iodoethane as a catalytic surfactant.<sup>27</sup>

As already mentioned, the films deposited by ALD grow conformally when the reactions proceed in the ideal self-limiting manner. Therefore, if a copper ALD process were found, it would most probably be exploited in the integrated circuit metallization. Even if not the entire copper layer was deposited by ALD, already a uniform conformally deposited seed layer for electrochemical deposition would gain enormous interest.

Because copper precursors like Cu(I)- $\beta$ -diketonates that react by disproportionation are not suitable for ALD, the ALD growth of copper thin films has been explored from Cu(II)- $\beta$ -diketonates and also from CuCl. Similarly to CVD, the main reducing agent studied has been hydrogen. Usually the processes have been quite specific to the substrate material and especially problems with adhesion were encountered. The ALD studies on copper deposition are summarized

in Table II.

Table II. An overview of the ALD deposited copper films.

Copper precursor	Reducing agent	Deposition temperature (°C)	Substrate	Impurities (at.%)	Resistivity (: S cm)	Growth rate (nm/cycle)	Ref.
CuCl	H <sub>2</sub>	360-410	Ta	Cl:<1	not reported	0.08	28, 29
Cu(thd) <sub>2</sub>	H <sub>2</sub>	175-300 (self-limiting at 190-260)	Pt/Pd seed	traces of C, O (film cooled under H <sub>2</sub> )	8.1 (60 nm) 41.2 (41 nm)	0.03 (190-260 °C)	28, 30
Cu(acac) <sub>2</sub>	H <sub>2</sub>	250	glass, Si, Ti, Al,	not reported	not reported	not reported	22
Cu(hfac) <sub>2</sub> @ xH <sub>2</sub> O	CH <sub>3</sub> OH	230-300	glass, Ta, TiN, TaN	C:5 O:4	5.33 (200 nm)	not reported	31
-“-	C <sub>2</sub> H <sub>5</sub> OH	-“-	-“-	C:3 O:3	about 2	-“-	-“-
-“-	HCHO- H <sub>2</sub> O	-“-	-“-	C: traces O:<2	1.78 (120 nm) 4.25 (20 nm)	-“-	-“-

ALD of copper from Cu(thd)<sub>2</sub> and H<sub>2</sub> was successful only on Pt/Pd seeded glass substrates and no deposition occurred on bare glass, Ta, Fe, TiN, Ni and In<sub>2</sub>O<sub>3</sub>:Sn substrates.<sup>28,30</sup> The growth on the Pt/Pd seed was explained by a more complete dissociation of the Cu(thd)<sub>2</sub> molecules due to the electron transfer from the substrate to the adsorbed molecule. Another quite possible reason is that the dissociation of molecular hydrogen into reactive hydrogen atoms is assisted by the Pt/Pd seed. The growth of copper on hydroxyl terminated (glass, In<sub>2</sub>O<sub>3</sub>:Sn) and oxidized metal (Ta, Fe, TiN, Ni) surfaces could not proceed, because one of the thd ligands is believed to remain bound with the adsorbed copper atom blocking the surface sites. A self-limiting growth with a rate of 0.03 nm/cycle corresponding to 0.17 monolayers of the (111) oriented copper was obtained between 190 and 260 °C on the Pt/Pd seeded glass substrates. The purity of the films cooled under hydrogen was excellent and only traces of carbon and oxygen could be detected by XPS. The resistivity and morphology were very dependent on the film thickness, but not on the deposition temperature inside the self-limiting temperature regime (“ALD-window”). The resistivity decreased with increasing film thickness so that the resistivity of a 60 nm thick film was only 8.1 : S cm and that of a 41 nm thick film as high as 41.2 : S cm. AFM and SEM studies showed that the films



consisted of individual grains, the size of which varied between 0.1 and 0.3 : m being larger with the thicker films. At temperatures below the self-limiting growth regime the growth rate decreased abruptly until no growth could be observed. At higher temperatures the thermal decomposition of  $\text{Cu}(\text{thd})_2$  took place and the films were contaminated with carbon. These Cu films were deposited in a reactor built by Mårtensson and Carlsson,<sup>28,30</sup> but the process could not be reproduced in a commercial F-120 reactor.<sup>III</sup> This was attributed to several factors including too low hydrogen partial pressure and too high linear gas flow across the substrate surface. The linear gas flow velocity was almost a factor of 10 higher in the F-120 reactor than in the reactor used in the successful copper depositions experiments.

Some brief studies with  $\text{Cu}(\text{acac})_2$  and  $\text{H}_2$  have been carried out, and a film with a clear metallic reflectivity was deposited on Ti and Al. However, on glass only a moderately transparent green-blue film and on silicon only weak indications of any deposit formation were observed. According to XPS, copper was present on all the sample surfaces but its chemical state depended on the substrate material so that the relative amount of  $\text{Cu}^{2+}$  increased in a series Ti, Si < Al < glass.<sup>22</sup>

Mårtensson et al. used also hydrogen as a reducing agent for  $\text{CuCl}$ .<sup>28,29</sup> Tantalum was the only studied substrate and copper films were deposited between 360 and 410 °C with a typical rate of 0.08 nm/cycle. However, a fast substrate reduction process contributed to the growth causing an initial film thickness of about 30 nm. The films were polycrystalline exhibiting a grain size of 1 - 4 : m, but also some grains of a 10 : m size were observed. The concentration of chlorine in the films was below 1 at.% though the surface concentration was about 7 at.%.

The most promising results so far have been obtained by using  $\text{Cu}(\text{hfac})_2 \cdot x\text{H}_2\text{O}$  and formalin ( $\text{HCHO} \cdot x\text{H}_2\text{O}$ ) as precursors.<sup>31</sup> The deposition was carried out on glass, Ta, TiN and TaN. The growth of copper films was observed already at about 230 °C, but the best results were achieved at 300 °C. A typical ALD cycle consisted of pulse length of 12 s for the reactants and 20 s for the purge pulses. These are quite long compared to the conventional ALD pulse lengths which are typically below 1 s in the F-120 flow type reactors used in their study. However, the films appeared bright copper colored showing an excellent conformality over high aspect ratio trenches. The resistivity of a 120 nm film was 1.78 : S cm and increased with decreasing film thickness so that the resistivity of a 20 nm thick copper film was 4.25 : S cm. The higher resistivity of the thinner films was attributed to the interface scattering of the electrons. The films were quite free from impurities and only less than 2 at.% oxygen was detected by XPS. Also methanol and ethanol were used as reducing agents but the results were not as promising as with formalin. The resistivities achieved with ethanol for 77 nm thick films grown on different substrates were around 2 : S cm. The dominant impurities were carbon and oxygen (both about 3 at.%). The results

obtained with methanol were not as good as with ethanol and these films appeared reddish indicating a significant amount of carbon incorporation. The adhesion of the copper films depended on the substrate material. The adherence was good on TiN and TaN, but the films deposited on glass and Ta did not pass the Scotch tape test. Alcohols have been proven to be effective reducing agents also in the CVD growth of copper. They have been proposed to act as agents delivering atomic hydrogen which assists in the reduction process. The ability of a certain alcohol to produce atomic hydrogen is dependent on the bond strength of hydrogen-primary carbon, and therefore it is understandable that ethanol is a better reducing agent for copper than methanol.<sup>32,33</sup>

Except for the recent study with formalin the results obtained have been quite modest. Since ALD has a lot to offer for IC manufacturing, especially for future generations, many different approaches to deposit copper have to be studied.

### 3.2.2. Molybdenum

Molybdenum is a suitable material for metallization in integrated circuits due to its relatively low resistivity ( $5.2 \text{ } \mu\Omega \text{ cm}$ ), inertness, high-temperature stability (m.p.  $2625 \text{ } ^\circ\text{C}$ ), low thermal expansion coefficient and etchability. The most common deposition method for molybdenum is sputtering, but also CVD has been examined. Molybdenum can be deposited by CVD from  $\text{MoF}_6$ ,  $\text{MoCl}_5$  and  $\text{Mo(CO)}_6$ , and usually  $\text{H}_2$  has been used as a reducing agent. The typical deposition temperatures vary between  $200 - 500 \text{ } ^\circ\text{C}$  for  $\text{MoF}_6$ ,  $500 - 1100 \text{ } ^\circ\text{C}$  for  $\text{MoCl}_5$  and  $200 - 600 \text{ } ^\circ\text{C}$  for  $\text{Mo(CO)}_6$ .<sup>34</sup>

Except for the study reported in this thesis, the deposition of molybdenum by ALD has not been attempted. A molybdenum ALD process might, however, be of interest especially in the manufacturing of thin film electroluminescent (TFEL) displays. ALD was originally developed for making TFEL displays and it has been employed in TFEL production since 80's.<sup>4,5,35-38</sup> TFEL devices consist of a film stack electrode - insulator - luminescent layer - insulator - electrode deposited on glass. If soda lime glass is used, it is first passivated with an ion barrier layer. In conventional TFEL devices the bottom electrode is transparent and metal is deposited as the other electrode on top of the film stack. In TFEL devices with an inverted structure, on the other hand, metal electrode is deposited already as the first film of the stack on the ion barrier, and will therefore be subjected to deposition steps of the subsequent films. Hence the requirements for this metal electrode material are more demanding, like high melting point and thermal expansion coefficient matching to glass substrate. In addition, to obtain good contrast, the electrode material has to have a small reflection coefficient in the visible region. Aluminium is the currently used electrode material in the conventional TFEL devices but it can not be used in the inverted

structures. Molybdenum along with tungsten, on the other hand, could be used as an electrode both in the conventional and inverted TFEL structures, since it fulfills the above demands.<sup>38</sup> In both cases, a Mo ALD process could be combined with the preceding ALD process steps, i.e., deposition of the insulator - phosphor - insulator films in the conventional structures and ion barrier in the inverted structures, and thereby a major part of the film stack could be deposited by a continuous ALD process.

### 3.3. ALD of Transition Metal Nitrides

Transition metal nitrides are important in many areas of microelectronics, although the most important application is perhaps a diffusion barrier between metals and silicon. Use of a diffusion barrier is necessary since the presence of copper in silicon results in highly adverse effects which weaken the properties of the electric circuits and eventually lead to total destruction of the device. Hence, the purpose of the diffusion barrier is to keep these reacting materials separated during the whole IC fabrication process and also to maintain the electrical integrity of the contact junction. The barrier may also function as an adhesion promoter, since copper is known to adhere poorly on SiO<sub>2</sub> and also on the various low-k materials considered for use in the future.<sup>2</sup>

The shrinkage of IC device dimensions puts great demands on the barrier.<sup>2,39</sup> The barrier must provide the required performance at continuously reduced thicknesses in order not to reduce the cross sectional area of the actual copper interconnect and thus increase the wire resistance. It has been predicted that the maximum allowable barrier thickness reduces from 17 to 10 nm and below during the next five years.<sup>1</sup> Conformality is crucial and the barrier must also meet number of other requirements like low resistivity and impurity contents.

The diffusion barriers can be divided into four classes, namely sacrificial, stuffed, passive and amorphous, according to the mechanism by which they suppress the chemical reaction of the separated materials.<sup>40</sup> The transition metal nitrides are characterized to be mainly passive or amorphous. The most often studied diffusion barrier has been TiN which has already been used with good results between aluminium and silicon. It is a polycrystalline material exhibiting typically a columnar type morphology. Therefore the diffusion mainly takes place through grain boundaries which are the main reason for the barrier breakdown.<sup>2</sup> In order to eliminate the grain boundaries the material should be either single crystal or amorphous. Single crystals are difficult to achieve and therefore amorphous materials are preferred. Much effort has been invested in finding the most suitable diffusion barrier material and also the deposition method. Since ALD provides good controllability and conformality it is a promising technique to meet the future challenges.

### 3.3.1. TiN

The deposition of TiN films, like other nitride films, has been performed with various PVD and CVD techniques. These methods, however, suffer from various downsides as described previously. In the traditional CVD processes, TiN films are deposited from  $\text{TiCl}_4$ ,  $\text{H}_2$  and  $\text{N}_2$  at temperatures above  $750\text{ }^\circ\text{C}$  which is well above that tolerated in the manufacturing of the future circuits.<sup>41</sup> If  $\text{NH}_3$  is used instead of  $\text{H}_2$  and  $\text{N}_2$ , reasonably good quality films can be deposited at temperatures exceeding  $550\text{ }^\circ\text{C}$  but this is still above the desired temperature ( $400\text{ }^\circ\text{C}$ ).<sup>42-47</sup> Therefore, alternative precursors, particularly alkylamides,<sup>48-57</sup> as well as additional energy sources, like plasma<sup>50,52</sup> and hot filament activation<sup>58</sup> of nitrogen sources, and post- or intermediate<sup>54,55,59</sup> deposition plasma treatments have been examined. For example, by  $\text{N}_2/\text{H}_2$  plasma post treatment the resistivity and the chlorine content of TiN films deposited by CVD from  $\text{TiCl}_4$  and  $\text{NH}_3$  could be reduced by about 70 % and 30 %, respectively.<sup>59</sup>

As in CVD, majority of the ALD grown TiN films have been deposited from titanium tetrachloride and ammonia. In order to reduce the deposition temperature and also to deposit films with amorphous structure titanium alkylamides have been studied. The ALD deposited TiN films usually exhibit better characteristics compared to the respective films made by CVD at same temperature. It is possible that the quality of the ALD deposited TiN films could even be improved, for example, with plasma treatments but its exploitation is only at a beginning. The ALD studies on TiN deposition are summarized in Table III.

Table III. An overview of the ALD deposited TiN and Ti-Si-N films.

