# Atomic Vapor Depositions of Metal Insulator Metal capacitors: Investigation, Development and Integration

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## Abstract

Metal-Insulator-Metal (MIM) capacitors are one of the most essential passive components in radio frequency devices and analog/mixed-signal integrated circuits. However, depending on the applications, MIM capacitors can require up to 50 % of the chip area. This strongly affects the ability to reduce the size of the chips, but the reduction and downscaling of the chips are crucial in order to reduce the cost, and therefore increase the functionality and performance of the devices. To achieve a higher capacitance per unit area for providing the analog scaling is the main objective. Since capacitance is a direct function of the dielectric constant of the insulator, the replacement of currently used silicon oxide or silicon nitride films with the new alternative dielectrics which have higher permittivity values is a very promising approach.

The work is focused on the preparation and characterization of alternative dielectrics, namely HfO<sub>2</sub>, SrTaO and TiTaO as well as of TiN electrode. The study showed that these dielectrics are very promising materials for future Si based technologies.

Metall-Isolator-Metall (MIM) Kondensatoren gehören zu den wichtigsten passiven Komponenten in Hochfrequenzbauelementen und Schaltkreisen für Analog/Mischsignale. Unabhängig von der Anwendung beanspruchen MIM-Kondensatoren bis zu 50 % der Chipfläche. Dies unterstützt maßgeblich die Chipfläche zu reduzieren, die stark die Kosten aber auch die Funktionalität und Leistung des Chip bestimmt. Eine Steigerung der Kapazität pro Fläche (Kapazitätsdichte) ist aus diesem Grund der Schwerpunkt bei der weiteren analogen Skalierung von Bauelementen. Weil die Kapazität eine direkte Funktion der Dielektrizitätskonstante des Isolators ist, ist das Ersetzen des gegenwärtig genutzten Siliziumoxid oder Siliziumnitrid durch alternative Dielektrika mit höheren Dielektrizitätskonstanten ein vielversprechender Ansatz.

Die vorliegende Arbeit ist hauptsächlich auf die Präparation und Charakterisierung solcher alternativer Dielektrika, wie HfO<sub>2</sub>, Sr-Ta-O und Ti-Ta-O sowie dazugehöriger TiN -elektroden gerichtet. Die durchgeführten Untersuchungen zeigten, dass diese Dielektrika aussichtsreiche Materialien für zukünftige siliziumbasierte Technologien darstellen können.

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# List of abbreviations

**acac** – acetyacetonate.

- A/D Analog-Digital.
- AVD Atomic Vapor Deposition.
- ALD Atomic Layer Deposition.
- BiCMOS Bipolar CMOS.
- **BEOL** Back End Of Line.
- **BJT** Bipolar Junction Transistor.
- CMOS Complementary MOS.

C<sub>p</sub> – cyclopentadienyl.

- cps counts per second.
- CPU Central Processing Unit.
- CSD Chemical Solution Deposition.

C-V – Capacitance–Voltage.

**CVD** – Chemical Vapor Deposition.

D/A – Digital-Analog.

- DBS Dual Beam Spectroscopy.
- dmae dimethylaminoethoxide.
- Ebd Breakdown Field.

Et – Ethyl.

FEOL – Front End of Line.

FET – Field Effect Transistor.

- FN Fowler-Nordheim.
- ITRS -- International Technology Roadmap for Semiconductors.
- LDS Liquid Delivery System.

me – Methoxyethoxide.

Me – Methyl.

MIM – Metal Insulator Metal.

mmp - 1-methoxy-2-methyl-2-propxide.

MOS – Metal Oxide Semiconductor.

MOSFET – Metal Oxide Semiconductor Field Effect Transistor.

NVM – Non Volatile Memory.

NMOS – n-type MOS.

**OBu**<sup>t</sup> – tertbutoxide.

**OPr<sup>i</sup>** – isopropoxide.

**PECVD** – Plasma Enhanced CVD.

PIP – Polysilicon Insulator Polysilicon.

PF - Poole-Frenkel.

PLD – Pulsed Layer Deposition.

PMOS – p-type MOS.

**ppm** – Parts per Million

PVD – Physical Vapor Deposition.

PZT – PbZrTiO<sub>3</sub>.

RF - Radio Frequency.

**RIE** – Reactive Ion Etching.

SAW – Surface Acoustic Wave.

 $\textbf{SBT}-SrBi_2Ta_2O_{9.}$ 

SE – Spectroscopic Ellipsometry.

**SEM** – Scanning Electron Microscopy.

STA – Sr-Ta-O.

STO – Sr-Ti-O.

t-Bu – Tertbutyl.

**TBTDET** - tertbutylimido-tris(diethlyamido)tantalum.

TDDB – Time Dependent Dielectric Breakdown.

TDEAT - tetrakis(diethylamido)titanium.

TDMAT - tetrakis(dimethylamido)titanium.

TEM – Transmission Electron Microscopy.

TEMAHf – Tetrakis(ethylmethylamido)hafnium.

TEMAT – Tetrakis(ethylmethylamido)titanium.

thd – 2,2,6,6,-tetramethyl-3,5,-heaptadionate.

TTO – Ti-Ta-O.

 $\phi$  – Photoelectron take off angle.

**XPS** – X-Ray Photoelectron Spectroscopy.

**XRD** – X-Ray Diffraction.

XRR – X-Ray Reflectivity.

# Overview

#### Goal of the study

During the last decades a tremendous progress was made in Silicon based semiconductor technologies due to the miniaturization of semiconductor devices such as field effect transistors (FET) in complementary metal oxide semiconductor (CMOS) logic devices. This was achieved due to the fundamental aspect of silicon that reacts with oxygen and composes excellent dielectric SiO<sub>2</sub> and therefore presenting the wonderful properties of the silicon/silicon dioxide interface. By scaling SiO<sub>2</sub> it was possible to double the number of transistors per unit area every 18-24 months when new technology nodes were introduced. The 45 nm node (gate length) is reached and optimized and is already used in the Central Processing Units (CPUs) of computers nowadays. The scaling phenomenon is known as the Moore's Law. By continuing this scaling it is possible to increase the speed of CPU etc., but the power losses become too high which makes the devices not suitable and convenient for wireless and broadband communication applications. By staying with the higher gate lengths of transistors (250 nm or 130 nm) it is possible to reduce the leakage currents, but to make the chip more "competitive" the functionality of it has to be expanded. This approach is called "More than Moore". One of the most advanced technologies in this field is called Bipolar Complimentary Metal Oxide Semiconductor (BiCMOS) technology, in which digital and analog parts are placed on the same chip to increase the performance of the devices. The integration of passive devices into these semiconductor devices is an enabling technology that drives a higher degree of system-level integration for portable communication devices.

Examples of passive devices are Metal–Insulator–Metal (MIM) capacitors, Varactors, Non–Volatile Memories (NVM) or Surface–Acoustic–Wave (SAW) filters. Among them, MIM capacitors are one of the key building blocks in analog/mixed signal Radio Frequency (RF) CMOS circuits. However, to increase the functionality, performance and reliability of devices, reduction in feature size of passives is also necessary. To achieve a higher capacitance density per unit area for providing the analog scaling is the main objective, while currently used TiN/SiO<sub>2</sub>/TiN MIM stacks possess capacitance density of only 1 fF/µm<sup>2</sup>. Since capacitance is directly proportional to the

dielectric constant of the material, the replacement of currently used SiO<sub>2</sub> and silicon nitride (Si<sub>3</sub>N<sub>4</sub>) films with the new alternative dielectrics which have a high–*k* value is very promising approach. Unfortunately, miniaturization of MIM capacitors and implementation of new materials also raises difficulties in fulfilling the challenges defined by the International Roadmap for Semiconductors (ITRS)<sup>1</sup>: capacitance–voltage (C-V) linearity and leakage currents have to be decreased while quality factor, breakdown voltage and capacitance density should increase.