Material/ precursors substrate	Deposition temperature (°C)	Crystallinity	Impurities (at.%)	Resistivity (: S cm)	Growth rate (nm/ cycle)	Ref.
TiN/ TiCl <sub>4</sub> , NH <sub>3</sub> on glass	500	polycryst. (200) dom.	Cl:<0.5 O:9 H:<0.4	250	0.017	7
TiN/ TiCl <sub>4</sub> , NH <sub>3</sub> on glass	500	polycryst. (200) dom.	Cl: few	240-360	0.02-0.03	9
TiN/ TiCl <sub>4</sub> -Zn-NH <sub>3</sub> on glass	400-500	polycryst. (111) dom.	Cl: 6(400°C) <0.5(500 °C) Zn:<0.1 O:3 H:<0.4	200 (400 °C) 50 (500 °C)	0.013 (400 °C) 0.019 (500 °C)	7, 10
TiN/ TiCl <sub>4</sub> -NH <sub>3</sub> on glass	350-500	polycryst. (200) dom. (400-425 °C) (111) dom. (450-500 °C)	I:2 (350 °C) <0.5 (>400 °C) O:40 (350 °C) 10 (475-500 °C)	380 (400 °C) 150 (450 °C) 70 (500 °C)	0.005 (350 °C) 0.012 (400 °C) 0.032 (500 °C)	8
TiN/ TiCl <sub>4</sub> -NH <sub>3</sub> on Si	350-450	polycryst. (200) dom.	Cl:2.5 (350 °C) 0.5 (400 °C) <0.5 (450 °C)	350 (350 °C) 140 (400 °C) 75 (450 °C)	0.04	60
TiN/ TiCl <sub>4</sub> -NH <sub>3</sub> on SiO <sub>2</sub>	350-400	not reported	Cl:3 (350 °C) 1.5 (400 °C)	400-500 (350 °C) 150-250 (400 °C)	not reported	61
TiN/ TiCl <sub>3</sub> +Ti <sub>2</sub> Cl <sub>6</sub> (TiCl <sub>4</sub> +Ti)- NH <sub>3</sub> on Si	300-400	polycryst.	Cl: 9.3 (300 °C) 3.8 (350 °C) 1.2 (400 °C)	400 (350 °C) <200 (400 °C)	0.037 (400 °C)	62
TiN/ TEMAT-NH <sub>3</sub> on SiO <sub>2</sub>	150-400 (self-limiting at 170-210)	amorphous (170-210 °C)	C:4 H:6	not reported	0.6	63
TiN/ TEMAT-NH <sub>3</sub> on Si	150-240 (self-limiting at 150-220)	amorphous	not reported	<230 (<180 °C) >8000 (>180 °C)	0.45 (150-220 °C)	64
Ti-Si-N/ TDMAT-SiH <sub>4</sub> - NH <sub>3</sub> on SiO <sub>2</sub>	180	amorphous matrix with nanocrystalline phases	Si:18-21 C:<1.5	30000 (Si:18 at.%) 5000 (Si:0 at.%)	0.20 (18 at.% Si) - 0.44 (0 at.% Si)	65, 66

Ritala et al.<sup>7,10</sup> have deposited TiN films from  $\text{TiCl}_4$  and  $\text{NH}_3$  with and without Zn as an additional reducing agent. The deposition rate of the films was quite low, below 0.02 nm/cycle in each case. This corresponds to 0.1 monolayers/cycle if the (111) growth direction is assumed. The films were deposited without zinc only at 500 °C. The amount of chlorine impurities was below the detection limit of RBS and less than 0.4 at. % of hydrogen could be detected in the film by NRB. The oxygen content of the films was, however, quite high. A 140 nm thick film contained about 9 at. % oxygen. The resistivity of the films over 100 nm in thickness was about 250 : S cm. The film properties were improved when zinc was pulsed in between the  $\text{TiCl}_4$  and  $\text{NH}_3$  pulses. The chlorine content of the films deposited at 400 °C was 6 at. % and the resistivity was 200 : S cm, which is even slightly lower than in the films deposited without zinc at 500 °C. No zinc could be detected with either EDX or RBS which is important considering the tendency of zinc to dissolve into silicon. The oxygen content of the films deposited with the  $\text{TiCl}_4$  - Zn -  $\text{NH}_3$  process was lower (3 at. %) than with the  $\text{TiCl}_4$  -  $\text{NH}_3$  process. In general, oxygen seemed to be quite uniformly distributed in the film and its content was the highest in the thinnest films. Therefore, it was suspected that oxygen incorporation took place after the film growth through grain boundary diffusion. The films grown with and without zinc consisted of cubic TiN, although the direction of the most preferred orientation was different. The most preferred orientation of the films deposited with zinc was (111), i.e., the films consisted mainly of alternately stacked titanium and nitrogen layers. On the other hand, the (100) direction was the most dominant for the films prepared without zinc, and hence these films were built up of planes containing equal amounts of titanium and nitrogen. The difference in the orientations of the films deposited by different processes was explained by the capability of zinc to remove chlorine from the surface, after which the remaining Ti atoms could arrange to the structure with the lowest surface energy, i.e., the (111) orientation.

Jeon et al.<sup>60</sup> and Satta et al.<sup>61</sup> have also deposited TiN films from  $\text{TiCl}_4$  and  $\text{NH}_3$ . Good quality films were prepared already at 350 °C and the chlorine content was only about 3 at. %. The most probable reason for the better results than Ritala et al.<sup>7</sup> is the higher  $\text{NH}_3$  flow rate used. Jeon et al. deposited TiN films using the flow rate of 75 sccm, which is nearly ten times higher than used by Ritala et al. Also the oxygen distribution in the films seemed to differ, since according to AES spectra only the topmost surface and the interface between substrate and the film contained oxygen.<sup>60</sup> The resistivities of these films were the same or even lower than those of the films deposited by the  $\text{TiCl}_4$  - Zn -  $\text{NH}_3$ <sup>7,10</sup> process at the same temperatures.<sup>60,61</sup> At 350 °C the only reflection observed in the XRD pattern was (200) but at 400 and 450 °C, both (111) and (220) peaks were observed along with the most intensive (200) peak. The TiN film deposited at 350 °C exhibited a columnar structure, but the microstructure of the film deposited at 450 °C was somewhat randomly oriented. This change in the microstructure was attributed to the surface mobility of adsorbed molecules. Bulk diffusion and recrystallization contributed to the film growth

at 450 °C in addition to the surface diffusion of the adsorbed molecules which was the only contributing factor at 350 °C.<sup>60</sup>

One of the problems with the ALD of TiN films is the low growth rate. In order to increase that, *in situ* reduced titanium chloride has been used as a titanium source and NH<sub>3</sub> with a flow rate of 100 sccm as a nitrogen source.<sup>62</sup> The *in situ* reduction was realized by pulsing TiCl<sub>4</sub> over a hot titanium metal. The gas phase products of the reduction reaction and thereby the actual titanium sources were assumed to be TiCl<sub>3</sub> and Ti<sub>2</sub>Cl<sub>6</sub>. The growth rate could be increased to 0.037 nm/cycle at 400 °C, whereas the growth rate without the *in situ* reduction saturated at 0.017 nm/cycle. In addition, the saturation was achieved extremely fast with 0.1 and 0.05 s pulse times for NH<sub>3</sub> and TiCl<sub>4</sub> pulses, respectively. This was attributed to the fast surface reactions and efficient transportation of the precursors. The chlorine content of the films decreased with increasing deposition temperatures, being 9.3 and 1.2 at.% at 300 and 400 °C, respectively. The resistivity of these TiN films was comparable (below 200 : S cm at 400 °C) to those deposited strictly from TiCl<sub>4</sub><sup>7,10,60,61</sup>

Another titanium halide that has been studied in the ALD of TiN films is TiI<sub>4</sub>.<sup>8</sup> Due to lower dissociation energy of the bond Ti-I ( $D_0 = 296$  kJ/mol) compared to the bond Ti-Cl ( $D_0 = 429$  kJ/mol),<sup>67</sup> the deposition of TiN films from TiI<sub>4</sub> and NH<sub>3</sub> can be carried out at lower temperatures than from TiCl<sub>4</sub> and NH<sub>3</sub><sup>7</sup> at the otherwise same deposition conditions. The iodine content of the films deposited at 350 °C was 2 at.% and it decreased below 0.5 at.% at temperatures exceeding 400 °C. The oxygen content was comparable (10 at.% at 400 °C) to the films deposited by TiCl<sub>4</sub>-NH<sub>3</sub> process, and even 40 at.% oxygen was detected in the films deposited at 350 °C. Similarly to the TiCl<sub>4</sub> based processes, the resistivity of the films decreased as a function of the deposition temperature being 380 and 70 : S cm at 400 and 500 °C, respectively. According to XRD analysis the films deposited below 400 °C were amorphous, which may be due to the high oxygen content or the low thickness (below 60 nm). The films deposited at higher temperatures were polycrystalline TiN with the cubic structure. In each film only one reflection was detected in XRD. However, the direction of the most preferred orientation was dependent on the deposition temperature so that the films grown at 400 and 425 °C were oriented into the (100) direction while those grown at higher temperatures were oriented into the (111) direction. It seemed that by using TiI<sub>4</sub> the energetically most favorable orientation, i.e., (111), could be obtained, but in the respective TiCl<sub>4</sub> based processes<sup>7,10</sup> the use of zinc was necessary in order to achieve this. Most likely the more easier breakability of the Ti-I bond than the Ti-Cl bond enables the surface to reorganize.

Different titanium alkylamides have been used in CVD of TiN films. Amorphous TiN films could

be grown at low temperatures with variable resistivities depending, for example, on the alkylamide.<sup>53</sup> Although these compounds include the Ti-N bond, use of an external nitrogen source, conventionally  $\text{NH}_3$ , was beneficial since the films deposited through transamination reactions were better than those achieved with the simple decomposition of the alkylamides.<sup>51,52,56,57</sup> With ALD, amorphous TiN films have been deposited from  $\text{Ti}[\text{N}(\text{C}_2\text{H}_5\text{CH}_3)_2]_4$  (tetrakis(ethylmethyldamido)titanium, TEMAT) and  $\text{NH}_3$ .<sup>63,64</sup> The saturative pulse length of TEMAT depended on the deposition temperature. The film thickness saturated with pulse times exceeding 3 s and 10 s at 200 and 175 °C, respectively. On the other hand, with  $\text{NH}_3$  (flow 250 sccm) longer pulse times of 10 and 20 s were needed to saturate the growth rate to 0.5 and 0.6 nm/cycle, respectively.<sup>63</sup> Film growth was controlled by self-limited ALD reactions in the temperature range of 170 - 210 °C<sup>63</sup> or 150 - 220 °C.<sup>64</sup> At higher temperatures TEMAT decomposed and CVD type of reactions occurred. The growth rate of these films varied between 0.5 - 0.6 nm/cycle, which is more than ten times higher than in the halide based processes. These growth rates are well above the ideal monolayer per cycle (ML/cycle) growth which is 0.245 nm, if the (111) direction is considered. This is inconsistent with the normal ALD process because the film thickness per cycle should be limited to at or below 1 ML. This behavior was thought to be due to rechemisorption of the excess TEMAT and  $\text{NH}_3$ . Kinetic modeling of this kind of film growth has been studied by Lim et al.<sup>68</sup> and the growth rate was found to depend on the lengths of the precursor pulses. The purity of the ALD produced films was rather good and only 4 at.% carbon and 6 at.% hydrogen were incorporated into the film.<sup>63</sup> The step coverage of the films was excellent, above 90 %, whereas for MOCVD TiN films it is usually poor.<sup>51,52,57</sup> The resistivity of the TiN films deposited by ALD at lower temperatures (180-190 °C) varied between 210 and 230 : S cm, but increased dramatically as the temperature was increased.<sup>64</sup> Also the diffusion barrier behavior of both as-deposited and post-annealed 45 nm thick TiN films at temperatures between 550 and 700 °C were investigated. The post-annealing did not seem to have an effect on the film properties and the increase of temperature above 650 °C resulted in interdiffusion and probable formation of  $\text{Cu}_3\text{Si}$ .<sup>64</sup>

Titanium-silicon-nitride, Ti-Si-N, films were grown by ALD from  $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$  (tetrakis(dimethylamino)titanium, TDMAT), silane ( $\text{SiH}_4$ ) and ammonia at substrate temperature of 180 °C.<sup>65,66</sup> Silane was supplied either as a separate pulse between or after the subsequent TDMAT and  $\text{NH}_3$  pulses or simultaneously with  $\text{NH}_3$ . The silicon content of the film depended on the deposition sequence in question. With the TDMAT -  $\text{SiH}_4$  -  $\text{NH}_3$  process the silicon content saturated to 18 at.%, with the TDMAT - ( $\text{SiH}_4 + \text{NH}_3$ ; 1:1 ratio) process to 23 at.% and with the TDMAT -  $\text{NH}_3$  -  $\text{SiH}_4$  process to 21 at.%. In the film with a composition of  $\text{Ti}_{0.32}\text{Si}_{0.18}\text{N}_{0.50}$  less than 1.5 at.% of carbon was incorporated. The step coverage was almost 100 % and according to TEM the film consisted mainly of amorphous phase, although some nanocrystallites were embedded.<sup>65</sup> The resistivity was reported to be about 30000 : S cm for a film with 18 at.% of silicon. This is



very high as compared to typical diffusion barriers but the authors suspected that the films grown at higher temperatures should display better electrical properties.<sup>66</sup> The barrier capability of a 10 nm  $\text{Ti}_{0.32}\text{Si}_{0.18}\text{N}_{0.50}$  was tested by capacitance-voltage measurements. These revealed that the Ti-Si-N film prevented the diffusion of Cu up to 800 °C for 1 hour when the annealing was carried out in  $\text{H}_2(10\%)\text{-Ar}(90\%)$ .<sup>69</sup> In addition to the Ti-Si-N films, also TiN films were grown from TDMAT and  $\text{NH}_3$  at 180 °C. The growth rate of 0.44 nm/cycle was comparable to the films deposited from TEMAT<sup>63,63</sup> and the resistivity was lower (5000 : S cm) than that of the Ti-Si-N films.<sup>66</sup>

It can be concluded that although quite many ALD studies have been carried out to deposit TiN diffusion barriers, the low temperature studies have been quite limited. This is mainly because ammonia has been used as a nitrogen source and since it has a relatively high dissociation energy (449 kJ/mol)<sup>70</sup> it is not effective enough at low temperatures. Therefore especially the studies on more effective nitrogen sources than ammonia are needed in order to deposit good quality films at low temperatures. An alternative way to decrease the deposition temperature is to use plasma activation but its exploitation is only at a beginning.<sup>21,71</sup>

### 3.3.2. Other Transition Metal Nitrides

So far, the ALD of transition metal nitride films other than TiN has been only quite sparsely examined. However, the interest especially into the ALD of TaN films has increased since TaN is suspected to exhibit better diffusion barrier characteristics than TiN.<sup>2,72,73</sup> The better barrier properties of TaN films are attributed to a disordered grain boundary structure that makes copper atom diffusion through the film more inefficient compared to TiN that has a columnar grain structure.<sup>72</sup> In addition, tantalum is stable with copper whereas titanium can form cuprides.<sup>73</sup> The summary of the ALD deposited transition metal nitride films is presented in Table IV.

Table IV. An overview of the ALD deposited TaN<sub>x</sub>, MoN<sub>x</sub> and NbN films.