A variety of high–k materials are investigated as alternative dielectrics to replace the SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub>. Among them, Hafnium Oxide (HfO<sub>2</sub>), Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) and Tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) are the most researched single high–k dielectrics. Recently systems of two metals such as, Sr-Ti-O, Sr-Ta-O or Ti-Ta-O have attracted attention due to their high bulk value of permittivity. In addition, the electrical properties of MIM capacitors are not only determined by the dielectric itself. Bottom electrode material and its interface with the dielectric also play a significant role on the properties such as capacitance density, capacitance voltage linearity or leakage current. The electrode has to exhibit a high work function to limit leakages, a low resistivity to reduce the metal losses, a high resistance to oxidation and good compatibility with the insulator. Therefore the choices of the dielectric and electrode material as well as engineering aspects are critical to meet the specifications.

Due to the thermal budget of the Back end of line (BEOL) process, where MIM capacitors are located, one of the main difficulties is to get good quality dielectric as well as electrode layers at the maximum allowed temperature of 400°C. At this point, the appropriate deposition technique has to be applied. Mainly, the thin films of the simple oxides such as HfO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> as well as metal TiN electrodes are deposited by the Physical Vapor Deposition (PVD) techniques but Chemical Vapor Deposition (CVD) based techniques are the ones to come into consideration due to the good composition control for ternary oxides, high uniformity of the films, good doping control, and most importantly, they give excellent conformal step coverage on non–planar device geometries. An Atomic Vapor Deposition (AVD) technique, which is a very advanced modification of CVD, was used as the deposition tool for getting all the thin films used in this work.

The **main goals and objectives** of this PhD thesis were to develop the Atomic Vapor Deposition processes for TiN as electrode material as well as for alternative high–k dielectrics namely HfO<sub>2</sub>, SrTaO and TiTaO for MIM applications for future Si based technologies. In order to fulfil the requirements defined by the ITRS roadmap, influence of

deposition parameters such as process or annealing temperatures and pressure on the composition, microstructure and electrical properties of MIM capacitors were investigated.

As it is very difficult to find the one which fulfils all the requirements, attempts to combine single oxides to build MIM stacks or three dimensional (3D) approaches are also investigated as a possible solution to increase the capacitance density. Additionally, the final goal was to integrate the  $HfO_2$  as a dielectric and TiN as electrode material in MIM for BiCMOS technology.

#### **Organization of the thesis**

The general properties of MIM capacitors and the principles of deposition technique are described in *Chapter I*. The particular attention is dedicated to the scaling of MIMs and to the key requirements for alternative dielectrics. A literature review of explored oxides and possible solutions in engineering the devices are also presented.

*Chapter II* gives a short overview on the theoretical and experimental principles applied in this study. Deposition and characterization instruments are also specified.

The results of optimization and development of the AVD process to obtain uniform, low resistivity TiN metal layers are described in *Chapter III*. The influence of process temperature and concentration of the Ti precursor on TiN layer properties such as resistivity, roughness, morphology and stoichiometry is investigated.

*Chapter IV* summarizes the results of the HfO<sub>2</sub> based MIM capacitors. This chapter is divided into two parts. The first one deals with the optimization of deposition process to get high quality HfO<sub>2</sub> films as well as the physical and electrical characterization of them. In addition, the role of the interface between TiN and HfO<sub>2</sub> and the comparison of two different electrode materials is also studied. The integration process and electrical results of integrated TiN/HfO<sub>2</sub>/TiN MIM stack will be presented in the second part of the chapter.

Alternative dielectrics (SrTaO and TiTaO) are investigated in *Chapter V*. A special point here is dedicated to the development of the AVD process itself in order to find the suitable deposition conditions for theses oxides. Finally, depositions of HfO<sub>2</sub> and TiN in trenched Si wafers are explored as a possible design of three dimensional MIM capacitors.

*Chapter VI* summarizes all the results obtained in this research study and states some recommendations for future efforts.

# Chapter I

## 1. Introduction

### **1.1. MIM Capacitors**

The rapid increase in wireless communications products has energized the need for process technologies that support both digital and analog (mixed–signal) devices at radio frequencies (RF). Silicon–Germanium Bipolar Complimentary Metal Oxide Semiconductor (SiGe BiCMOS) technologies<sup>2</sup> are ideal for many wireless applications. In these technologies high speed conventional active CMOS<sup>3</sup> digital cells are being mixed with Bipolar Junction Transistor (BJT) modules in so called Front–End–Of–Line (FEOL) as well as with the key passive components which are required for any highly integrated mixed–signal chip. These passive elements include process–enabled elements (such as resistors and vertical capacitors) as well as design–enabled elements such as inductors, varactors and lateral capacitors. In analog/mixed–signal circuits these passives are used for a variety of active functions such as tuning, filtering, impedance matching or gain control and are key blocks in e.g analog frequency tuning circuits, filters, digital/analog–analog/digital (D/A–A/D) converters and many others.<sup>4,5</sup>

One of the most dominant passive devices are capacitors. Three types of capacitors have been developed in SiGe technologies – MOS<sup>6</sup> (polysilicon gated capacitors on single crystal silicon), PIP<sup>7</sup> (polysilicon–insulator–polysilicon), and Metal–Insulator–Metal (MIM)<sup>8,9</sup> capacitors. Each of them has their own place for use in different applications depending on capacitance desired and performance at the application frequency. Traditionally MOS and PIP capacitors are integrated during front end processing by using doped monocrystalline Si substrate, polycrystalline Si with the combination of respective Si–oxides or Si–oxynitrides. Because of the vicinity to the Si substrate, these devices suffer from increased performance degradation especially when

used at high RF frequencies, therefore there is a high demand for low loss, low parasitics, but high quality capacitors in the interconnect levels.

By far most popular analog/mixed–signal capacitors are MIM capacitors, which have the inherent advantage of low–resistivity metal wiring and of thick interlevel dielectric which physically distances the devices from the relatively low–resistivity substrate. In IHP BiCMOS technology they are implemented between 2<sup>nd</sup> and 3<sup>rd</sup> Aluminium metallization layers in a Back–End–Of–Line (BEOL) process, which is shown in complete cross section of BiCMOS view in Fig. 1.1



Fig. 1.1. Cross section view of BiCMOS technology.

The placement of MIMs in the interconnect levels significantly reduces the parasitic capacitance of the substrate and therefore are very preferred by the circuit designers. The price paid for this benefit is that a large area of the chip is consumed, affecting the ability to reduce the form factor of the chip. Capacitors may require up to 50 % of the chip area, depending on the application and hardly shrink from one technology node to the other. This point is illustrated in Fig. 1.2, which presents the impressive area covered by MIM capacitors as well as inductors in the layout of typical RF receiving circuit embedded in mobile phones.



Fig. 1.2. Layout of a RF reception circuit for cell phones.<sup>10</sup>

In order to decrease the capacitor footprint, several options to increase the unit capacitance are available. As can be seen from parallel place capacitor formula (Eq. 1.1), the capacitance is a direct function of the dielectric constant of the insulator and is inversely proportional to the film thickness:

$$C = \frac{\varepsilon_0 kA}{d} \tag{1.1}$$

where, *C* is the capacitance,  $\mathcal{E}_0$  – the permittivity of free space, *A* – area and *d* – dielectric thickness, respectively.