Material/ precursors substrate	Deposition temperature (°C)	Crystallinity	Impurities (at.%)	Resistivity (: S cm)	Growth rate (nm/ cycle)	Ref.
TaN <sub>x</sub> / TaCl <sub>5</sub> -NH <sub>3</sub> on glass	200-500	amorphous (<400 °C) polycryst. Ta <sub>3</sub> N <sub>5</sub> (at 400 °C and above)	Cl:<0.1 H:<0.1 O:3-5 (450-500 °C)	>200x10 <sup>6</sup> (<400 °C) 5x10 <sup>5</sup> (>400 °C)	0.012 (200 °C) 0.024 (>350 °C)	74
TaN <sub>x</sub> / TaCl <sub>5</sub> -NH <sub>3</sub> on glass	500	polycryst. Ta <sub>3</sub> N <sub>5</sub>	not detected	41170 (Ta <sub>3</sub> N <sub>5</sub> )	0.02-0.03	9
TaN/ TaCl <sub>5</sub> -Zn- NH <sub>3</sub> on glass	400-500	polycryst. TaN (111) dom. at 450 and 500 °C	Cl:4 (400 °C) 0.3 (450 °C) 0.1 (500 °C) H:0.5 (400 °C) <0.1 (500 °C) Zn:0.5 (400 °C) <0.1 (500 °C) O:3-4	900	0.02 (400 °C) 0.015 (500 °C)	74
TaN/ TBTDET- H RF plasma (13.56 MHz, 100 W) on SiO <sub>2</sub>	260	polycryst. TaN (111) dom.	C:15	400	0.08	71
MoN <sub>x</sub> / MoCl <sub>5</sub> -NH <sub>3</sub> on glass	500	polycryst. Mo <sub>2</sub> N (111) dom. MoN (200) dom.	not detected	260 (Mo <sub>2</sub> N) 250 (MoN)	0.02-0.03	9
NbN/ NbCl <sub>5</sub> -NH <sub>3</sub> on glass	500	polycryst. NbN (111) dom.	not detected	200-240	0.02-0.03	9
NbN/ NbCl <sub>5</sub> -NH <sub>3</sub> on glass	500	polycryst. Nb <sub>4</sub> N <sub>5</sub> , NbN or Nb <sub>4</sub> N <sub>3</sub>	Cl:<0.3	550	0.025	75, 10
NbN/ NbCl <sub>5</sub> -Zn- NH <sub>3</sub> on glass	500	polycryst. Nb <sub>4</sub> N <sub>5</sub> , NbN or Nb <sub>4</sub> N <sub>3</sub>	Cl, Zn:<0.3	200	0.018	75, 10
WN <sub>x</sub> / WF <sub>6</sub> -NH <sub>3</sub> on SiO <sub>2</sub>	327-527	polycryst. W <sub>2</sub> N (111) dom.	C:5 O:3.6	4500	0.25	76

Tantalum nitride films have been deposited by Ritala et al.<sup>74</sup> from  $\text{TaCl}_5$  and  $\text{NH}_3$  with (between 400-500 °C) and without (between 200-500 °C) Zn as an additional reducing agent. This approach is similar to the previously described TiN processes by the same group.<sup>7</sup> The use of Zn was crucial for achieving low resistivity TaN films whereas the films obtained without Zn were dielectric  $\text{Ta}_3\text{N}_5$ . Thus, the reducing power of  $\text{NH}_3$  seems to be too weak to reduce Ta(V) into Ta(III). The composition of  $\text{Ta}_3\text{N}_5$  films was strongly dependent on the deposition temperature and the purest films were obtained at 450 and 500 °C, the chlorine and hydrogen contents being below 0.1 at.%. The oxygen content, on the other hand, showed no temperature dependence and all the films deposited above 300 °C contained 3 - 5 at.% oxygen. Metallic TaN with a resistivity of 900 : S cm was deposited using an exposure sequence  $\text{TaCl}_5$  - Zn -  $\text{NH}_3$ . The resistivity and also the oxygen contents (3-4 at.%) exhibited no significant temperature dependence, but the chlorine, hydrogen and zinc contents were different in the films deposited at various temperatures. For example the chlorine content decreased from 4 to below 0.1 at.% in the films deposited at 400 and 500 °C, respectively.

A novel approach into the ALD of nitride films is plasma-enhanced atomic layer deposition (PEALD) which has been utilized in the deposition of TaN films at 260 °C from  $(\text{NEt}_2)_3\text{Ta}=\text{NBu}^t$  (*tert*-butylimidotris(diethylamido)tantalum, TBTDET) and hydrogen radicals (RF plasma 13.56 MHz, power 100 W).<sup>71</sup> As compared to the other ALD deposited TaN films, PEALD yielded superior TaN films with a resistivity of 400 : S cm. The growth rate with 3 s TBTDET and 10 s hydrogen plasma pulse times was 0.08 nm/cycle, but it decreased slightly down to 0.07 nm/cycle as the pulse time of hydrogen plasma increased to 30 s. However, the lowest resistivity was obtained using a long pulse time of 30 s for hydrogen plasma. The probable reason for this was attributed to the increased film density with the longer hydrogen plasma pulse times. According to AES analysis the films were slightly Ta rich and the carbon content in the films was about 15 at.%. As expected for ALD deposited films, the step coverage was excellent even on the holes having a slightly negative slope.

The ALD of  $\text{MoN}_x$  films has been only briefly reported.<sup>9</sup> Cubic ( $\beta$ - $\text{Mo}_2\text{N}$ ) and hexagonal ( $\alpha$ - $\text{MoN}$ ) have been deposited from  $\text{MoCl}_5$  and  $\text{NH}_3$  at 500 °C. According to RBS and XRF the films contained no impurities and although they had different stoichiometry, the resistivity was almost the same (260 and 250 : S cm for  $\text{Mo}_2\text{N}$  and  $\text{MoN}$  films, respectively).

Zinc has also been used in the deposition of NbN from  $\text{NbCl}_5$  and  $\text{NH}_3$ .<sup>10,75</sup> Its use was not as crucial as in the deposition of  $\text{TaN}_x$  films and good quality films could also be grown without zinc. NbN films were free of chlorine residues, but the growth rate was low, only 0.025 nm/cycle for  $\text{NbCl}_5$  -  $\text{NH}_3$  and 0.018 nm/cycle for  $\text{NbCl}_5$  - Zn -  $\text{NH}_3$  processes. According to XRD the films

were polycrystalline, but no unambiguous discrimination could be made with the different phases. By using zinc the resistivity could be decreased from 550 to 200 : S cm. Hiltunen et al.<sup>9</sup> studied also the superconducting properties of <sup>\*</sup>-NbN films and found that they became superconducting below 10 K.

Klaus et al.<sup>76</sup> have deposited tungsten nitride films from WF<sub>6</sub> and NH<sub>3</sub>. According to XRD the films were cubic W<sub>2</sub>N and the size of the crystallites estimated from the width of the most dominant peak (111) was only about 11 nm. The growth rate saturated to about 0.25 nm/cycle between temperatures 327 and 527 °C, which agrees well with the lattice constant derived from the (111) peak of W<sub>2</sub>N (0.24 nm). XPS analysis showed only low amounts of C, O and F impurities, where C and O were considered to result most likely from CO residues in the diffusion pumped deposition chamber. The resistivities obtained were 4500 : S cm.

### 3.4. Characterization of ALD Processes

Surface reactions may be characterized either by analyzing the surface or the gas phase, preferably both. This is not, however, easy and studies on characterizing the surface reactions occurring during the ALD growth, especially in the flow-type reactors, have been quite sparse. The commonly used flow-type reactors operate in a pressure range of 1 - 10 mbar, which rules out those frequently used surface analyzing techniques which require ultra high vacuum (UHV) conditions. One approach to overcome this problem is to carry out the reactions under conditions which allow their convenient examination, e.g. in UHV or in a chamber from which the substrates can be inertly transferred to UHV.<sup>77-80</sup> In addition, infrared spectroscopy, which is a commonly used method in studying surface species, is not suited for thin film studies on planar substrates because the surface area is too small to obtain adequate signal-to-noise ratio. Therefore the reactions have been carried out on high surface area substrates and the characterization has been performed afterwards with not only FTIR but also with NMR and elemental analysis.<sup>20,76-79,81-83</sup> However, these results do not necessarily describe the situation during the film deposition processes in the flow-type ALD reactors because of the difference in either the pressure or time scale. In order to better understand the reactions taking place during the ALD growth and thereby to improve the processes, it is important to be able to characterize the surface reactions also *in situ* under real conditions. A valuable tool for the *in situ* ALD studies is the quartz crystal microbalance (QCM), which gives real time results from the weight changes on the crystal surface and helps in interpretation of the growth mechanisms.<sup>84-89</sup> Also optical methods, like spectroscopic ellipsometry,<sup>20,76</sup> surface photo absorption (SPA)<sup>90</sup> and reflectance difference spectroscopy (RDS),<sup>91</sup> have been used to study ALD reactions *in situ*. However, supplementary methods are commonly needed for the optical methods in order to interpret the obtained data in chemical terms.

Mass spectrometry is a promising way to characterize the surface reactions by analyzing the gaseous reaction byproducts and has already been utilized in CVD studies.<sup>32,92,93</sup> However, the mass spectrometry studies on ALD processes in flow-type reactors require complicated differentially pumped sampling setups, which is most likely the reason for its limited utilization until now.<sup>11,12,89,94,95</sup>

## 4. EXPERIMENTAL

In this section the main features of the experimental techniques are described. More detailed information can be found from the corresponding papers and from the cited references.

### 4.1. Film Growth

The films were grown onto 5x5 cm<sup>2</sup> substrates using a commercial flow-type F-120 ALD reactor (ASM Microchemistry Ltd., Espoo, Finland)<sup>5</sup> operated under a pressure of 10 mbar. Nitrogen (purity 99.999% or higher) was used as a carrier and a purging gas. In most of the experiments the substrates were soda lime glass, but also Al<sub>2</sub>O<sub>3</sub>, Si, TiN and different metals were used.

The reactants were evaporated either from internal or external sources depending on the vapor pressure. The reactants whose vapor pressure at ambient temperature exceeds 10 mbar were evaporated outside the reactor. The reactant flow was controlled with the aid of solenoid and needle valves. The pulsing of the reactant vapors generated inside the reactor was accomplished by means of inert gas valving.

### 4.2. Film Characterization

Film thicknesses were determined at approximately 3 cm from the leading edge of the substrate with energy dispersive X-ray spectroscopy (EDX) using a Link ISIS EDX spectrometer installed to a Zeiss DSM 962 scanning electron microscope (SEM) [II-V] and with time-of-flight elastic recoil detection analysis (TOF-ERDA) [VI]. A GMR electron probe thin film microanalysis program was used to analyze the EDX results.<sup>96</sup> The thickness of copper films [I] was measured by a Sloan Dektak II profilometer.

EDX was used for the routine analysis of the film constituents, and TOF-ERDA<sup>97,98</sup> was used in order to obtain a more detailed information about the film composition, including depth profiles of the elements.

Surface morphology and cross sections were studied by SEM using Zeiss DSM 962 or JEOL JSM 840 scanning electron microscopes. Sheet resistance was measured by the standard four-point probe method.

Crystallinity of the films was analyzed by Philips MPD 1880 or by Bruker AXS D8 advance powder X-ray diffractometers (XRD) using Cu K<sup>α</sup> radiation. Both the grazing incidence method

with an incidence angle of  $1^\circ$  and the standard  $2 - 2\theta$  scan were used. The Bruker AXS D8 equipment was also used in X-ray reflectance (XRR) mode in order to determine the exact thickness of the Ti(Al)N films tested for barrier characteristics [V].

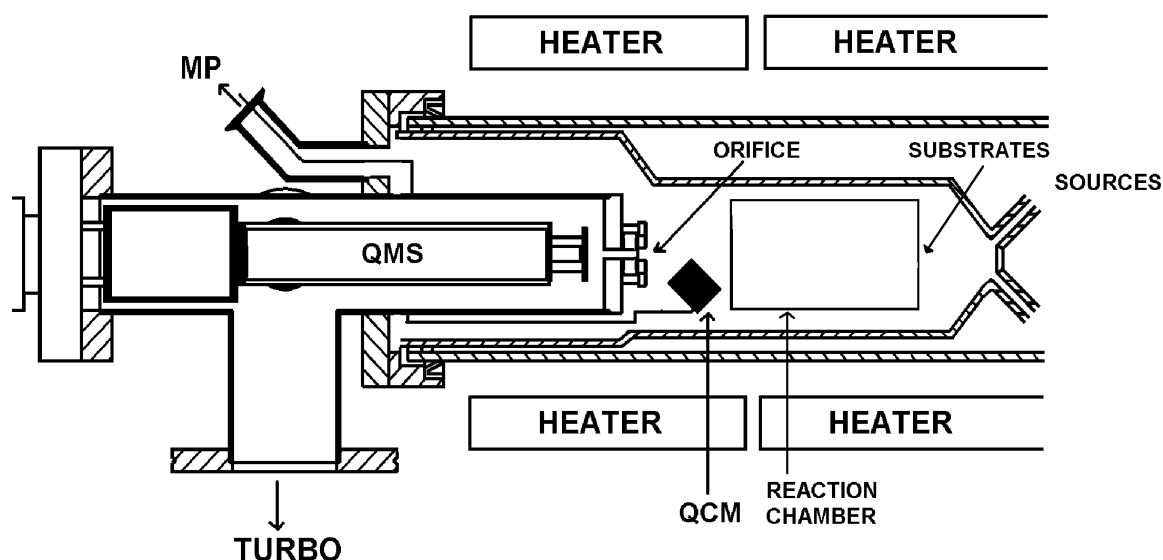
In order to study the diffusion barrier characteristics Cu/TiN/Si [III] and Cu/Ti(Al)N/Si [V] structures were prepared. A copper film was deposited by ALD on the TiN films and electron beam evaporated on the Ti(Al)N films. After annealing at different temperatures the samples were subsequently analyzed by the sheet resistance and XRD measurements, and also by the so called “Secco” etch method.<sup>99</sup> The “Secco” etch solution consists of 0.15 M  $K_2Cr_2O_7$  and HF in a 1:2 ratio. Before the “Secco” etch copper films were etched away by a dilute  $HNO_3/H_2O$  solution, and TiN and Ti(Al)N films by a mixture of  $NH_4OH$ ,  $H_2O_2$  and  $H_2O$  in a ratio of 1:2:6. In addition, the barrier capabilities of the TiN films were studied by XPS and SEM. An increase in the sheet resistance and an appearance of new peaks in the XRD pattern after annealing at different temperatures were the indications of a formation of copper silicides,  $Cu_xSi$ , and thereby of the barrier breakdown. Also the “Secco” etch test probes the formation of  $Cu_xSi$ , since the “Secco” etch solution dissolves  $Cu_xSi$  leaving inverted pyramidal shaped holes observable with a microscope.

#### 4.3. Design of the MS-ALD equipment

In order to carry out the *in situ* mass spectrometry studies, a flow-type ALD reactor F-120 was at first modified to meet the requirements of MS studies. The reactions between trimethylaluminium and water were studied with different sampling setups to find the most optimal conditions for the *in situ* studies. The integration of an ALD reactor and a mass spectrometer involves several critical issues<sup>95</sup> that have been solved as follows:

- The pressure in the main chamber of the ALD reactor is about 2 mbar and the operating pressure of QMS is below  $10^{-4}$  mbar. Therefore a pressure reduction is needed. This was realized by using either a short and small diameter glass capillary [VII] or orifice with a small diameter [VIII] (Fig. 2).
- When solid precursors with only modest vapor pressure are used as reactants in ALD, condensation into the capillary/orifice can be possible. In order to avoid this, the QMS sampling was performed at elevated temperatures close to the substrate temperature. To keep the detector and electronics close to room temperature, the QMS was inserted partly into the resistively heated ALD reactor tube in a region where a rather steep temperature gradient exists.

The amount of byproducts released in one cycle is typically in the order of  $10^{14}$  molecules per  $1 \text{ cm}^2$  surface. To ensure that detectable amounts of byproducts are formed, the reaction chamber was enlarged and loaded with the glass substrates so that the total surface area was about  $3500 \text{ cm}^2$ . In a normal F-120 reactor the surface area is only about  $50 \text{ cm}^2$ .<sup>5</sup>



*Figure 2.* Schematics of the sampling in the MS-ALD equipment used for studying the ALD of TiN and Ti(Al)N thin films. The reactants and carrier gas are coming from the right and are pumped by a mechanical pump (MP). A small part of the flow is pumped by a turbo pump through the orifice and analyzed by the QMS. The equipment used for studying the  $\text{Al}_2\text{O}_3$  film growth was quite similar, but instead of an orifice a capillary was used for sampling. QCM was not used in these studies.