During the past decade most MIM capacitors in manufacturing were using silicon oxide  $(SiO_2)^{11}$  as insulator and TiN as electrode material. A typical cross sectional Scanning Electron Microscopy (SEM) picture of SiGe BiCMOS planar MIM is shown in Fig. 1.3. In this MIM capacitor, 50 nm SiO<sub>2</sub> is used between two layers of TiN electrodes, but due to the small *k* value of SiO<sub>2</sub> (k = 3.9)<sup>12</sup>, the capacitance density (C/A) of such MIM stack is about 1 fF/µm<sup>2</sup> and this value, according to ITRS<sup>1</sup> should be increased for future applications. As can be seen from equation (1.1), capacitance density could be easily increased by reducing the thickness of dielectric but it would lead to unacceptable high leakage currents and low breakdown voltages.



Fig. 1.3. Cross sectional SEM picture of integrated 50nm SiO<sub>2</sub> between TiN electrodes.

Another way to increase the capacitance is to replace SiO<sub>2</sub> by materials with higher *k* values. So, SiO<sub>2</sub> was progressively replaced by silicon nitride<sup>13</sup> (the *k* value of Si<sub>3</sub>N<sub>4</sub> is 7.5<sup>14</sup>) or silicon oxynitride.<sup>15</sup> In this case, a density of 2 fF/ $\mu$ m<sup>2</sup> was reached, but even such values are too low for the long term requirement of capacitance density which is shown in Fig. 1.4. One can see that a density of 5 fF/ $\mu$ m<sup>2</sup> is already required from year 2010–2011 and values as high as 12 fF/ $\mu$ m<sup>2</sup> for the next decade.



Fig. 1.4. Requirements from the roadmaps of semiconductor industries for capacitance

density as a function of year.

In addition to the high capacitance density, several other critical parameters for MIM capacitors are required and could be summarized as following:

- ✓ High Capacitance–Voltage (*C*–*V*) linearity over broad voltage range (linearity coefficient  $\alpha$  must be smaller than 100 ppm/V<sup>2</sup>);
- ✓ Low leakage currents ( lower than  $10^{-8}$  A/cm<sup>2</sup> at ± 2V);
- ✓ High dielectric breakdown voltage and reliability;
- ✓ High quality factor (reciprocal dielectric loss tangent) *Q* must be higher than 50 at 5 GHz.
- ✓ Small temperature dependence of capacitance;
- ✓ Low parasitic capacitance;

In the following sections the most important parameters will be discussed in more details.

#### **1.1.1. Capacitance Voltage Linearity**

A key characteristic regarding the performance of MIM capacitors is capacitance voltage linearity, which indicates the dependence of capacitance on the applied bias. For applications, the variation of capacitance in the device must be as stable as possible with respect to applied voltage. This stability of capacitance variation is commonly described by the following polynomial law<sup>16</sup>:

$$C(V) = C_0 (\alpha V^2 + 1)$$
(1.2)

where  $C_0$  is the capacitance at zero bias voltage, and  $\alpha$  represents the quadratic capacitance coefficient.

The allowed capacitance voltage linearity coefficient  $\alpha$  is strictly defined by ITRS Roadmap and has to be lower than 100 ppm/V<sup>2</sup>. This requirement is schematically illustrated in a grey line in Fig. 1.5, where capacitance density is plotted against applied voltage.



Fig. 1.5. Capacitance–Voltage curves voltage of allowed nonlinearity (grey line) and typical of high-k material (black line).

One of the most severe challenges of introducing alternative high-k dielectrics in MIM capacitors is to keep this capacitance–voltage linearity coefficient  $\alpha$  in the allowed range. Usually, MIM capacitors with alternative high-k materials exhibit strong positive parabola (high  $\alpha$  values) as shown in black line in Fig. 1.5, but the microscopic origin of this nonlinear behaviour is still unclear. Probably, capacitance voltage nonlinearity is related with the high degree of electric field polarization and carrier injections<sup>17</sup>. Other physical mechanisms are also reported, such as free carrier injection or space charge relaxation<sup>18</sup>, where space charges can form an accumulation layer next to the electrodes, leading to double layer capacitance. This effect is also called electrode polarization.<sup>19</sup> This model varies with frequency, but it is negligible in the case of HfO2.<sup>20</sup> Nonlinear metaloxygen bond polarizability was also proposed as the microscopic origin of nonlinearity of Al<sub>2</sub>O<sub>3</sub><sup>21</sup> but it is not suitable for other oxides. Recently, Miao<sup>22</sup> reported that carbon contamination also effects voltage linearity in HfO2 films. The authors showed that it is possible to minimize the alpha value when carbon amount is reduced in the HfO<sub>2</sub> films. Another microscopic model for nonlinearities in C-V characteristics of high-k MIM capacitors, based on fundamental physical mechanisms, such as electrostriction, Coulomb interaction between the electrodes and nonlinear optical effects is presented by Wenger.<sup>23</sup>

According to this model the quadratic voltage coefficient  $\alpha$  strongly depends on the thickness of dielectric layer and can be identified as:

$$\alpha = \frac{2n_2n_0}{k_0d^2}$$
(1.3)

where

 $n_0$  is linear refractive index of the dielectric material;

 $n_2$  – nonlinear refractive index;

 $k_0$  – dielectric constant;

d – thickness of dielectric layer.

As can be seen, the coefficient  $\alpha$  is dependent on the refractive index  $n_{0}$ , the linear dielectric constant  $k_0$  and nonlinear refractive index  $n_2$ , whereby  $n_2$  strongly depends on  $k_0$ . According to this model,  $n_2$  is a function of dielectric constant and Young's modulus, which shows the elastic properties of the insulator.

#### **1.1.2. Leakage current**

Leakage current density is also a crucial parameter for MIM capacitors, particularly at higher voltages. Since the standard thickness of dielectrics is 40–50 nm for MIM applications, the quantum phenomenon, where mobile charge carriers (electrons or holes) can tunnel through an insulating material creating conduction paths in it, does not occur. Therefore, conduction only becomes possible as a result of the presence of sites from which electrons or holes can be activated. According to the behaviour of dielectrics under electric fields, several conduction mechanisms can be identified. Fowler-Nordheim (FN) tunneling<sup>24</sup>, Schottky emission<sup>23</sup> or Poole-Frenkel (PF) emission<sup>25</sup> are schematically shown in a), b) and c) parts of Fig. 1.6.



Fig. 1.6. Illustrations of a) FN tunnelling, b) Schottky and c) PF conduction mechanisms.

FN tunnelling has been shown to be the dominant current mechanism in MOS structures, especially for thick oxides. The basic idea of FN mechanism is that quantum mechanical tunnelling from the adjacent conductor into the insulator limits the current through the structure. Once the carriers have tunnelled into the insulator they are free to move within the valence or conduction band of the insulator. It is important to stress that this mechanism is typically the case for thick oxides and high electric fields.

If electrons are activated by the high electric field directly into the conduction band the situation is known as Schottky emission. If, however, the electrons are activated not directly into the conduction band, but into the next potential sites, usually in additional energy states called traps, which are created by structural defects in dielectric, this process is named Poole–Frenkel emission. PF mechanism seems to be the dominant mechanism in case of HfO<sub>2</sub>.<sup>26,27</sup>

### **1.1.3. Breakdown Voltage and reliability**

The dielectric breakdown is also important parameter which has to be taken into consideration while it is the determining factor in the reliability (oxide lifetime) of MIM devices. Reliability can be defined as a probability that MIM device will perform a required function under stated conditions for a stated period of time. The field  $E_{bd}$  at which the dielectric breaks down is referred to breakdown strength of the material. Depending on the applications, the values of breakdown strengths as high as 10 MV/cm are required for

alternative high–*k* oxides. At these high electric fields, a gradual degradation of the insulating oxide occurs resulting in growth of conduction paths which means that the insulating properties of dielectrics are irreversibly lost. This time-depending-dielectric-breakdown (TDDB) phenomenon and its relation to the proceeding degradation are intensively investigated. It is well known that defects, contamination and metal impurities are hazardous for a sufficient lifetime of the MIM capacitors, but even today, a complete understanding of the oxide breakdown problem, and its implications on the reliability of real devices, is rather complicated and not been understood yet.

Nevertheless, simplified physical mechanisms, which explain the breakdown mechanisms in the case of SiO<sub>2</sub>, exist. By far, the most developed ones are so called  $E^{28}$  and  $I/E^{29}$  models. The I/E model suggests that the breakdown process is current driven and should show an exponential dependence with I/E, due to FN conduction, but his model has a singularity at E=0 which is troublesome. This singularity would imply that the dielectric will not degrade in the absence of electric field but it is known that thermal/diffusion processes degrade all materials over time, even in the absence of electric field.

The *E* model also called the Thermochemical model explains that a local electrical field distorts polar molecular bonds thereby lowering the enthalpy of activation energy required for bond breakage in the dielectric. Although this model fits better the experimental results collected over a wide range of electric fields, and temperatures than the 1/E model does, it can not also explain all the processes during the breakdown. In addition, this model also establishes the relationship between  $E_{bd}$  and the dielectric constant *k*:

$$E_{bd} \sim (k)^{-1/2}$$
 (1.4)

This relationship is visually illustrated in Fig.1.7 and is found to be very universal and is in the good agreement with k values of dielectric materials as a function of breakdown strength.



Fig. 1.7. Breakdown strength versus dielectric constant. Correlation from Eq. 1.4. is valid nearly for two decades of dielectric constant.<sup>28</sup>

#### **1.1.4. Quality factor**

Unfortunately, no dielectric material is perfect and as a result the loss, sometimes called  $tan\delta$  or dissipation factor, of a capacitor must be recognized. In the case of MIM capacitors, losses are one of the most important issues for reactive elements. High-performance MIM devices must have low losses or high  $1/tan\delta$  ratio which is called quality factor. The quality factor, usually termed Q, can be defined at a frequency f by

$$Q = 2\pi f \text{ (energy stored/average power dissipated)}$$
(1.5)

where Q is dimensionless and is proportional to the ratio of energy stored C to energy lost per unit time. These losses are due to electrode resistance  $R_S$  and resistance of dielectric  $R_P$ ). It is affected by the cut–off frequency of the component, fixed by C and inductance  $L_S$ as schematically expressed in Fig. 1.8.<sup>10</sup>



Fig. 1.8. Frequency dependent behaviour of capacitor Q factor.

As can be seen, the quality factor is affected by the resistance of the dielectric at lower frequencies and is mainly influenced by the capacitance of the dielectric and resistance of the electrode material at middle frequencies. Achieving the highest capacitance density while preserving the other capacitor properties (leakage, stability and reliability) is the best way to diminish both the size and parasitic influences of metal electrodes, and thus improve the Q factor.

## **1.2.** Alternative high-k dielectrics

All these listed and briefly explained requirements could be fulfilled by one of the two approaches: 1) Introduction of high–k materials with the k value in the range of 25–150; or 2) integration of three–dimensional (3D) MIM capacitors. Both ways were selected and described in this work.

A good alternative dielectric should have a k value higher than that of SiO<sub>2</sub>, a high band gap to limit the leakage currents, a high breakdown field to meet reliability specifications and has to be deposited at a temperature below 400°C to be compatible with BEOL constrains.

Al<sub>2</sub>O<sub>3</sub> was first investigated as a dielectric to replace Si<sub>3</sub>N<sub>4</sub> while it presents large band gap and breakdown fields, but it's highly nonlinear properties observed with TiN electrodes limits its applications to capacitor applications.<sup>30, 31</sup> HfO<sub>2</sub><sup>32</sup> and Ta<sub>2</sub>O<sub>5</sub><sup>33</sup> are the most widely investigated materials for MIMs due to their readiness in DRAM and transistor applications. For more complex research, metal oxides such as SrTaO, TiTaO, PrTi<sub>x</sub>O<sub>y</sub> or BaHfO<sub>3</sub> are investigated as alternative dielectrics to name a few.<sup>34,35,36,37</sup> A very nice review of high–*k* dielectric materials for microelectronics is published by Wallace et al.<sup>38</sup>. The main properties of widely used alternative dielectrics are summarized in table I.

High– <i>k</i> dielectric	Band gap [eV]	k value	Breakdown strength [MV/cm]	Crystal structure
SiO <sub>2</sub>	9	3.9	15	amorphous
Si <sub>3</sub> N <sub>4</sub>	5.3	7	10	amorphous
Al <sub>2</sub> O <sub>3</sub>	8.7	9	8	Crystalline >900°C
HfO <sub>2</sub>	5.9	16–40	6	Crystalline >450°C
Ta <sub>2</sub> O <sub>5</sub>	4.5	25	5	Crystalline >600°C
SrTaO	4.5-4.8	20–100	4	Crystalline >700°C
TiO <sub>2</sub>	3.5	80	2	Crystalline >400°C
TiTaO	3.1	20–26	Soft breakdown	Crystalline >900°C,

Table I. Properties of alternative dielectrics.

The choice of the oxide for MIM applications is limited to the thermal budget issue mentioned above. For example a lot of ternary oxides, which have a perovskite structure, including BaHfO<sub>3</sub> or BaZrO<sub>3</sub> have a k value of around 80 but higher temperatures (typically in the range of 800–900°C) are required for crystallization. Ferroelectric PbZrTiO<sub>3</sub> (PZT) can reach the relative permittivity of around 800°C but again it needs the temperature for crystallization of 700°C. On the contrary, there are some perovskite materials that crystallize at lower temperature. S. Van Elshocht et al. found that SrTiO<sub>3</sub> (STO) crystallizes in a perovskite structure already at 550°C which boosts the k value to 153.<sup>39</sup>

All these mentioned high–k dielectrics can be deposited either by Physical Vapor Deposition or Chemical Vapor Deposition based methods. The vapor phase techniques Metal Organic CVD (MOCVD) or Atomic Layer Deposition (ALD) are more preferred than PVD techniques for the deposition of these oxides, as they offer the potential for large area growth, and have advantages of good composition control, high films uniformity, good doping control, and most importantly, they give excellent conformal step coverage on non–planar device geometries.

The comparison of MIM results of investigated oxides is rather difficult while reports on high–k dielectrics were often done with different unit capacitance, with different voltage and thermal linearity measured at different frequencies, i.e., 100 kHz, 500 kHz or 1 MHz. In addition the reported leakage is also measured with different bias and temperatures. The properties of the alternative dielectrics, which were investigated in this work, are briefly presented in the next sections.