The quadrupole mass spectrometer (QMS) used in studying the trimethylaluminium - water [VII] ALD process was a Leybold TSP 300 with a Faraday cup detector. In the study of the reactions in the ALD growth of TiN and Ti(Al)N films from titanium tetrachloride, trimethylaluminium and ammonia [VIII], the QMS used was a Hiden HAL/3F 501 RC with an electron multiplier detector. The sampling and pressure reduction needed for the measurements was accomplished through a  $200 : \text{m}$  diameter, 3 mm long capillary [VII] and  $50 : \text{m}$  orifice [VIII].



## 5. RESULTS OF THE DEPOSITED METALS

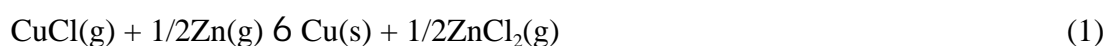
In this chapter the results of the copper and molybdenum films reported by the author are summarized. In addition to the published papers [I, II] some results of previously unpublished copper deposition studies are briefly reported.

### 5.1. Copper

#### 5.1.1. CuCl and Zn [I]

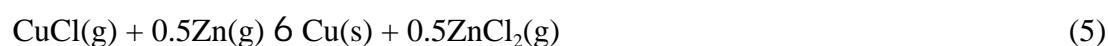
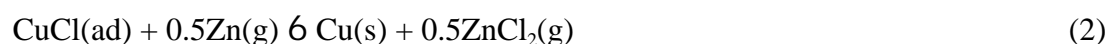
The deposition of copper films is mainly discussed on the basis of the paper [I], but also some results of the CuCl - Zn deposition studies previously reported by the author<sup>100</sup> have been added.

*Film growth.* The film growth from copper chloride and zinc is thermodynamically more favorable than from copper chloride and molecular hydrogen as calculated by HSC Chemistry for Windows program. Interestingly, ) G for reaction



is more negative at lower temperatures and therefore the growth of copper films should be thermodynamically more favorable at lower temperatures.<sup>101</sup> Accordingly, copper films could be deposited on glass substrates covered by thin Al<sub>2</sub>O<sub>3</sub> film using Zn, but no film growth could be observed when H<sub>2</sub> was used as a reducing agent. The deposition temperature range of the CuCl - Zn process was restricted to 440 - 500 °C, the lower limit being dictated by the evaporation temperature of Zn and the upper limit by the temperature sensitivity of the glass substrates and glass parts of the reactor. The pulse lengths of 0.5, 1.0, 1.5 and 2.0 s were used for both CuCl and Zn and the purge length after both reactant pulses was 0.5 s. The films were the most uniform when equal pulse lengths were used. The films deposited at 500 °C were continuous, but at lower temperatures the film grew only at the first half of the substrate. This is somewhat strange, because according to the thermodynamics the growth of Cu should be more favorable at lower temperatures. Therefore, only the films deposited at 500 °C with equal pulse lengths were analyzed. No saturation of the growth rate, characteristic for ALD, could be achieved. The film thickness depended strongly on the length of the CuCl pulse and the thickness profiles were very steep, the thickness of the films being higher at the leading edge of the substrate. In addition, even the growth rate of the thinnest films, i.e., those deposited with the shortest (0.5 s) CuCl pulse times, was already about 1 nm/cycle, which is about five times higher than the ideal layer-by-layer growth rate of (111) oriented copper.

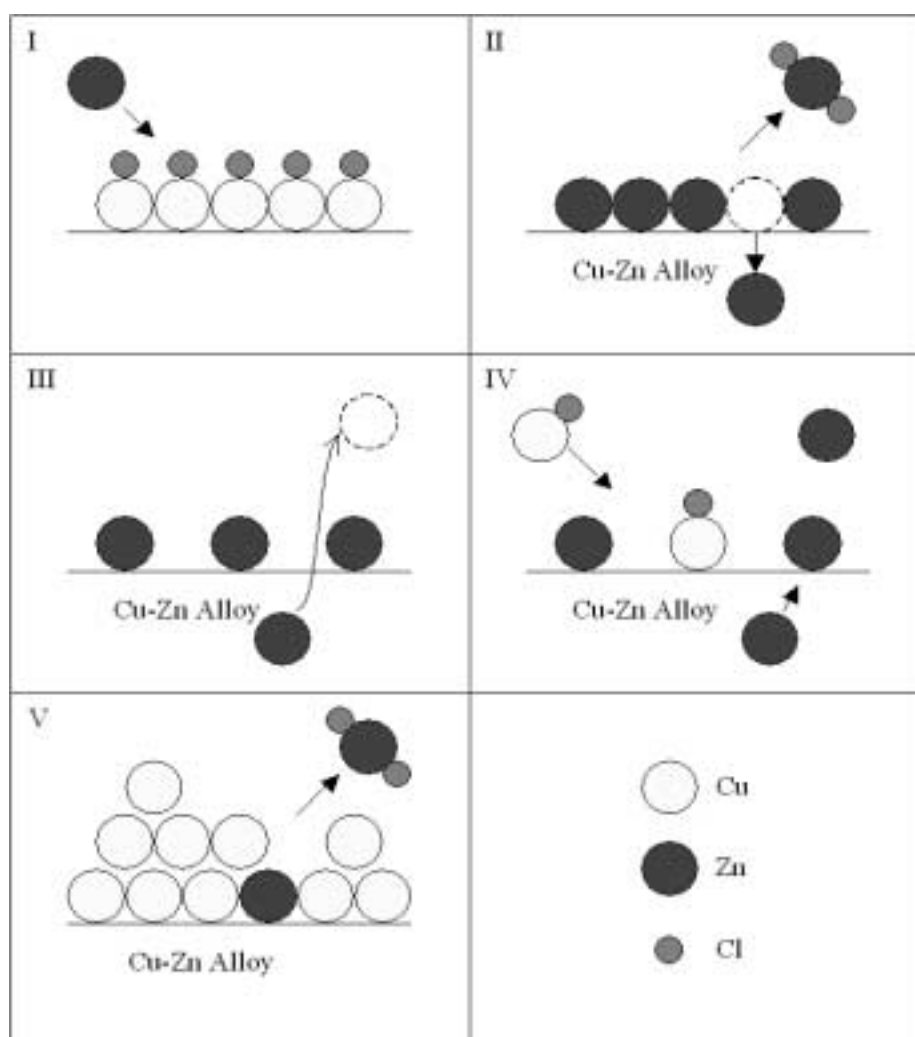
One major concern with the CuCl - Zn precursor combination was interpreted to be the solubility of zinc into copper, i.e., brass formation, which complicated the film growth. Since the growth rate of the films was higher than 1 ML per cycle and no self-limiting growth mechanism could be observed, it is obvious that zinc dissolved into copper. The schematics of the suspected film growth is presented in Fig. 3. First copper is formed as desired by the reductive exchange reaction (Eq. 2). But then the dissolution (Eq. 3) and a continuous outdiffusion (Eq. 4) of zinc begins to complicate the process and destroys the self-limiting growth mechanism leading to a CVD-type of growth (Eq. 5).



The dissolution and outdiffusion of zinc were later, however, noticed to have even more significant effect on the deposition of copper films. When the films were grown with 20 s purge lengths after the Zn pulse copper was grown only onto the leading edge of the substrate and nothing was deposited at the rest of the substrate. Most likely with the longer purge lengths all the dissolved zinc had been outdiffused and no CVD-type reactions leading to the deposition of copper took place. Therefore, the most dominant reactions leading to the deposition of copper from CuCl and Zn involved the outdiffusion of zinc and hence the deposition of copper behaved by no means like an ideal ALD process.

*Film properties.* The impurity contents of the films were not dependent on the pulse lengths used, but approximately equal amounts of impurities were detected by EDX in each film deposited at 500 °C. Although zinc dissolved into copper, the zinc contents in the final films were only around 3 at.%. No chlorine could be observed indicating an effective reduction of CuCl by Zn. The thinnest films consisted of separate Cu agglomerates with diameters of a few micrometers, and in between them there were some smaller agglomerates. With increasing film thicknesses the morphology changed and the agglomerates grew into contact with each other forming a network of agglomerates and eventually a dense and continuous film. The thickest films consisted of well developed grains with lateral diameters of 1 - 2 : m. The films exhibited poor adhesion on Al<sub>2</sub>O<sub>3</sub> as they did not pass the standard Scotch tape test. Some experiments were also carried out on aluminium foil, soda lime glass, and titanium and niobium nitride films, but only the adhesion on aluminium foil was good and the films passed the tape test. The deposited copper films were polycrystalline and oriented towards the (111) and (200) directions and no impurity phases were detected. The ratio of the (111) and (200) intensities was higher with thinner films, indicating that these films exhibited better

resistance to oxide and silicide formation and also to electromigration.<sup>24,102</sup> Resistivity could not be analyzed, because the Cu films consisted of large grains which stayed isolated so long that after the formation of a continuous film the sheet resistance was too low for a reliable measurement.



*Figure 3.* Schematics of the copper film growth from CuCl and Zn.

I) Zn is pulsed onto saturated CuCl surface.

II) Zn reacts first with the adsorbed CuCl resulting in formation of elemental copper and volatile  $\text{ZnCl}_2$ . The excess Zn dissolves into copper forming a Cu-Zn alloy.

III) After the termination of the Zn pulse, the Cu-Zn alloy tries to equilibrate itself with the gas phase resulting in an outdiffusion of Zn.

IV) The outdiffusion of Zn occurs continuously also during the subsequent CuCl pulse resulting in CVD-like reactions.

V) As a result the film grows fast and the self-limiting growth mechanism is destroyed.

### 5.1.2. Experiments With Different Copper Precursors and Reducing Agents

In addition to paper [I], numerous studies on different copper precursors and reducing agents have been carried out in order to deposit copper films. In this chapter a summary of these copper deposition studies is presented. The experimental data is listed in Table V with brief comments on the results obtained. The deposition of copper by ALD turned out to be especially difficult and in many cases either the film did not grow at all or the quality of the deposited film was poor. Therefore only the most interesting results are discussed in the following. The deposition studies were carried out with high number of deposition cycles, usually 3000. To examine if the precursors reacted preferably in the gas phase rather than on the surface, some experiments were also carried out by pulsing the precursors onto the substrates simultaneously. This kind of approach resembles CVD and was named as pulsed CVD. However, since the aim of this thesis was to study ALD, the pulsed CVD studies are just listed in Table V but not discussed any further.

Table V. Summary of the unpublished copper deposition studies carried out by the author.

Reducing agent / substrate	Deposition temperature (°C)	Comments
<b><i>Cu(hfac)<sub>2</sub>•H<sub>2</sub>O</i></b>		
Zn / Al <sub>2</sub> O <sub>3</sub>	250-400	- a brownish film, probably oxidized copper
H <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub> +H <sub>2</sub> O / Al <sub>2</sub> O <sub>3</sub> , TiN(O), Al	250-400	- no growth on Al <sub>2</sub> O <sub>3</sub> and TiN(O) - on Al, with H <sub>2</sub> +H <sub>2</sub> O, a brownish film at 325 °C
NH <sub>3</sub> / glass, Al <sub>2</sub> O <sub>3</sub>	250	- a discontinuous film
<b><i>CuCl</i></b>		
SnCl <sub>2</sub> / glass	400, 500	- no ALD growth - copper with pulsed CVD
SnI <sub>2</sub> / glass	500	- a greenish film at the leading edge of the substrate
NH <sub>3</sub> / glass, <i>in situ</i> TiN	400, 500	- a nonconductive thin copper film
hydroquinone, C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> / glass, Al <sub>2</sub> O <sub>3</sub> , TiN(O)	430-500	- a greenish discontinuous film
azo-t-butane, (CH <sub>3</sub> ) <sub>3</sub> CN=NC(CH <sub>3</sub> ) <sub>3</sub> / glass	450	- a black film at the leading edge of the substrate with pulsed CVD
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NBH <sub>3</sub> / glass, Al <sub>2</sub> O <sub>3</sub>	400	- a discontinuous copper film
N <sub>2</sub> H <sub>5</sub> OH / Al <sub>2</sub> O <sub>3</sub> , Pt, TiN(O)	500 and 480	- by ALD nonconductive Cu film with separate grains of diameter > 1 : m. - by pulsed CVD nonconductive Cu film with separate grains of diameter > 2 : m

DMHy / Al <sub>2</sub> O <sub>3</sub> , TiN(O)	400, 500	- at 500 °C continuous and conductive copper film, Cl: 0 at.% (EDX), growth rate: 0.07 nm/cycle, resistivity: about 25 : S cm. - at 400 °C copper film only on half of the substrate
<sup>t</sup> BuNH <sub>2</sub> / glass, TiN(O)	400, 500	- only a thin oxidized copper film
trimethylsilylasetylene C <sub>5</sub> H <sub>10</sub> Si / glass, TiN(O), Pt	400, 500	- on glass and TiN nonconductive copper with very poor adhesion - on Pt probably alloying of Cu and Pt
Cp <sub>2</sub> TiCl / glass, TiN(O)	400	- a continuous nonconductive copper film
CpTi(C <sub>7</sub> H <sub>7</sub> ) / glass, TiN(O), <i>in situ</i> TiN	400, 500	- at 400 °C continuous conductive copper, Cl:0.6 at.%, Ti:0.03 at.%, growth rate 0.2 nm/cycle - at 500 °C conductive film but worse than at 400 °C
TiCl <sub>3</sub> / glass, TiN(O)	500	- no growth
allylNH <sub>2</sub> / glass, TiN(O)	400	- conductive copper, Cl:0.5, growth rate 0.04 nm/cycle
TMA / glass, TiN(O)	400	- by ALD a very thin copper film - by pulsed CVD a conductive copper film
<b><i>CuI</i></b>		
SnI <sub>2</sub> / glass	400	- no growth
Zn / glass	500	- some copper at the leading edge of the substrate
<b><i>Cu(thd)<sub>2</sub></i></b>		
NH <sub>3</sub> / glass, Al <sub>2</sub> O <sub>3</sub>	280 and 350	- at 280 °C Cu <sub>3</sub> N or Cu. Cu <sub>3</sub> N turned to copper when annealed at 475 °C - at 350 °C a greenish film
hydroquinone, C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> / glass, Al <sub>2</sub> O <sub>3</sub> , TiN(O), Pt	250-400	- by ALD only a discontinuous greenish film - by pulsed CVD continuous conducting films at 350 - 400 °C - an extra hydroquinone pulse after pulsed CVD growth was noticed to enhance the growth
azo-t-butane, (CH <sub>3</sub> ) <sub>3</sub> CN=NC(CH <sub>3</sub> ) <sub>3</sub> / glass	280	- no growth
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> NBH <sub>3</sub> / glass, Al <sub>2</sub> O <sub>3</sub> , TiN(O)	250-300	- a greenish or brownish film
N <sub>2</sub> H <sub>5</sub> OH / Al <sub>2</sub> O <sub>3</sub> , Pt	250	- by ALD a greenish film - by pulsed CVD a conductive Cu film consisting of continuous network of micron size grains

DMHy / glass	250, 300	- a discontinuous yellow film at 300 °C
trimethylsilylasetylene C <sub>5</sub> H <sub>10</sub> Si / glass, TiN(O)	250, 300	- no growth
Sr(C <sub>5</sub> <sup>i</sup> Pr <sub>3</sub> H <sub>2</sub> ) / glass, Al <sub>2</sub> O <sub>3</sub> , TiN(O)	200-300	- best film deposited at 250 °C on TiN(O), Sr: 0 at.%, growth rate at on 0.01 nm/cycle (EDX), resistivity about 44 : S cm
Cp <sub>2</sub> TiCl / glass, TiN(O)	250	- no growth
CpTi(C <sub>7</sub> H <sub>7</sub> )/ glass, TiN(O)	250	- no growth
TMA / glass, TiN(O)	250, 300	- a very thin copper film
DEAH / glass, Al <sub>2</sub> O <sub>3</sub>	250, 300	- a faint copper film at 250 °C
<b>(Et<sub>3</sub>P)CuCp</b>		
DMHy / glass	150	- no growth
methyl acrylate, C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> / glass, Pt	120-150	- a copper film on Pt resulting from decomposition of (Et <sub>3</sub> P)CuCp on Pt surface
TMA / glass, TiN(O)	150	- a faint copper film

Copper(II)1,1,1,5,5,5-hexafluoro-2,4-heptanedionato, Cu(hfac)<sub>2</sub>, is one of the most studied copper precursors in CVD of copper films and most often H<sub>2</sub> with or without H<sub>2</sub>O has been used as a reducing agent.<sup>26</sup> However, the ALD from these reagents did not produce any film on oxide surfaces. Some copper could be deposited on aluminium foil at 325 °C, but the film was very thin and brownish. Although not analyzed, it is likely that the film contained quite a large amount of carbon resulting from the decomposition of Cu(hfac)<sub>2</sub>.