#### <u>1.2.1. HfO<sub>2</sub></u>

Among various high–k dielectric candidates, HfO<sub>2</sub> has been intensively investigated as gate dielectric of MOSFETs due to its high dielectric constant, excellent thermal stability and high band gap.<sup>40</sup> Indeed, Hf based gate insulators are nowadays standard in Intel transistors.<sup>41</sup> Due to the proper electrical behaviour of MOS capacitors with HfO<sub>2</sub>, researches have investigated it as a possible dielectric for MIM applications. HfO<sub>2</sub> has a relatively high band gap of ~ 5.9 eV and a relatively wide range of permittivity which depends on its crystalline phase. Under standard conditions HfO<sub>2</sub> tends to crystallize in the monoclinic phase with a k value of ~16, with a decrease of k value compared to the amorphous phase (which has a k value of ~ 20), while cubic phase has almost twice this permittivity.<sup>39</sup>

MIM capacitors have been studied for RF and analog/mixed signal technologies using HfO<sub>2</sub> as dielectric which can be obtained by various techniques, such as reactive sputtering<sup>42</sup>, Pulsed Layer Deposition (PLD)<sup>43</sup>, ALD<sup>32</sup> or MOCVD.<sup>44,45</sup> Reported capacitance densities vary from 3 to 13 fF/ $\mu$ m<sup>2</sup> depending on the dielectric thickness. The thickness also influences the nonlinearity coefficients  $\alpha$  from 831 to 45 ppm/V<sup>2</sup>. Observed leakage currents are in the range from 1.55 · 10<sup>-6</sup> to 2 · 10<sup>-9</sup> A/cm<sup>2</sup> depending on the measured temperature and voltage.

Although a variety of precursors have been investigated and tested for obtaining HfO<sub>2</sub> thin films, unfortunately, there were a number of problems associated with them. For instance HfCl<sub>4</sub> is a low volatility solid which needs substrate temperatures of at least 800°C for oxide deposition.<sup>46</sup> The  $\beta$ -diketonates, [Hf(thd)<sub>4</sub>] (thd = 2,2,6,6,-tetramethyl-3,5,heaptadionate. [Hf(acac)<sub>4</sub>] (acac = acetvacetonate) were also tested<sup>47</sup>, but these precursors are relatively involatile and also require relatively high growth temperatures. Furthermore, oxides films deposited from  $\beta$ -diketonates are often contaminated with carbon. Although high purity HfO<sub>2</sub> films have been grown at 300°C using the eight-coordinate monomers [Hf(NO<sub>3</sub>]<sup>48</sup>, but the long term stability of these complexes is a problem. The organometallic precursors, [(MeCp)<sub>2</sub>HfMe(mmp)] (Cp = cyclopentadienyl) (mmp = 1methoxy-2-methyl-2-proposide) and  $[(MeCp)_2HfMe(OPr^i)]$  (OPr<sup>i</sup> = isoproposide) have been also used to deposit HfO<sub>2</sub>.<sup>49</sup> Hf alkoxides are attractive MOCVD precursors as they allow low deposition temperatures, and under optimum growth conditions allow the deposition of carbon-free films. However, the majority of simple [Hf(OR)<sub>4</sub>] complexes are dimeric or polymeric with limited volatility due to the tendency of Hf<sup>V</sup> atoms to expand their coordination sphere to six seven or eight.<sup>50</sup> The use of the sterically demanding  $[OBu^{t}]$  (OBu<sup>t</sup> = tertbutoxide) or  $[OPr^{t}]$  ligands produces the volatile monomeric complexes  $[Hf(OBu^{t})_{4}]^{51}$  or  $[Hf(OPr^{i})_{4}]^{52}$  which can be used as precursors for HfO<sub>2</sub>. However, these 4-coordinate complexes are highly reactive and moisture sensitive with a short life time and a tendency to block the MOCVD reactor inlet lines. [Hf(mmp)<sub>4</sub>], which contain the donor functionalized ligand mmp are more saturated and therefore much less moisture sensitive than  $[Hf(OBu^{t})_{4}]$ . Since the initial study by Bastianini<sup>53</sup> on the MOCVD of ZrO<sub>2</sub> using  $[Zr(NEt_2)_4]$  (Et = Ethyl), the analogous Hf alkylamides have been intensively investigated. Tetrakis(dimethylamido)hafnium [Hf(NMe<sub>2</sub>)<sub>4</sub>] is solid at room temperature, but it becomes liquid at higher temperatures and is also used as CVD precursor.<sup>54</sup> A source that is liquid and stable at room temperature can be obtained by substituting CH<sub>3</sub> with  $C_2H_5$  in the precursor molecule and tetrakis(ethylmethylamido)hafnium [Hf(NEtMe)<sub>4</sub>]<sup>55</sup> or tetrakis(diethylamido)hafnium [Hf(NEt<sub>2</sub>)<sub>4</sub>]<sup>56</sup> are considered as being novel precursors for MOCVD. The biggest advantage of these alkylamides is that they allow growing HfO<sub>2</sub> films at very low deposition temperatures (starting from ~ 250°C) due the high boiling point (~ 40–110°C at 0.1 Torr). However, a potential disadvantage of [Hf(NR<sub>2</sub>)<sub>4</sub>] complexes is their reactivity with air and moisture that could lead to difficulties in handling and storage, but maintaining it in the proper way the precursor in this study was kept for very long time (> 3 years) without any changes in films properties. Tetrakis(ethylmethylamido)hafnium (TEMAHf) was chosen as a precursor for HfO<sub>2</sub> in this work, because it is liquid at room temperature, has convenient thermal characteristics (high vapor pressure of ~ 14 mbar at 140°C), reasonable reactivity with oxygen and high growths rates.

#### <u>1.2.2. Ta<sub>2</sub>O<sub>5</sub></u>

Ta<sub>2</sub>O<sub>5</sub> appears to be the candidate of choice since it has been in use in DRAM for more than a decade. It has a *k* value of 25, a bind gap of 4.5 eV and can be deposited at low temperature, < 450°C, making it suitable for the fabrication of MIM structures in the BEOL that requires a low thermal budget. By far the best recorded single Ta<sub>2</sub>O<sub>5</sub> MIM possesses 5 fF/µm<sup>2</sup> and  $\alpha$  value of 13 ppm/V<sup>2</sup> with TiN metallization.<sup>30,57</sup> Despite the good properties of linearity a reported leakage current density of these films is ~ 5.5  $\cdot 10^{-4}$  A/cm<sup>2</sup>, which is about three orders of magnitude higher compared to the ones of HfO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>. This poor leakage could limit its use in mobile applications, but these high leakage currents can be engineered by integration of electrodes with a higher work function and better chemical stability with Ta<sub>2</sub>O<sub>5</sub>, such as Ru or Pt<sup>58</sup>. Remmel et. al.<sup>59</sup> claimed that the leakage of Ta<sub>2</sub>O<sub>5</sub> based MIM capacitors is heavily dependent upon the quality of dielectric/electrode interface and the leakage currents can be suppressed to the level of  $10^{-8}$  A/cm<sup>2</sup> at 1 V.

There are several deposition techniques available for the  $Ta_2O_5$  films, such as more recently, MOCVD<sup>18</sup>, ALD<sup>60</sup> or Plasma Enhanced CVD (PECVD). For CVD of  $Ta_2O_5$  thin films various precursors have been studied so far. Tantalum halides (TaX<sub>5</sub>,

X = F, Cl) are solids and suffer from low volatility and the difficulties in delivery. <sup>61,62</sup> The most commonly used liquid precursor is  $[Ta(OEt)_5]_2$ . It has a relatively low vapor pressure but the films contain carbon impurities.<sup>63</sup> Senzaki et. al. demonstrated that tertbutylimido-tris(diethlyamido)tantalum, t-BuN=Ta(NEt<sub>2</sub>)<sub>3</sub>, (t-Bu = tertbutyl) (TBTDET) in combination with oxygen could be successfully applied to provide Ta<sub>2</sub>O<sub>5</sub> films in CVD process at the temperatures as low as 400°C.<sup>64,65</sup> TBTDET was chosen and used in this work.

#### <u>1.2.3. Sr-Ta-O system</u>

A possible solution to increase the dielectric permittivity of  $Ta_2O_5$  is to mix it with SrO to form strontium tantalates. Several phases in the SrTaO system have been reported and could be written under the  $Sr_xTa_2O_{5+x}$  formula, where x could be 1, 2, 4, and 6.<sup>66</sup> The  $Sr_5Ta_4O_{15}$  has been also observed.<sup>67</sup> Recently,  $SrTa_2O_6$  (STA) has been discussed in addition as it has promising properties in the amorphous form, which has a *k* value of 40, as well as in the crystalline form, which is around 100.<sup>68</sup> Some other ceramics of strontium tantalates and their *k* values are summarized in Fig. 1.9.<sup>66,67,69</sup>



Fig. 1.9. Dielectric constants of SrTaO bulk materials as a function of Sr content.

Different phases of STA, which contain perovskite–like building blocks, are known for some time, but the processing of ceramics needs high temperature.<sup>70</sup> However, along with the development of CVD methods for thin films of ferroelectric SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> (SBT), precursors became available, which allow for a straightforward depositions of STA thin films by Chemical Solution deposition (CSD)<sup>71</sup> sol–gel<sup>72</sup>, ALD<sup>73</sup> or MOCVD.<sup>74</sup>

Conventional strontium and tantalum precursors in CVD include  $Sr(thd)_2$  or  $Sr(thd)_2$ -tetraglyme (tetraglyme = 2,5,8,11,14-Pentaoxapentadecane) and  $Ta(OC_2H_5)_5$  or  $Ta(OPr^i)_4(thd)$ . However, these precursors are generally incompatible, because of their different physical properties and decomposition characteristics. A potential solution to this problem is the use of so called single–source precursors such as Sr-Ta alkoxides that contain the elements required in the oxide films in a single stoichiometric compound. A potential advantage of single–source precursors is that the metal/metal ratio in the precursor should be also matched the ratio in the deposited film.

Complexes such as  $Sr[Ta(OEt)_6]_2$  have been investigated for CVD of SBT, but a potential disadvantage of these precursors is that they can decompose in the gas phase after vaporization, leading to a separation of the  $[Sr(OEt)_2]$  and  $[Ta(OEt)_5]$  components. In order to stabilize these heterometal complexes and inhibit decomposition, bidentate donor-functionalized ligands such as dimethylaminoethoxide (dmae) or methoxyethoxide (me) have been introduced to produce the novel  $Sr[Ta(OEt)_5(me)]_2$  and  $Sr[Ta(OEt)_5(dmae)]_2$  complexes, which have been shown to undergo less dissociation than the parent  $Sr[Ta(OEt)_6]_2$ . These two complexes were tested in this work.

The thin films of STA have been investigated as gate dielectric for MOS transistors<sup>75</sup> as well as in MIM capacitors. Chae et. al<sup>76</sup> and Goux et. al<sup>77</sup> reported that the obtained *k* value of amorphous films was ~ 25, and the leakage current was as low as  $10^{-10}$  A/cm<sup>2</sup>. These amorphous layers could be crystallized by post–annealing at a temperature  $\geq$  700°C. The orthorhombic phase was dominant within the broad range of compositions (Sr/Ta 0.4–0.7) and for stoichiometric SrTa<sub>2</sub>O<sub>6</sub> the dielectric permittivity reached the values of 100–110 but the leakage currents decreased by 2–4 orders of magnitude. <sup>74</sup> The reported *C–V* nonlinearity value  $\alpha$  for 20 nm STA film was 300 ppm/V<sup>2</sup>.<sup>77</sup>

#### <u>1.2.4. Ti–Ta–O system</u>

TiO<sub>2</sub> is a potential candidate, since it displays very high k value of ~ 80, but the small band gap (3.5 eV) and the corresponding small (1.2 eV) conduction band offset to the Si directly correlate with high leakage currents, making the material unlikely for device applications. Another factor that causes high leakage currents is the crystallization of TiO<sub>2</sub>, which starts even at low temperatures such as 400°C.

To overcome these problems  $TiO_2$  can be mixed with  $Ta_2O_5$  to avoid the crystallization of  $TiO_2$  and to increase the conduction band offset. Additionally, the dielectric constant can be increased by mixing these oxides. It was shown by Cava back in 1995, that for ceramic bulk materials (processed at 1400°C) the dielectric constant of  $Ta_2O_5$  can be increased by nearly a factor of four – from 35 to 126 – through the addition of 8 % titanium oxide.<sup>78</sup> The variation of dielectric constants in  $(Ta_2O_5)_{1-x}(TiO_2)_x$  ceramics is illustrated in Fig. 1.10.



Fig. 1.10. Variation of dielectric constant in  $(Ta_2O_5)_{1-x}(TiO_2)_x$  ceramics at 20°C as a function of composition x.<sup>78</sup>

The possible explanation of this high–k value could be related with the metastable monoclinic phase of the particular composition of the ceramic crystal. The crystal structure of Ta<sub>2</sub>O<sub>5</sub> itself is complex, involving highly distorted TaO<sub>7</sub> and TaO<sub>6</sub> coordination

polyhedra, in a structure whose periodicity is known to be sensitive to small quantities of additives.<sup>79</sup> The authors claimed that accommodation of Ti atoms in the distorted coordination geometries afforded by the  $Ta_2O_5$  structural framework is what causes the enhancement of the dielectric constant in the present case.

Very few literature reports exist which deal with TiTaO thin films although the bulk properties are particularly very promising. Gan et. al. studied the dielectric properties of  $(Ta_2O_5)_{1-x}(TiO_2)_x$  thin films deposited by rf magnetron sputtering.<sup>80</sup> The deposited films were amorphous and had a maximum k value of 30 for 8 % doping of TiO<sub>2</sub>. The annealing forces layers to crystallize to the mentioned metastable phase and the k value was boosted to 55, but is still much lower than the value reported on bulks.

An attempt of depositing TiTaO films by CVD at 500°C using two starting precursors:  $[Ta(OEt)_4(dmaae)]$  (dmae = dimethylaminoethoxide) and  $[Ti(OEt)_2(dmae)_2]$  was also reported.<sup>81</sup> Only amorphous layers were reported for low titanium concentration. Nevertheless, the film deposited from 67 % dissolution presented very slight reflection peaks which allowed identifying the TiO<sub>2</sub> anatase structure.

The only results of TiTaO based MIM capacitors were reported by Chiang et. al.<sup>82</sup> Amorphous, 17 nm thick Ti<sub>x</sub>Ta<sub>1-x</sub>O (x~0.6) stacks with TaN/Ta as bottom electrode were obtained. High capacitance density of 23 fF/ $\mu$ m<sup>2</sup> was obtained for the films grown at 400°C, giving a high–*k* value of ~ 39. It is know that TiO<sub>2</sub> has large leakage current due to its conduction through grain boundaries of the polycrystalline films. In contrast with TiO<sub>2</sub> leakage behaviour, TiTaO MIM capacitors have ~ 5 to 7 orders of magnitude lower leakage currents (1.2·10<sup>-6</sup> A/cm<sup>2</sup>) than that of TiO<sub>2</sub> devices. The extracted quadratic voltage linearity *a* was 81 ppm/V<sup>2</sup> at 1 GHz.