Two different hydrazine derivatives; hydrazine hydrate (N<sub>2</sub>H<sub>5</sub>OH) and dimethylhydrazine ((CH<sub>3</sub>)<sub>2</sub>NNH<sub>2</sub>, DMHy) were used as reducing agents for CuCl and Cu(thd)<sub>2</sub>, and some studies were also carried out with (Et<sub>3</sub>P)CuCp. Hydrazine derivatives were able to reduce CuCl, although only nonconductive Cu films were deposited when N<sub>2</sub>H<sub>5</sub>OH was used as a reducing agent. According to SEM, these films consisted of separate grains more than 1 : m in diameter which explains the nonconductivity. On the other hand, conducting and continuous films could be grown at 500 °C when DMHy was used as a reducing agent. According to TOF-ERDA analysis the film was quite pure and below 1 at.% of carbon, chlorine and hydrogen impurities were incorporated into the film. However, the film was difficult to analyze because of the rough surface, and therefore it is possible that the amount of impurities was actually higher. A resistivity of about 25 : S cm was measured for a Cu film deposited on Al<sub>2</sub>O<sub>3</sub>. However, for some reason, the Cu film could be deposited only

on half of the substrate at 400 °C. Hydrazine derivatives were not able to reduce the other tested copper precursors.

The reducing ability of two amines, namely *tert*-butylamine ( $((\text{CH}_3)_3\text{CNH}_2, \text{}^t\text{BuNH}_2)$ ) and allylamine ( $(\text{CH}_2=\text{CHCH}_2\text{NH}_2, \text{allylNH}_2)$ ) were also studied with CuCl. With  $\text{}^t\text{BuNH}_2$  no copper film could be deposited. By contrast, with allyl $\text{NH}_2$  a conductive, continuous and almost chlorine free (0.5 at.% according to EDX analysis) copper film was deposited with a growth rate of 0.04 nm/cycle already at 400 °C. According to SEM analysis the film consisted of continuous network of grains about 1 : m in lateral diameter. The adhesion was poor since the film did not pass the standard Scotch tape adhesion test.

Titanium cyclopentadienyls,  $\text{Cp}_2\text{Ti(III)Cl}$  and  $\text{CpTi(II)(C}_7\text{H}_7)$ , were supposed to reduce CuCl by reacting with adsorbed chlorine species and forming higher oxidation state gaseous titanium compounds. By using  $\text{Cp}_2\text{TiCl}$  only nonconductive copper films could be deposited at 400 °C, but  $\text{CpTi(C}_7\text{H}_7)$  proved to be a more effective reducing agent. With  $\text{CpTi(C}_7\text{H}_7)$  a conductive and quite pure (Cl:0.6 at.%, Ti:0.03 at.% as analyzed by EDX) copper film was deposited at 400 °C. Also this film consisted of a continuous network of grains about 1 : m in lateral diameter (Fig. 4) and did not pass the standard Scotch tape adhesion test.

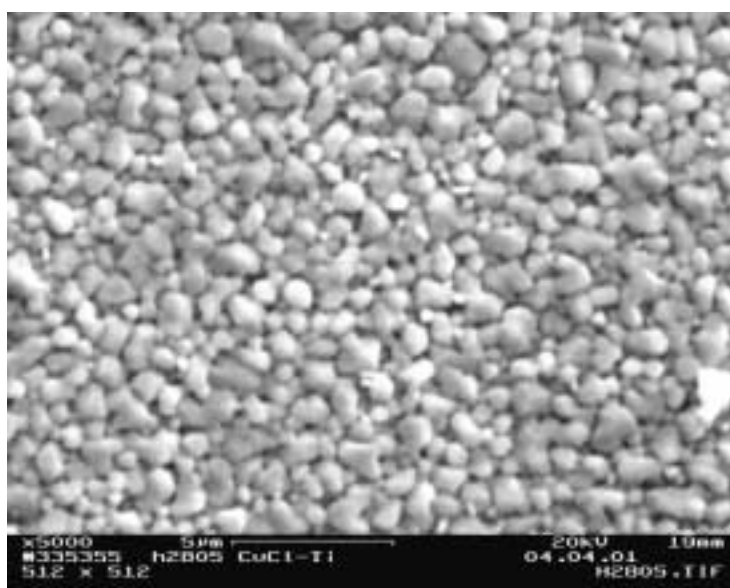


Figure 4. SEM image of a copper film about 600 nm in thickness deposited from CuCl and  $\text{CpTi(II)(C}_7\text{H}_7)$ .

Cyclopentadienyl compounds are known to dissociate at low temperatures and this property was exploited in the deposition of copper films from  $\text{Cu}(\text{thd})_2$  and  $\text{Sr}(\text{C}_5^i\text{Pr}_3\text{H}_2)_2$ .  $\text{Sr}(\text{C}_5^i\text{Pr}_3\text{H}_2)_2$  was hoped to react with  $\text{Cu}(\text{thd})_2$  by ligand exchange reaction forming volatile  $\text{Sr}(\text{thd})_2$  and copper cyclopentadienyl which would subsequently dissociate and produce a copper film. The deposition of copper from these reagents was studied within a temperature range of 200 - 300 °C, and the best film was obtained at 250 °C on TiN(O). The resistivity of this film (about 30 nm in thickness) was about 44 : S cm and no strontium could be detected by EDX.

The reducing capability of  $\text{NH}_3$  was studied with  $\text{CuCl}$  and  $\text{Cu}(\text{thd})_2$ . Pinkas et al.<sup>103</sup> discussed the mechanistic role of  $\text{NH}_3$  in CVD of copper from  $\text{Cu}(\text{hfac})_2$ . According to them,  $\text{NH}_3$  works similarly to  $\text{H}_2\text{O}$ , transferring a proton to the hfac ligand, although the acidity of protons in  $\text{NH}_3$  is much lower than in  $\text{H}_2\text{O}$ . In their experiments a mixture of metallic copper and  $\text{Cu}_3\text{N}$  film was deposited at 450 °C. In our experiments only a very thin and nonconductive Cu film could be deposited from  $\text{CuCl}$  at 400 and 500 °C, and either  $\text{Cu}_3\text{N}$  or Cu films were obtained from  $\text{Cu}(\text{thd})_2$  at 280 °C. Deposition of  $\text{Cu}_3\text{N}$  films by reactive sputtering in nitrogen plasma has been reported by Maya et al.<sup>104,105</sup> who also noted that the pyrolysis of  $\text{Cu}_3\text{N}$  under dynamic vacuum releases nitrogen and forms a Cu film. This kind of an approach was also studied for the ALD deposited  $\text{Cu}_3\text{N}$  film. The temperature in the reactor was increased to 475 °C after the deposition, and a thin copper film with holes was produced.

## 5.2. Molybdenum

### 5.2.1. $\text{MoCl}_5$ and Zn (II)

*Film growth.* Similarly to the Cu - Zn process, the reduction of  $\text{MoCl}_5$  by Zn is thermodynamically more favorable process than reduction by  $\text{H}_2$ .<sup>101</sup> Molybdenum films were deposited between 400 and 500 °C on glass substrates covered by a thin  $\text{Al}_2\text{O}_3$  film or on bare soda lime glass. The evaporation temperature of Zn was reduced to 390 °C as compared to 435 °C used in the CuCl - Zn process to widen the deposition temperature range. Because significant outdiffusion of Zn was noticed to occur during the deposition of copper films from CuCl and Zn, the length of purge pulse after Zn was varied between 0.5 and 3.0 s in order to find out what kind of an effect it has on the growth rate and the Zn content. The best growth temperature was concluded to be 420 °C since the growth rate was then the highest and the amount of Zn residues did not decrease remarkably at higher temperatures. The chlorine content did not correlate with the deposition temperature and in the films deposited between 400 and 480 °C it varied rather randomly between 0.7 and 2 at.% as analyzed by EDX. In the film deposited at 500 °C the chlorine content was exceptionally high (about 5 at.%). As suspected, the purge length after Zn had an effect on both the zinc residue content



and the growth rate. In the films deposited at 420 °C the zinc content was about 2 at.% with 0.5 - 1.5 s purge lengths, but with longer purge lengths only about 0.5 at.% of Zn could be detected. At the same time the growth rate decreased from 0.08 to 0.04 nm/cycle. The film thickness exhibited quite well the linear increase as a function of deposition cycles when short purge lengths after Zn were used. Deviations from the linearity appeared with longer purge lengths and the films grown with 3000 cycles were even thicker than the films grown with a higher number of cycles.

It seems that there exists a direct relationship between the growth rate and zinc content, and it is possible that some of the zinc dissolved into the molybdenum film, and during purging out-diffused from there. The film growth from MoCl<sub>5</sub> and Zn is suspected to occur analogously to that in the deposition of copper from CuCl and Zn. In addition to dissolution and outdiffusion of zinc leading to CVD-like deposition and therefore lost of self-limiting growth mechanism, this process is further complicated by the etching of Mo by MoCl<sub>5</sub> (Eq. 6).



If outdiffusion of Zn is still occurring during the MoCl<sub>5</sub> pulse (short purging after the Zn pulse) Zn most likely reacts with MoCl<sub>5</sub> forming Mo and gaseous ZnCl<sub>2</sub> (CVD-like growth) and the growth rate of the film is high. On the other hand, if most of the dissolved Zn is already outdiffused before the MoCl<sub>5</sub> pulse (long purging after Zn pulse), the etching reaction may start to dominate and this in turn decreases the growth rate. The etching and CVD kind of growth had also an effect on the thickness profiles of the molybdenum films. The films deposited with longer purging (1.5-3.0 s) were thinner on the leading edge of the substrate than on the latter half, and this kind of a profile originates most likely from the etching. On the other hand, with short purging (0.5-1.0 s) the film on the first half of the substrate was thicker than that on the latter, and this can be attributed to the CVD kind of growth. The low growth rate at higher temperatures (>420 °C) was caused by the etching of Mo by MoCl<sub>5</sub> in addition to the outdiffusion of Zn which both become more remarkable at higher temperatures. Altogether the deposition of Mo from MoCl<sub>5</sub> and Zn involves many complicating reactions and one has to compromise between high growth rates and low zinc contents.

*Film properties.* As already noted, the amount of Zn residues was dependent on the purge length after the Zn pulse. On the other hand, the oxygen content seemed to depend on the zinc content. The films deposited at 420 °C with short (0.5 s) purging and therefore high Zn contents contained quite a lot of oxygen (about 30 at.%) in their outermost halves. By contrast, the amount of oxygen in the film grown with 3.0 s purging (low Zn contents) was very low. It was concluded that the oxygen incorporation took place after the film growth when the film was exposed to air since the inner

halves of the films were almost oxygen free. The morphology of the molybdenum films was very different from the rough copper films and according to SEM the film was built up of densely packed grains and had mainly a smooth surface. The XRD analysis showed that the films were polycrystalline molybdenum and the most dominant reflection was (110). The resistivity, as expected, was dependent on the Zn contents. The lowest resistivity of about  $15 \text{ } \Omega \text{ cm}$  was achieved when the Zn contents were below 1 at.%. This is somewhat higher than that of bulk Mo ( $5.7 \text{ } \Omega \text{ cm}$ ) but on the other hand lower than those achieved by CVD from  $\text{MoCl}_5$ <sup>106</sup> or  $\text{MoF}_6$ <sup>107</sup> and  $\text{H}_2$  without post-annealing. According to the Scotch tape test the adhesion was very good onto both  $\text{Al}_2\text{O}_3$  and soda lime glass substrates.