#### **1.2.5. Multilayers of dielectrics**

Since no single layer high–*k* dielectric can satisfy all the ITRS requirements of high unit capacitance with low leakage and alpha value, there are numerous attempts in engineering such high–*k* dielectric stacks in recent years. From a) sandwiching  $Ta_2O_5$  between  $Al_2O_3^{83}$  to b)  $Ta_2O_5/Al_2O_3$  stack layers<sup>30</sup> to c) the intermixing film of Hf-Al-O<sup>84</sup> to d) multiple laminates of  $Al_2O_3/HfO_2/Al_2O_3^{85}$  and  $Ta_2O_5/HfO_2/Ta_2O_5$  multilayered dielectric stacks.<sup>57</sup> Each of these dielectric architecture aims is to merge the best properties of each single material in a new MIM stack. For instance, the leakage current can be

reduced via increasing the energy band gap by intermixing HfO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> and improving the interface condition between the electrode and the oxide. Indeed, the leakage current has improved compared to the single layer of those dielectrics, however, the voltage linearity has also degraded due to the Al<sub>2</sub>O<sub>3</sub>. The price to pay for decreasing leakage current is the reduction of capacitance because the total capacitance of the stack is defined by that of the lowest *k*. Al<sub>2</sub>O<sub>3</sub> has a *k* value of 9 and therefore reduced capacitance density from 2.86 to 2.47 fF/µm<sup>2</sup> when Al<sub>2</sub>O<sub>3</sub> barrier increased from 0 to 3 nm, while keeping the constant thickness of HfO<sub>2</sub> (57nm).<sup>86</sup> Therefore, one would prefer to employ films with similar dielectric constants. The Ta<sub>2</sub>O<sub>5</sub>/HfO<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub> stack with NH<sub>3</sub> plasma treatment of both interfaces exhibits a capacitance density of  $4 \text{ fF}/\mu\text{m}^2$  and leakage current density of  $\sim 1 \cdot 10^{-7} \text{ A/cm}^{2.57}$ 

Efforts have also been made to improve the leakage behaviour and alpha value of  $HfO_2$ , by doping it with Terbium (Tb).<sup>87</sup> It has been shown that addition of 4 % of Tb improves the alpha value from 4631 ppm/V<sup>2</sup> to 2667 ppm/V<sup>2</sup> and leakage current density decreases by one order of magnitude. This improvement has been attributed to the reduced number of traps when doped with Tb. Kim et al. demonstrated another well-engineered high–*k* stack of SiO<sub>2</sub>/HfO<sub>2</sub>. <sup>88</sup> The authors combined the effect of the negative parabolic C–*V* curve of SiO<sub>2</sub> with the strong positive parabola of HfO<sub>2</sub>. Capacitance voltage nonlinearity of 14 ppm/V<sup>2</sup> and the capacitance density of 7 fF/µm<sup>2</sup> were achieved for a 12 nm MIM stack.

## **1.3. 3D architectures**

However, achieving high densities with planar architectures still faces the limitations associated to high–k materials: capacitance above 5 fF/µm<sup>2</sup> can hardly be reached without degrading electrical reliability parameters. The architecture for module integration has to evolve to further increase in capacitance density. In this way, three–dimensional damascene MIM capacitors with increased inter–electrode area are proposed by adding a deposition of the bottom electrode before the dielectric layer. This point is illustrates in Fig. 1.11 b) and is compared to a standard planar MIM architecture in Fig.1.11 a).

Employment of such 3D MIM capacitors allows increasing the capacitance density by a factor of three or higher, depending on the width and depth of trenches compared to planar approaches.<sup>89</sup> In this point conformal deposition techniques such as AVD or ALD are applied and make such approach feasible.



Fig. 1.11. Schematic cross-sections of damascene MIM capacitors integration among interconnect levels (Metal 2 and Metal 3) for a) a planar architecture and b) a high density 3D architecture.

These architectures were successfully integrated with  $Si_3N_4^{90}$  to reach capacitance densities of 5 fF/µm<sup>2</sup> and 17 fF/µm<sup>2</sup> with Ta<sub>2</sub>O<sub>5</sub>.<sup>91</sup> The extracted other criteria (i.e. leakages, breakdown voltages) were similar to those obtained using a conventional planar architectures. The 3D architectures can be also extendable to deeper trenches (up to 1:10) to reach higher densities. In this way, further capacitance density increases were demonstrated: 30 fF/µm<sup>2</sup> by integrating the MIM structure with Ta<sub>2</sub>O<sub>5</sub>/HfO<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub> dielectrics among a 3 µm thick Cu level,<sup>92</sup> and 35 fF/µm<sup>2</sup> with Al<sub>2</sub>O<sub>3</sub> by extending the MIM capacitor on multiple interconnect levels.<sup>93</sup>

### **1.4. TiN and TaN electrodes**

For forming the MIM stack it is critical to have good metal bottom electrodes. Titanium Nitride (TiN) is a material with many remarkable properties (e.g. extreme hardness or corrosion resistance) which led TiN to be used in a wide range of applications.<sup>94,95,96</sup> Relatively high conductivity, chemical inertness, suitable work function and diffusion barrier properties of TiN have led to its employment in semiconductor Al metallization technologies<sup>97</sup>. A "diffusion barrier" layer means that TiN is placed between two metal or semiconductor layers to prevent intermixing and undesired interactions, while still permitting electrical current to flow.

The main properties of TiN are summarized in Table II and compared to those of TaN. TiN is stable over wide compositional ranges. The primary nitride phase, TiN, crystallizes in rock salt structure with a lattice parameter of 4.24 Å. The increase or decrease of the N content influences the external properties such as color or lattice constant. For example, the lattice parameter and the hardness are observed to be maximal for stoichiometric TiN.<sup>98</sup>

	TiN	TaN
Structure	cubic	hexagonal
Range of composition	TiN <sub>0.5-1.1</sub>	TaN <sub>0.5-1.6</sub>
Colour	golden	golden
Density [g/cm <sup>3</sup> ]	5.4	13.7
Melting point [°C]	2950	3090
Refractive index (544 nm)	1.89	2.2
Resistivity (bulk) [ $\mu\Omega$ ·cm]	~ 20	~ 200
Work Function [eV]	4.7 -5.0	4.4

Table II. Properties of TiN and TaN (Assembled from<sup>99,100</sup>)

The properties of TiN are extremely sensitive not only to the nitrogen fraction, but also to impurities as well, especially oxygen. Controlling oxygen content is of extreme importance, since the free energy of formation for titanium oxides are much more favourable than for TiN and some amount of undesirable titanium oxide or titaniumoxynitride may form even with the small amount of oxygen present.<sup>101</sup> It is known that a dense amorphous and insulating interfacial oxide grows on the surface of TiN and TaN even at room temperature<sup>102,103</sup> and can affect capacitance density or capacitance voltage linearity. This effect as well as incorporation of oxygen in TiN layers and its influence on the resistivity will be discussed in more details in *chapters III* and *IV* respectively.

TiN is most commonly deposited by reactive sputtering,<sup>104,105,106</sup> often from a titanium metal target in a nitrogen–containing atmosphere. Sputtered films can be produced with a good stoichiometry control and purity, and resistivity as low as  $30-40 \ \mu\Omega$ ·cm, but conformality is difficult to achieve. The non-line-of-site techniques such as MOCVD<sup>107,108,109</sup> or ALD<sup>110</sup> offer many advantages such as high growth rate and especially good conformality for deposition in trenches.