## 6. RESULTS OF THE DEPOSITED TRANSITION METAL NITRIDES

In this chapter the results reported by the author of the ALD deposited titanium, tantalum, molybdenum and niobium nitride films are summarized. The main focus is on the deposition of TiN films and the deposition of the other transition metal nitrides is briefly reported only in chapter 6.1. More comprehensive description of the results with figures can be found from the corresponding papers [IV - VI]

### 6.1. 1,1-Dimethylhydrazine as a Nitrogen Source [IV]

Traditionally ammonia has been used as a nitrogen source in the ALD of nitride films. However, since a transition metal is most often at a higher oxidation state in a transition metal precursor than in the desired nitride material, the reduction properties of the nitrogen source are important. Ammonia is not a very effective reducing agent and in order to avoid using the undesired zinc as an additional reducing agent, alternative approaches have been sought. One possibility is to use a more reactive nitrogen source like hydrazine ( $\text{N}_2\text{H}_4$ ) or its more safe derivatives, instead of  $\text{NH}_3$ . Hydrazine and its derivatives have lower dissociation energies than  $\text{NH}_3$  ( $E_{\text{D}}(\text{H}_2\text{N}-\text{H}) = 449$  kJ/mol),<sup>70</sup> which makes them attractive nitrogen sources. The dissociation energies of N-N bond in hydrazine and hydrazinelike compounds are quite similar to each other;  $E_{\text{D}}(\text{H}_2\text{N}-\text{NH}_2) = 275$  kJ/mol,  $E_{\text{D}}((\text{CH}_3)(\text{H})\text{N}-\text{NH}_2) = 268$  kJ/mol,  $E_{\text{D}}((\text{CH}_3)_2\text{N}-\text{NH}_2) = 247$  kJ/mol and  $E_{\text{D}}((\text{C}_6\text{H}_5)\text{NH}-\text{NH}_2) = 219$  kJ/mol.<sup>108</sup> They have successfully been used in CVD<sup>48,109-112</sup> and also in ALD<sup>113</sup> of nitride films. In this thesis the use of unsymmetrical dimethylhydrazine,  $(\text{CH}_3)_2\text{NNH}_2$  (DMHy), in the ALD of TiN,  $\text{TaN}_x$ , NbN and  $\text{MoN}_x$  thin films is reported. The main aim of these studies was to find out if DMHy would work as a better nitrogen source than  $\text{NH}_3$ . In order to compare the effectivity of DMHy and  $\text{NH}_3$  some NbN and  $\text{MoN}_x$  films were also deposited with  $\text{NH}_3$ , since these have previously been studied only briefly.<sup>9,10,75</sup>

*Film growth.* The transition metal nitride films were deposited from the corresponding chlorides ( $\text{TiCl}_4$ ,  $\text{TaCl}_5$ ,  $\text{NbCl}_5$  and  $\text{MoCl}_5$ ) and DMHy at different temperatures, TiN between 200 and 500 °C,  $\text{TaN}_x$  between 300 and 400 °C, and both NbN and  $\text{MoN}_x$  only at 400 °C. The growth rate of the TiN films increased as a function of temperature between 200 and 450 °C (from about 0.01 to 0.03 nm/cycle), but at 500 °C was only about 0.02 nm/cycle. Except at 200 °C, these growth rates are higher than achieved even with the  $\text{TiCl}_4$  - Zn -  $\text{NH}_3$  process at 500 °C.<sup>7,10</sup> The growth rates of  $\text{TaN}_x$  (0.013 - 0.031 nm/cycle), NbN (0.023 nm/cycle) and  $\text{MoN}_x$  (0.057 nm/cycle) films deposited with DMHy are mainly comparable to those deposited with  $\text{NH}_3$ .<sup>9,10,74,75,IV</sup>

*Film properties.* As in the growth of nitride films in general, the chlorine content of the deposited TiN films decreased as a function of the deposition temperature. According to the EDX analysis the amount of chlorine decreased from 23 at.% at 200 °C to about 2 at.% at and above 400 °C. Also the resistivity decreased with increasing temperature until at 350 °C where it was the lowest, about 500 : S cm. For comparison, at 400 °C, the chlorine content of the films deposited with the TiCl<sub>4</sub> - Zn - NH<sub>3</sub> process was higher (6 at.%) than in the films deposited with DMHy, but on the other hand the resistivity was lower (200 : S cm).<sup>7,10</sup> The TOF-ERDA analysis showed that the film deposited at 400 °C with DMHy contained 13 at.% carbon and 14 at.% oxygen uniformly distributed through the whole film, which most likely was the reason for the higher resistivity of these films. The reason for the high carbon contents was attributed to the decomposition of DMHy and the oxygen incorporation was thought to take place after the film was exposed to air. Although not analyzed, the carbon was suspected to be present as a carbide rather than CH<sub>x</sub> species since the hydrogen content was only 2 at.% in the films deposited at 300 and 400 °C. Since carbides<sup>114</sup> and carbonitrides<sup>115,116</sup> are also considered as possible diffusion barrier materials, the high carbon content is not necessarily a major problem. The oxygen content, on the other hand, has been high also in the TiN films deposited by ALD from TiCl<sub>4</sub> and NH<sub>3</sub>,<sup>7,8</sup> and in general the TiN films have been found to oxidize rather easily.<sup>117-121</sup> According to XRD the films were weakly crystalline and only one reflection corresponding to (200) of cubic TiN was detected. This differs from the other halide based ALD TiN processes which resulted in the films with strong reflections (Table III). Since amorphous films are considered to function better as diffusion barriers, DMHy seems to be a more potential nitrogen source than NH<sub>3</sub>.

The MoN<sub>x</sub> films deposited with DMHy exhibited better characteristics than the films deposited with NH<sub>3</sub> even when Zn was used as an additional reducing agent. The resistivity of the MoN<sub>x</sub> film deposited with DMHy at 400 °C was only about 900 : S cm, which was four times less than that achieved with Zn and NH<sub>3</sub> at the same temperature. According to TOF-ERDA analysis the MoN<sub>x</sub> films deposited with DMHy contained quite much carbon (10 at.%), but the amounts of other impurities were quite low (O: 2 at.%, H: 2 at.%, and Cl: 3 at.%). Peaks obtained from the XRD analysis were weak, slightly shifted and broad, but were assigned to the cubic Mo<sub>2</sub>N. However, TOF-ERDA analysis showed that the Mo:N ratio was close to 1:1. It is possible that the extra nitrogen was present in the Mo<sub>2</sub>N matrix or the matrix was amorphous MoN with nanocrystallites of Mo<sub>2</sub>N. In addition, it must be noted that the differences in the reference d values of Mo<sub>2</sub>N and MoN are only minor and therefore these two phases are difficult to distinguish.

The TaN<sub>x</sub> and NbN films deposited with DMHy were not as good as the corresponding TiN and MoN<sub>x</sub> films. In the case of TaN<sub>x</sub>, DMHy did not bring any improvement to the conductivity and partly transparent Ta<sub>3</sub>N<sub>5</sub> films were obtained. The chlorine content of TaN<sub>x</sub> films, as determined

by EDX, decreased with increasing temperature from 14 to below 0.5 at.%. So, according to these results DMHy is not efficient enough for reducing tantalum from the oxidation state +V to +III, and use of an extra reducing agent like zinc<sup>74</sup> is necessary in order to obtain conducting TaN. On the other hand, the resistivity of the NbN films deposited with DMHy at 400 °C was considerably lower (about 2900 : S cm) than that obtained with NH<sub>3</sub> (>10000 : S cm) at the same temperature. DMHy was also a more effective chlorine removing agent as the films deposited at 400 °C with DMHy and NH<sub>3</sub> contained 5 and 15 at.% of chlorine, respectively. According to XRD, the film was either tetragonal Nb<sub>4</sub>N<sub>3</sub> or cubic \*-NbN.

In conclusion, the films deposited with DMHy exhibited better characteristics than the films deposited with NH<sub>3</sub> at low temperatures although the resistivities and impurity contents were still quite high. The impurity contents and resistivities could probably be reduced by using other hydrazine derivatives.

## 6.2. *Tert*-Butylamine and Allylamine as Nitrogen Sources [VI]

In addition to hydrazine derivatives, various amines are considered more effective nitrogen sources than ammonia in the deposition of transition metal nitrides. Similarly to hydrazines, the effectiveness of amines as compared to NH<sub>3</sub> is based on lower dissociation energy. In this thesis the use of *tert*-butylamine ((CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>, <sup>t</sup>BuNH<sub>2</sub>) and allylamine (CH<sub>2</sub>=CHCH<sub>2</sub>NH<sub>2</sub>, allylNH<sub>2</sub>) in the ALD of TiN films at 400 °C was examined. The dissociation energies of <sup>t</sup>BuNH<sub>2</sub> and allylNH<sub>2</sub> are 346 and 290 kJ/mol,<sup>122</sup> respectively, which are both well below the dissociation energy of NH<sub>3</sub> (449 kJ/mol).<sup>70</sup> <sup>t</sup>BuNH<sub>2</sub> and allylNH<sub>2</sub> have also been studied in the ALD of TaN films.<sup>123</sup> As compared to the Ta<sub>3</sub>N<sub>5</sub> films deposited with DMHy,<sup>IV</sup> the amines proved to be more effective nitrogen sources and conductive TaN films could be deposited with both studied amines. <sup>t</sup>BuNH<sub>2</sub> has successfully been used also in CVD of TiN films from TiCl<sub>4</sub>. For example, Price et al.<sup>124</sup> deposited TiN films with a resistivity of about 300 : S cm at 400 °C and the films deposited by Williams et al.<sup>125</sup> at 630 °C exhibited a resistivity of 287 : S cm.

In this work films were deposited with different pulsing schemes where the pulsing order of the reactants was varied. TiCl<sub>4</sub> and TiI<sub>4</sub> were used as titanium sources. Since the films deposited from TiI<sub>4</sub> and allylNH<sub>2</sub> with and without NH<sub>3</sub> were of variable quality and worse than the films deposited from TiCl<sub>4</sub>, the results are not reported here. The flow rate used for <sup>t</sup>BuNH<sub>2</sub> was 16 sccm and for allylNH<sub>2</sub> two different, 7 and 16 sccm, flow rates were used.

*Film growth.* The addition of NH<sub>3</sub> was necessary when <sup>t</sup>BuNH<sub>2</sub> was used as a nitrogen source at low temperatures. Best results were obtained when NH<sub>3</sub> was pulsed simultaneously with <sup>t</sup>BuNH<sub>2</sub>.

The deposition rate of the films grown at 400 °C from  $t\text{BuNH}_2$  without  $\text{NH}_3$  was only 0.003 nm/cycle whereas by adding  $\text{NH}_3$  simultaneously with  $t\text{BuNH}_2$  the rate increased to 0.015 and 0.011 nm/cycle with  $\text{TiCl}_4$  and  $\text{TiI}_4$ , respectively.

The addition of  $\text{NH}_3$  was not as crucial with allyl $\text{NH}_2$  and already at 400 °C the growth rate of 0.015 nm/cycle could be achieved without  $\text{NH}_3$  with both flow rates of allyl $\text{NH}_2$ . The addition of  $\text{NH}_3$  increased the growth rate to 0.02 nm/cycle.

*Film properties.* Only about 1 at.% of chlorine and 0.5 at.% of iodine was detected in the films deposited at 400 °C when  $\text{NH}_3$  was pulsed simultaneously with  $t\text{BuNH}_2$ . The amount of halide impurities decreased as a function of deposition temperature. Similar behavior as a function of temperature was also found when the films were grown from allyl $\text{NH}_2$  though the amounts detected were higher. For example, the amount of chlorine in the films deposited at 400 °C was about 7 and 4 at.% without and with  $\text{NH}_3$ , respectively. The films deposited with  $t\text{BuNH}_2$  contained only minor amounts of carbon and hydrogen impurities (below 1 at.%) whereas in the films deposited with allyl $\text{NH}_2$  the amounts were higher. In the films deposited at 400 °C with only allyl $\text{NH}_2$  (flow rate 7 sccm) the amounts of carbon and hydrogen were about 9 and 5 at.%, respectively. By adding  $\text{NH}_3$  these could be decreased to about 6 at.% and 3 at.%. Each film contained lots of oxygen (over 10 at.%) which has been found typical for titanium nitride films in general as discussed with DMHy.

The resistivity of the film deposited from  $\text{TiCl}_4$ ,  $t\text{BuNH}_2$  and  $\text{NH}_3$  at 400 °C was about 310 : S cm and decreased to about 170 : S cm at 450 °C, whereas the lowest resistivity with allyl $\text{NH}_2$  was about 330 : S cm. According to XRD analysis the films were only weakly crystalline. A film of about 60 nm in thickness deposited from  $\text{TiCl}_4$ ,  $t\text{BuNH}_2$  and  $\text{NH}_3$  at 400 °C seemed nearly amorphous, since only a very weak XRD peak was detected with the standard 2 - 2 $\theta$  scan using 10 s time/step. The addition of  $\text{NH}_3$  and also the flow rate of allyl $\text{NH}_2$  seemed to have some kind of an effect on the crystallinity of the TiN films deposited from  $\text{TiCl}_4$  and allyl $\text{NH}_2$ . The films deposited with the higher flow rate of allyl $\text{NH}_2$  and/or with  $\text{NH}_3$  were more strongly oriented. It seemed that if a reflection appeared, it was (200) similarly to the TiN films deposited with DMHy.

For barrier applications it seems very promising that the TiN films deposited by using  $t\text{BuNH}_2$  and allyl $\text{NH}_2$  were only very weakly crystalline and the films deposited at temperatures desired in IC fabrication exhibited rather low resistivities. In the future it would be interesting to study also the barrier capabilities of these films.

### 6.3. Trimethylaluminium as a Reducing Agent [V]

An alternative to using a more effective nitrogen source than ammonia in the deposition of nitride films is to use an extra reducing agent in addition to ammonia. In fact, metal chloride - zinc - ammonia processes exhibit this kind of an approach.<sup>7,10,74,75</sup> However, since the use of zinc in electronic applications is undesirable, some aluminium alkyls and hydrides, namely trimethylaluminium (TMA), di-isobutyl aluminium hydride (DIBAH) and diethylaluminium hydride (DEAH) have been studied in this thesis. TMA proved to be an effective reducing agent and the properties of TiN, TaN<sub>x</sub>, MoN<sub>x</sub> and NbN films could be enhanced as compared to the films deposited with only NH<sub>3</sub> at 400 °C. The effectiveness of TMA as a reducing agent was based on the relatively low dissociation energy of the Al-CH<sub>3</sub> bond (approximately 280 kJ/mol)<sup>126</sup> as compared to the strong Al-Cl (420.7 kJ/mol)<sup>127</sup> and C-Cl (327.2 kJ/mol) bonds.<sup>127</sup> Therefore, TMA was supposed to extract chlorine from the adsorbed titanium species forming aluminium and methyl chlorides and reducing titanium. The surface reactions taking place in the ALD of Ti(Al)N films were studied in more detail in paper [VIII] by means of mass spectrometry. Though the Al-H bond was suspected to provide atomic hydrogen and thereby to exhibit even better reducing properties than TMA, the films deposited with DIBAH and DEAH were not as good as those deposited with TMA. DIBAH and DEAH were noticed to decompose at low temperatures (~200-300 °C) forming metallic aluminium already in the precursor tube. Therefore lower deposition temperatures than with TMA (decomposes above 300 °C) had to be used with DIBAH and DEAH, but unfortunately at these temperatures the reactivity of NH<sub>3</sub> is quite low. The effectiveness of TMA has been studied in more detail in the ALD of titanium<sup>V</sup> and tantalum nitride films.<sup>128</sup> Here only the studies on the Ti(Al)N films deposited using TMA as an additional reducing agent [V] are summarized.

*Film growth.* Four different deposition schemes where the pulsing order or the pulse time of the reactants was varied were used to study the Ti(Al)N deposition from TiCl<sub>4</sub>, TMA and NH<sub>3</sub> within a temperature range of 250 - 400 °C. The growth rate was found to be strongly dependent on both the deposition temperature and the deposition sequence in question. With all the schemes the growth rate increased rather linearly as a function of temperature. The highest growth rates (about 0.09 nm/cycle) were obtained when NH<sub>3</sub> was pulsed two times during one deposition cycle, i.e., after both TiCl<sub>4</sub> and TMA pulses. The growth rate of the films deposited with the deposition scheme TiCl<sub>4</sub> - TMA - NH<sub>3</sub> at 400 °C varied between about 0.045 and 0.06 nm/cycle depending on the length of the NH<sub>3</sub> pulse (0.5 or 1.0 s). Almost without exception the growth rates of the Ti(Al)N films were at each deposition temperature higher than those achieved with the previous ALD deposited TiN films.<sup>7,8,10</sup> However, the growth rates are still lower than the ideal growth rate of the (111) oriented TiN films (0.245 nm/cycle). As the growth rate increased as a function of the deposition temperature no so called "ALD-window" was found. This kind of behavior has

previously been observed with the ALD of AlN films from TMA and NH<sub>3</sub> and was then attributed to the thermal decomposition of TMA.<sup>129</sup>

*Film properties.* The amount of chlorine impurities decreased with increasing temperature being about 20 at. % in the Ti(Al)N films deposited at 250 °C and between 2 and 6 at. % at 400 °C. Slightly higher amounts of chlorine residues were found in the films deposited with the scheme TiCl<sub>4</sub> - NH<sub>3</sub> - TMA than with the other schemes. The aluminium content was found to be more dependent on the deposition scheme than the chlorine content. The aluminium content was the highest in the films deposited with the scheme TiCl<sub>4</sub> - NH<sub>3</sub> - TMA - NH<sub>3</sub>. This is understandable since this scheme involves a pulsing subsequence - NH<sub>3</sub> - TMA - NH<sub>3</sub> -, which is known to deposit AlN. Interestingly, at 350 °C the aluminium content seemed to be the highest in the Ti(Al)N films deposited with the all other schemes except TiCl<sub>4</sub> - NH<sub>3</sub> - TMA. This kind of temperature dependence resulted most likely from the decomposition of TMA, which has been reported to begin, for example, with TMA adsorbed on porous alumina above 300 °C.<sup>130</sup> The aluminium content was the lowest in the films deposited with the scheme TiCl<sub>4</sub> - NH<sub>3</sub> - TMA. Thereby, it seems that when dosed right after TMA, TiCl<sub>4</sub> most effectively removes aluminium containing species, probably by forming gaseous aluminium chlorides. A significant improvement to the other ALD deposited TiN films was the much lower oxygen contents of the Ti(Al)N films. Below 0.6 at. % of oxygen was detected by TOF-ERDA in all the studied Ti(Al)N films. The superior oxidation resistance of these films has been attributed to a thin passivating aluminium oxide layer formed on the surface of the Ti(Al)N film when exposed to air, and has been found typical also in the PVD and CVD deposited Ti(Al)N films.<sup>131-133</sup> The carbon contents were high, above 6 at. % in all the studied Ti(Al)N films. However, similarly to the TiN films deposited with DMHy,<sup>IV</sup> the corresponding hydrogen contents were lower suggesting that the carbon was present as a carbide rather than as CH<sub>x</sub> species.

The resistivity decreased strongly as a function of deposition temperature and was the lowest (140 : S cm) in the Ti(Al)N film deposited at 400 °C by the scheme TiCl<sub>4</sub> - TMA - NH<sub>3</sub> with an NH<sub>3</sub> pulse length of 1.0 s. This is comparable<sup>60-62,64</sup> or even lower<sup>7-9</sup> than those achieved with the other ALD deposited TiN films. In XRD the Ti(Al)N films exhibited reflections typical for the cubic TiN. The relative intensities of the two observed reflections were dependent on the aluminium concentration. With higher aluminium contents the (200) reflection was the most dominant and with lower aluminium contents the (111) reflection dominated. Thus it seemed that only when most of the Al atoms were removed from the surface, Ti and N atoms could arrange to a structure with the lowest surface energy, i.e., the (111) orientation. A continuous shift of the peak position to lower  $d$  values was observed for both (111) and (200) reflections as the aluminium content increased. This was attributed to the smaller size of Al atoms substituting the larger Ti atoms in the TiN lattice



and has been reported to occur also in other Ti(Al)N films.<sup>131, 134-137</sup>

Similar to the films deposited from DMHy, <sup>t</sup>BuNH<sub>2</sub> and allylNH<sub>2</sub>, also the Ti(Al)N films deposited using TMA as an additional reducing agent exhibited in general better characteristics than the TiN deposited by the NH<sub>3</sub> based processes at the corresponding temperatures. However, the decomposition of TMA can be considered as a drawback since it affects the film purity and also the controllability of the film growth.

#### 6.4. Barrier Properties [III, V]

In this chapter the barrier properties of the TiN films deposited previously by ALD<sup>7,8,10,III</sup> and of the Ti(Al)N films<sup>V</sup> described in this thesis are summarized. Since the barrier capability studies have usually been carried out with films of variable thicknesses and also at different annealing conditions, a comparison between different diffusion barrier films is difficult. However, at the end of this chapter some studies on barrier performance of different titanium nitride films is reviewed.

##### 6.4.1. TiN [III]

The barrier properties of TiN films deposited by three different ALD processes, i.e., TiI<sub>4</sub> - NH<sub>3</sub>,<sup>8</sup> TiCl<sub>4</sub> - NH<sub>3</sub><sup>7</sup> and TiCl<sub>4</sub> - Zn - NH<sub>3</sub><sup>7,10</sup> were investigated. TiN film was deposited on Si and on top of the TiN film a copper film was deposited by an ALD Cu(thd)<sub>2</sub> - H<sub>2</sub> process previously described by Mårtensson and Carlsson.<sup>30</sup> The original purpose was to grow the copper film immediately after the TiN film deposition, but for some reason the copper film could not be deposited in the F-120 reactor used for the deposition of TiN films. Hence the copper deposition had to be carried out in the reactor used by Mårtensson and Carlsson.

The TiN film, about 90 nm in thickness, deposited by the TiCl<sub>4</sub> - Zn - NH<sub>3</sub> process exhibited the best barrier properties and the Cu/TiN/Si test structure was stable at 700 °C. By contrast, the TiN films with comparable thicknesses deposited by the other processes failed after a 75 min anneal at 650 - 750 °C according to XPS. The TiN films deposited by the TiI<sub>4</sub> - NH<sub>3</sub> process seemed to exhibit the worst barrier properties and only in these samples etch pits appeared on the silicon surface after the “Secco” etching.

In order to study what kind of an effect the thickness of the TiN barrier had on the barrier properties, six TiN films with different thickness (5, 8, 14, 20, 44 and 90 nm) were examined. These films were deposited by the TiCl<sub>4</sub> - Zn - NH<sub>3</sub> process, since with the 90 nm film deposited by this process the interdiffusion of Cu and Si was best prevented. Despite some discrepancy, it

seemed that the failure temperature of the TiN barrier was almost directly dependent on the barrier thickness. However, remarkable changes in, for example, sheet resistances were obtained only after annealing at 650 or 700 °C for 75 min even in the samples with the thinnest TiN films. The surface morphology of the copper film changed with increasing annealing temperature independent of whether Si diffusion had occurred or not, whereas the TiN films seemed unaffected. SEM imaging showed enlarged grains, and eventually the copper film consisted of separate large grains. The areas between the copper grains were virtually copper free and consisted only of TiN. As a result, the sheet resistance of the samples increased. Etch pits and new peaks in the XRD pattern appeared only in the thinnest films. Based on the fact that TiN seemed to be unaffected even after extensive interdiffusion of copper and silicon, it was obvious that the diffusion proceeded along grain boundaries, which is believed to be the most dominant breakdown mechanism of TiN barriers.<sup>2</sup>

#### 6.4.2. Ti(Al)N [V]

Ternary transition metal nitrides are considered to exhibit better barrier properties than binary nitrides since the addition of a third element into a transition metal matrix disrupts the crystal lattice leading possibly to a formation of an amorphous film. Amorphous films do not contain grain boundaries which are believed to be the most important diffusion pathways.<sup>2</sup> By adding aluminium into the TiN matrix, the barrier properties were hence suspected to be improved. In addition, Ti(Al)N films have been reported to have higher thermal stability than TiN which further improves the diffusion barrier behavior.<sup>131-133,138</sup>

In order to study the barrier capabilities of the Ti(Al)N films, three about 10 nm thick Ti(Al)N films were deposited on Si by different schemes under conditions found to give good quality films with different characteristics, like aluminium content, resistivity and crystallinity. On top of these Ti(Al)N films, a copper film was deposited by electron beam evaporation. The deposited Ti(Al)N films showed quite comparable barrier characteristics, although different results of the breakdown temperature were obtained by various testing methods.

The “Secco” etch test was found to be the most sensitive method for detecting the formation of  $\text{Cu}_x\text{Si}$ . According to this test, the Ti(Al)N film deposited by the scheme  $\text{TiCl}_4 - \text{NH}_3 - \text{TMA} - \text{NH}_3$  at 400 °C exhibited the best barrier properties and it was noticed to fail only after annealing for 15 min at 600 °C. The breakdown temperature of the other films was 550 °C. On the other hand, although according to “Secco” test and XRD analysis the Ti(Al)N film deposited by the scheme  $\text{TiCl}_4 - \text{NH}_3 - \text{TMA}$  at 300 °C exhibited the worst barrier properties, a remarkable increase in the sheet resistance was observed only after annealing at 700 °C. With the other films an increase in

the sheet resistance was observed already at 650 °C.

As compared to some other ALD deposited titanium nitride films, the 10 nm thick Ti(Al)N films seemed to fail at quite low temperatures. An amorphous 40 nm thick TiN film deposited by ALD from TEMAT and NH<sub>3</sub> was analyzed to fail after annealing for 1 h at 650 °C.<sup>64</sup> Even better results were obtained with a 10 nm thick nearly amorphous (some nanocrystallites embedded) Ti-Si-N film deposited by ALD from TDMAT, SiH<sub>4</sub> and NH<sub>3</sub>, which was reported to perform well the role of copper diffusion barrier even after annealing for 1 h at 800 °C.<sup>69</sup> This is much better than what was achieved with Ti-Si-N films deposited by sputtering, the highest failure temperature being 650 °C for 30 min annealing.<sup>139</sup> Interdiffusion of Cu in a sputter deposited 100 nm thick TiN film has been reported to begin after 1 h annealing already at 500 °C, but only after annealing at 800 °C a new diffraction peak assigned to Cu<sub>4</sub>Si appeared in the XRD pattern.<sup>140</sup> On the other hand, leakage current measurements did not show deterioration of a diode junction after 30 s annealing up to 650 °C and 800 °C for sputter deposited 100 nm thick Ti<sub>55</sub>N<sub>45</sub> and Ti<sub>45</sub>N<sub>55</sub>, respectively.<sup>141</sup> Kim et al.<sup>55</sup> studied the barrier properties of three different about 20 nm thick CVD deposited TiN films. According to etch pit tests, a TiN film deposited from TiCl<sub>4</sub> and NH<sub>3</sub> failed already after annealing for 1 h at 450 °C, and the films deposited from TDMAT with and without *in situ* N<sub>2</sub> plasma treatment failed at 550 °C.

Though the barrier characteristics are not straightforwardly comparable because of different barrier thicknesses and testing methods, it seems that the breakdown temperature of the present Ti(Al)N films was somewhat lower than those of the other ALD deposited TiN films. The TiN films deposited by other methods, however, do not necessarily exhibit as good barrier properties as the ALD deposited films. Therefore, it seems that ALD is a suitable method for depositing barrier films.

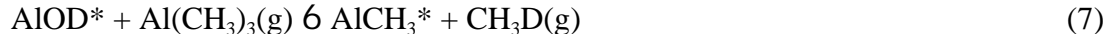
## 7. RESULTS OF THE IN SITU MASS SPECTROMETRY STUDIES

In this chapter the main results of the *in situ* mass spectrometry studies on the ALD growth of Al<sub>2</sub>O<sub>3</sub>, TiN and Ti(Al)N thin films are summarized. Detailed description of the experimental parameters is found from the corresponding articles [VII, VIII].

### 7.1. Growth Study of Al<sub>2</sub>O<sub>3</sub> from Trimethylaluminium and Water [VII]

The reactions between trimethylaluminium (Al(CH<sub>3</sub>)<sub>3</sub>, TMA) and deuterated water (D<sub>2</sub>O) during the ALD growth of Al<sub>2</sub>O<sub>3</sub> were studied in a temperature range of 150 to 400 °C. The deposition temperature and the water dose (flow rate was changed and the length of D<sub>2</sub>O pulse was kept the same) were the main parameters studied, since they were known to have the largest effect on the film growth.<sup>142</sup>

The only reaction product detected by the mass spectrometer was deuterated methane (CH<sub>3</sub>D), which formed during both Al(CH<sub>3</sub>)<sub>3</sub> and D<sub>2</sub>O pulses, and the film growth was thus concluded to proceed according to the following simplified reactions:



where \* denotes all the possible surface species. During the Al(CH<sub>3</sub>)<sub>3</sub> pulse the precursor reacts with the AlOD\* groups releasing methyl groups as deuterated methane and forming adsorbed AlCH<sub>3</sub>\* species (Eq. 7). Rest of the methyl groups are released during the following D<sub>2</sub>O pulse and the surface becomes again -OD terminated (Eq. 8).

After the Al(CH<sub>3</sub>)<sub>3</sub> pulse the surface contained in addition to the reactive Al(CH<sub>3</sub>)<sub>3</sub>\* groups also coordinatively unsaturated Al sites, denoted as Al-O-Al\*. Since the incoming D<sub>2</sub>O reacts also with these groups the Reaction 9 is possible:



The Reaction 8 could be studied by measuring the amount of CH<sub>3</sub>D produced, but the occurrence of the Reaction 9 could rather be seen during the next Al(CH<sub>3</sub>)<sub>3</sub> pulse since it affected the overall density of the AlOD\* groups. Because of the known high reactivity of aluminium alkyls towards water, the Reaction 8 was believed to go into completion before Reaction 9 became significant. On the other hand, since an increase in temperature was known to decrease the AlOD\* group

density through dehydroxylation,<sup>143-145</sup> i.e., inverse to Reaction 9, both the D<sub>2</sub>O dose and the deposition temperature had an important effect on the amount of CH<sub>3</sub>D produced and thereby on the dominating reaction mechanism. So, since parallel reactions were involved in the deposition of Al<sub>2</sub>O<sub>3</sub> from Al(CH<sub>3</sub>)<sub>3</sub> and D<sub>2</sub>O, the amounts of CH<sub>3</sub>D produced during the D<sub>2</sub>O and Al(CH<sub>3</sub>)<sub>3</sub> pulses were actually measures of Al(CH<sub>3</sub>)<sup>\*</sup> and AlOD<sup>\*</sup> groups, respectively, remaining on the surface after the preceding reactant and purge pulses.

The D<sub>2</sub>O dose required to saturate the Reaction 8, i.e., to react with all the methyl groups, was noticed to increase as a function of the deposition temperature. This was attributed to the decrease in the AlOD<sup>\*</sup> group density with increasing temperature. Also the amount of CH<sub>3</sub>D produced during the D<sub>2</sub>O pulse increased as a function of the deposition temperature with each D<sub>2</sub>O dose. According to these results it seemed that at low temperatures when the amount of available AlOD<sup>\*</sup> groups was high, Al(CH<sub>3</sub>)<sub>3</sub> lost most of its methyl groups already during the Al(CH<sub>3</sub>)<sub>3</sub> pulse. At high temperatures the situation was inverse and more methyl groups were released from the surface during the D<sub>2</sub>O pulse.

The behavior of the CH<sub>3</sub>D produced during the Al(CH<sub>3</sub>)<sub>3</sub> pulse was more complicated than during the D<sub>2</sub>O pulse. It seemed strange that by increasing the D<sub>2</sub>O dose more CH<sub>3</sub>D was produced during the Al(CH<sub>3</sub>)<sub>3</sub> pulse at each deposition temperature and no saturation was noticed. However, this was explained by the coexistence of the Reactions 8 and 9 and hence by the formation of additional AlOD<sup>\*</sup> groups during the D<sub>2</sub>O pulse with higher D<sub>2</sub>O doses. These additional AlOD<sup>\*</sup> groups reacted during the following Al(CH<sub>3</sub>)<sub>3</sub> pulse and produced CH<sub>3</sub>D. Such a mechanism is further supported by the observations of Matero et al.<sup>142</sup> where the growth rate saturated to different levels with low and high water flow rates. Previously already quite low water flow rates were believed to be saturative, because the growth rate could not essentially be increased by increasing the pulse length. However, according to Matero et al. it seems that in addition to pulse length also the flow rate had a remarkable effect on the surface chemistry.

As a conclusion, the results reported in paper [VII] agree quite well with the previous studies carried out with other methods.<sup>77,78</sup> The dehydroxylation of alumina played a key role in the ALD of Al<sub>2</sub>O<sub>3</sub> even in that sense that the degree of dehydroxylation determined whether Al(CH<sub>3</sub>)<sub>3</sub> adsorbed as -Al(CH<sub>3</sub>)<sub>2</sub> or as >Al(CH<sub>3</sub>). However, the D<sub>2</sub>O doses were analyzed to be saturative only according to QMS data in a way that it was large (i.e., flow rate and pulse length) enough to react saturatively with the Al-CH<sub>3</sub><sup>\*</sup> in Reaction 8, as verified by the absence of CH<sub>3</sub>D release during the subsequent D<sub>2</sub>O pulse. But as already noted, D<sub>2</sub>O can also react with the Al-O-Al<sup>\*</sup> groups (Reaction 9), though this could not be seen by QMS since no gaseous species were formed.

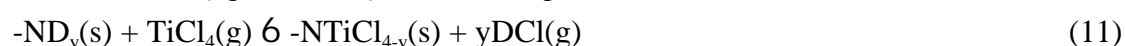
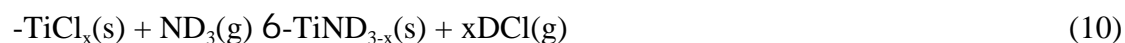
Later it became possible to study the saturation also by Quartz Crystal Microbalance (QCM), which enabled to examine the mass increment of the film during each cycle.<sup>11</sup> Because the mass changes analyzed by QCM were related to the adsorbate  $\text{Al}(\text{CH}_3)^*$  (after reaction with  $\text{Al}(\text{CH}_3)_3$ , Eq. 7) and  $\text{Al}_2\text{O}_3$  (after reaction with  $\text{D}_2\text{O}$ , Eqs. 8, 9), their ratio gave an estimate of the fraction of methyl groups released during the  $\text{Al}(\text{CH}_3)_3$  pulse. The same fraction could also be calculated from the QMS data by dividing the amount of  $\text{CH}_3\text{D}$  produced during the  $\text{Al}(\text{CH}_3)_3$  pulse by the total amount of  $\text{CH}_3\text{D}$  produced during one cycle. Such an analysis performed in paper [VII] on the QMS data showed that the amount of methyl groups released during each pulse was dependent on the deposition temperature. However, when the  $\text{D}_2\text{O}$  doses were optimized according to the QCM data, and thereby also the Reaction 9 was taken into account, much larger  $\text{D}_2\text{O}$  doses had to be used in order to obtain the saturative behavior. According to these later QMS and QCM studies, about half of the methyl groups was released during each reactant pulse and the deposition temperature did not have any major effect on the reaction mechanism.

## 7.2. Growth Study of TiN and Ti(Al)N thin films [VIII]

The surface reactions in the ALD of TiN and Ti(Al)N films from  $\text{TiCl}_4$ ,  $\text{Al}(\text{CH}_3)_3$  (TMA) and  $\text{ND}_3$  were studied in a temperature range of 300 to 400 °C. The main aim of this study was to find out how chlorine was released from the surface at different temperatures and how the addition of  $\text{Al}(\text{CH}_3)_3$  pulse in between the  $\text{TiCl}_4$  and  $\text{NH}_3$  pulses affected the reaction mechanism. Although the actual growth studies were carried out with four different deposition schemes, only the scheme  $\text{TiCl}_4$  -  $\text{Al}(\text{CH}_3)_3$  -  $\text{ND}_3$  was analyzed by means of *in situ* mass spectrometry. Because of the high temperatures, QCM could not be used in characterizing the reactions.

### *TiN*

In the deposition of TiN films from  $\text{TiCl}_4$  and  $\text{ND}_3$ , DCl was the only reaction byproduct detected during both pulses and the growth of TiN films most evidently proceeded according to the following reactions:



The total amount of DCl produced during one cycle increased as a function of deposition temperature. This can largely be attributed to a more effective removal of chlorine during the  $\text{ND}_3$  pulse since the relative amount of DCl released during the  $\text{ND}_3$  increased with the temperature. At low temperatures, a molecular adsorption of  $\text{ND}_3$  (Eq. 12) was also supposed to be possible, since

the amount of DCl produced was lower and also more chlorine has been noticed to be incorporated into the film.



According to the ratio of chlorine released during the two pulses, it seemed that  $\text{TiCl}_4$  adsorbed on the  $-\text{ND}_y$  covered surface as  $\text{TiCl}_x$ , where  $x$  increased as a function of temperature. This was concluded to be due to either the loss of the reactive  $-\text{ND}_y$  surface groups or their change from  $-\text{ND}_2$  to  $-\text{ND}$  groups when the temperature was increased. The first kind of a behavior has been noticed to be important in the ALD of oxide<sup>VII,11,12,85,88</sup> and sulfide<sup>146,147</sup> films, where the amount of reactive  $-\text{OH}$  and  $-\text{SH}$  surface groups decreased with increasing temperature. The latter, on the other hand, has been reported to occur in the ALD of AlN films.<sup>83</sup>

### *Ti(Al)N*

During the deposition of Ti(Al)N films several  $m/z$  ratios were observed, but in order to study the dominating reaction mechanism only the most abundant ions, namely  $\text{D}^{37}\text{Cl}^+$ ,  $\text{C}_2\text{H}_6^+$ ,  $\text{CH}_3^{35}\text{Cl}^+$ ,  $\text{Al}(\text{CH}_3)^{35}\text{Cl}^+$  and  $\text{CH}_3\text{D}^+$  were examined. In the Ti(Al)N growth studies<sup>V</sup> the  $\text{Al}(\text{CH}_3)_3$  dose had been noticed to have a profound effect on the characteristics of the films (Al content, resistivity, growth rate increased with increasing temperatures). However, the chlorine contents could not be decreased by increasing the  $\text{Al}(\text{CH}_3)_3$  dose. Since the  $\text{Al}(\text{CH}_3)_3$  dose apparently had an effect on the film growth, the reaction mechanism studies were carried out with low and high  $\text{Al}(\text{CH}_3)_3$  doses. The main focus was on DCl, since the amount of DCl was the most remarkable with the both types of  $\text{Al}(\text{CH}_3)_3$  doses. The amount of other reaction byproducts became considerable merely with the high  $\text{Al}(\text{CH}_3)_3$  dose. Unlike in the TiN film growth, the surface reactions were not entirely saturated with the used pulse lengths (5 s for each reactant). On the other hand, the growth of Ti(Al)N films can not be considered an ideal ALD process because of the  $\text{Al}(\text{CH}_3)_3$  decomposition possibility<sup>129</sup> and hence the use of longer pulse lengths is not reasoned. However, due to this unsaturative behavior, unreacted surface groups were left on the surface which led to a complicated behavior involving many parallel reactions.

With both  $\text{Al}(\text{CH}_3)_3$  doses DCl desorbed during each pulse. The desorption of DCl during the  $\text{Al}(\text{CH}_3)_3$  pulse implied that  $\text{Al}(\text{CH}_3)_3$  interacted with both  $-\text{TiCl}_x$  and  $-\text{ND}_y$  groups and resulted in the formation of DCl, since  $\text{Al}(\text{CH}_3)_3$  itself does not contain chlorine or deuterium atoms. One probable reaction pathway can be presented with the following unbalanced equation:



The reactions during the  $\text{Al}(\text{CH}_3)_3$  pulse may also proceed through radical mechanism. Indeed, in addition to DCl also ethane ( $\text{C}_2\text{H}_6$ ) was detected, though only with the high  $\text{Al}(\text{CH}_3)_3$  dose when the amount of released byproducts was higher. The deposition temperature had an effect on the amount of  $\text{C}_2\text{H}_6$  as more  $\text{C}_2\text{H}_6$  desorbed at higher temperatures. The desorption of  $\text{C}_2\text{H}_6$  was also detected during the  $\text{TiCl}_4$  and  $\text{ND}_3$  pulses and resulted most likely from their adsorption onto surface sites occupied by  $-\text{CH}_3$  groups. When the deposition of AlN from  $\text{Al}(\text{CH}_3)_3$  and  $\text{ND}_3$  was studied,  $\text{C}_2\text{H}_6$  was not detected. Since Al is at the same oxidation state (+III) in both  $\text{Al}(\text{CH}_3)_3$  and AlN, no reduction was then needed. Thereby it was concluded that the formation of  $\text{C}_2\text{H}_6$  during the deposition of Ti(Al)N films was an implication of  $\text{Al}(\text{CH}_3)_3$  acting as an additional reducing agent for titanium.

Although the Ti(Al)N films deposited already with low  $\text{Al}(\text{CH}_3)_3$  doses contained much less chlorine than the corresponding TiN films,<sup>v</sup> it seemed that the addition of  $\text{Al}(\text{CH}_3)_3$  did not change the basic surface reaction mechanism when the low  $\text{Al}(\text{CH}_3)_3$  was used. Most of the chlorine was still desorbed during the  $\text{ND}_3$  pulse as in the deposition of TiN films. However, the reaction mechanism seemed to change when the high  $\text{Al}(\text{CH}_3)_3$  dose was used. With the high  $\text{Al}(\text{CH}_3)_3$  dose about half of the chlorine was desorbed during the  $\text{TiCl}_4$  pulse at all the studied temperatures indicating that it adsorbed mainly as  $-\text{TiCl}_2$ . These results lead to a conclusion that after the  $\text{ND}_3$  pulse the surface consisted mainly of  $-\text{ND}$  sites with the low  $\text{Al}(\text{CH}_3)_3$  dose, and of  $-\text{ND}_2$  sites with the high  $\text{Al}(\text{CH}_3)_3$  dose. This difference was attributed to a more effective chlorine removing capacity of the high  $\text{Al}(\text{CH}_3)_3$  dose. More specifically: as there were less chlorine atoms on the surface after the high  $\text{Al}(\text{CH}_3)_3$  dose, the adsorbing  $\text{ND}_3$  molecules reacted mostly with only one chlorine and thus produced  $-\text{ND}_2$  groups.

The desorption of aluminium and methyl species was more difficult to study than the desorption of chlorine since the intensities detected were much lower. However, interestingly the mass spectrometry studies with the high  $\text{Al}(\text{CH}_3)_3$  dose seemed to correlate with the growth experiments, although the latter were carried out with a low  $\text{Al}(\text{CH}_3)_3$  dose, in what comes to the aluminium incorporation. The formation of the only detected aluminium species,  $\text{Al}(\text{CH}_3)_{3-x}\text{Cl}$ , was the weakest at 350 °C and the Al content of the deposited Ti(Al)N films was the highest at the same temperature. In addition, no  $\text{Al}(\text{CH}_3)_{3-x}\text{Cl}$  desorbed during the  $\text{ND}_3$  pulse, which is understandable since AlN films have been deposited by ALD from  $\text{Al}(\text{CH}_3)_3$  and  $\text{NH}_3$ <sup>129</sup> and also from  $\text{AlCl}_3$  and  $\text{NH}_3$ .<sup>148</sup> Far heading conclusions could not be drawn from the desorption of methyl species and carbon contents, since the decomposition degree of  $\text{Al}(\text{CH}_3)_3$  had a remarkable effect on the amount of detected methyl species.



## 8. CONCLUSIONS

The interest towards ALD has increased especially during the last few years. This is mainly due to the necessity of finding a thin film deposition method which would fulfill the demanding future requirements of microelectronics. Since the device dimensions are continuously decreasing and the aspect ratios increasing, a method by which thin films could be grown conformally even onto very deep trenches is needed. Due to the self-limiting growth mechanism achieved by pulsing the reactants alternately onto the substrates, ALD is one of the most promising methods to fulfill these future requirements. In this thesis ALD has been studied in depositing thin films for the future copper interconnect technology.

Copper, molybdenum and some transition metal nitrides, mainly TiN, were deposited by ALD. ALD of copper was tried by using many precursor combinations, but only a very few seemed promising. The deposition of copper did not usually proceed through the ideal self-limiting growth mechanism and the films showed quite rough structure and high resistivity. However, while ALD was originally developed to deposit compounds, the current studies with ALD metal deposition give further confidence that it is possible to grow also elements.

Copper and silicon are very reacting towards each other, and to prevent these unwanted reactions a diffusion barrier is needed. Transition metal nitrides are used as diffusion barriers and the main aim of the studies considering their ALD was to find appropriate chemistry which would enable low temperature deposition. Two different approaches were studied: TMA as an additional reducing agent and nitrogen sources more reactive than  $\text{NH}_3$ , namely DMHy,  $^t\text{BuNH}_2$  and allyl $\text{NH}_2$ . In each case, TiN films deposited at 400 °C showed better properties than the films obtained with the previous processes with the corresponding  $\text{NH}_3$  flow rate. For example, the resistivities were between about 100 and 500 :  $\Omega$  cm. Because of the decomposition of TMA, DMHy and allyl $\text{NH}_2$ , the amounts of carbon impurities were, however, quite high (several at.%). On the other hand, the films deposited with  $^t\text{BuNH}_2$  contained only minor amounts of carbon (below 1 at.%). The carbon was most likely present as carbide rather than as  $\text{CH}_x$  species since the amounts of hydrogen impurities were much lower.

To gain better understanding of the chemistry involved, *in situ* mass spectrometry studies on the ALD of  $\text{Al}_2\text{O}_3$ , TiN and Ti(Al)N were carried out. Since the deposition of  $\text{Al}_2\text{O}_3$  from  $\text{Al}(\text{CH}_3)_3$  and  $\text{H}_2\text{O}$  is considered to be one of the most ideal ALD processes it was a good process to start these novel experiments. It was found out that the dehydroxylation of  $\text{Al}_2\text{O}_3$  had an important effect on the growth. This was in agreement with the studies performed by other methods. The ALD of Ti(Al)N films from  $\text{TiCl}_4$ ,  $\text{Al}(\text{CH}_3)_3$  and  $\text{ND}_3$  was noticed to involve many parallel and

complicated reactions which depended on the  $\text{Al}(\text{CH}_3)_3$  dose. With the low  $\text{Al}(\text{CH}_3)_3$  dose most of the chlorine was released during the  $\text{ND}_3$  pulse similarly to the TiN process, but with the high dose most of the chlorine was released during the  $\text{TiCl}_4$  pulse. Also ethane could be detected during the deposition of Ti(Al)N films which implied that  $\text{Al}(\text{CH}_3)_3$  acts as an additional reducing agent releasing methyl radicals as suspected.

It can be concluded that ALD is an excellent method to fulfill the increasing demands of microelectronic industry. It offers many already found and still to be explored solutions to answer the future challenges. For understanding and developing ALD processes more profoundly, a valuable information is gained by *in situ* mass spectrometry studies.

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