The oldest CVD techniques employed TiCl<sub>4</sub> as a precursor, with ammonia or nitrogen as oxidants. TiCl<sub>4</sub> based TiN thin films have shown good step coverage with an aspect ratio of 7, as well as reasonable resistivities of few hundred  $\mu\Omega$ ·cm.<sup>111,112,113</sup> However, this inorganic chemistry for CVD TiN suffers from some severe drawbacks. Chlorine contamination in TiN films leads to serious corrosion in Al/Cu metallization. For reducing the content of chlorine to a low level (<1 at. % Cl), high substrate temperatures of more than 600°C are needed. The high-temperature process, however, cannot be applied in modern multilevel metallization schemes where other temperature sensitive layers are present on the substrate. An additional issue of this chemistry is the formation of adducts and NH<sub>4</sub>Cl salt particles, which brings severe problems in the production of microelectronic devices.<sup>114</sup> For lowering deposition temperature and overcoming the mentioned issues, new metal-organic precursors such as tetrakis(dialkylamido)Ti complexes and ammonia were employed to grow TiN layers at low temperatures (<400°C) which fits well with the thermal budget of BEOL. It has been understood that TiN films are deposited via transamination reaction<sup>115,116</sup> of titanium [Ti(NR<sub>2</sub>)<sub>4</sub>], where R = Methyl, Ethyl, or butyl complexes:

$$Ti(NR_2)_4 \xrightarrow{NH_3} TiN + by products$$
 (1.6)

Among these titanium amide complexes tetrakis(dimethylamido)titanium (TDMAT),<sup>117</sup> tetrakis(ethylmethylamido)titanium (TEMAT)<sup>118</sup> and tetrakis(diethylamido)titanium (TDEAT)<sup>119,120</sup> are the most studied. The first use of a metal amide compound and ammonia as precursor for obtaining nitride films was in 1990 by Fix,<sup>121</sup> who deposited TiN from TDMAT-NH<sub>3</sub> in atmospheric pressure CVD process. Later, Raaijmakers<sup>120</sup> found that films grown by low pressure CVD using TDMAT-NH<sub>3</sub> were inferior to those obtained from TDEAT-NH<sub>3</sub> under similar growth conditions. Films from TDMAT-NH<sub>3</sub> had higher resistivity (2400 and 660  $\mu\Omega$ ·cm), lower film density, higher oxygen and carbon content and lower conformality compared to those grown using TDEAT-NH<sub>3</sub>. This difference was explained by a minimum formation temperature of films deposited from several Ti alkylamides in air.<sup>122</sup> It was concluded that Ti alkylamides having higher molecular weight are apt to decompose at higher temperatures. This indicates a lower reactivity of heavier amides. A similar trend is expected to prevail in the case of reaction of the TDMAT and TDEAT wit NH<sub>3</sub>. Bulkier ligands are expected to be more effective in sterically hindered NH<sub>3</sub> from interacting with the metal center, thus effectively slowing down the transamination reaction. The lower reactivity of heavier Ti alkylamides is concurrent with a lower vapor pressure, however. At temperature of 60°C the vapor pressure of TDMAT is about 1 Torr, while that of TDEAT at the same temperature is only about 50 mTorr.<sup>117</sup> Because of the non-excessive reactivity to ammonia, TDEAT precursor was used for obtaining bottom as well as top electrodes for MIM capacitors in this work.

Due to the high thermal stability, chemical inertness and low resistivity TaN is also employed as a diffusion barrier in Cu metallization schemes.<sup>123</sup> It has a slightly higher bulk resistivity value compared to the one of TiN (see table II) and can also be easily fabricated using several kinds of techniques such as PVD method–reactive sputtering<sup>124,125</sup> or by MOCVD<sup>126,127</sup> with resistivity values of several hundreds  $\mu\Omega$ ·cm. In this work PVD deposited TaN substrates were used as bottom electrodes for MIM structures.
# **1.5. Deposition method**

Some process integration challenges should be realized to produce good quality thin films for MIM capacitors:

- ✓ Deposition temperature can not exceed 400°C to prevent the shorting of narrowly spaced large metal lines due to metal extrusions;
- Very thin high quality dielectric films (low defect density) with excellent thickness uniformity and control;
- ✓ Low resistivity of the electrodes and wiring to allow high switching speeds with high *Q* values, but without excessive heating.

To meet these requirements an advanced deposition technique has to be applied. In this work all thin films were deposited by Atomic Vapor Deposition (AVD). The main principles and basics of this technology will be discussed in the following section.

### **1.5.1. AVD Technology**

In the broadest sense Chemical Vapor Deposition involves the formation of a thin solid film on a heated substrate by a chemical reaction of vapor phase precursors. As CVD is a quite known deposition method, much details of it will not be presented here, but more information can be found in devoted books.<sup>128,129</sup>

Conventional CVD processes use in general gaseous precursors. They offer several advantages, such as easy composition control, uniform large area deposition and capability to cover non planar device structures. All these properties are still applicable in the case of solid/liquid precursors, but large numbers of these metal-organic sources, which are necessary for the deposition of alternative oxides, are characterized by low volatility, low thermal stability and instability in air. In classical MOCVD, the precursors are stored in containers, which are heated to a precisely controlled temperature. The obtained vapor is transported to the heated substrate where the thin film grows as the result of chemical reactions. Key steps of CVD reaction can be listed and indicated in Fig. 1.12:<sup>130</sup>

- ✓ Gas phase reactions of precursors in reactions zone to produce reactive intermediates and gaseous by-products;
- $\checkmark$  Mass transport of reactants to the substrate surface;
- $\checkmark$  Adsorption of the reactants to the substrate surface;
- Surface diffusion to growth sites, nucleation and surface chemical reactions leading to film formation
- $\checkmark$  Desorption of remaining fragments from reactions zone



Fig. 1.12. Precursor transport and reaction processes in CVD.

The difficulties of transporting low volatility metal precursors in MOCVD for obtaining complex oxides such as high-T<sub>c</sub> superconductors  $YBa_2Cu_3O_{7-\delta}^{131,132}$  or ferroelectric oxides PbTiO<sub>3</sub> and Pb(Zr,Ti)O<sub>3</sub><sup>133</sup> required a further development in MOCVD. The problem was that some metal oxide precursors such as metal alkoxides or  $\beta$ -diketonates have insufficient thermal stability to withstand heating for long periods. They can slowly decompose in the bubbler or in the inlet pipe work leading to poor layer

uniformity, irreproducible process conditions and reactor blockages or undergo annealing and crystallization, so that carrier gas pick-up rates change with time.

These challenges are successfully solved in AVD technology, which is also known as Pulsed Injection MOCVD (PI MOCVD)<sup>134</sup>. Instead of evaporating from a solid source in the bubbler, the precursor is dissolved in a liquid solvent and delivered through the stainless steel lines to pushing injectors, as sketched in Fig. 1.13. No temperature control of the Stainless Steel tanks as well as of lines is necessary and they are kept at ambient temperature prior to injection.



Fig. 1.13. Block diagram for liquid delivery (LDS) and evaporation system.<sup>135</sup>

Through the injectors (up to 4 are possible to use), which are mounted on top of the vaporizer, the liquid precursor is sprayed in discrete pulses in the micro liter range into properly heated Trijet<sup>®</sup> vaporizer. By injecting such small quantities of liquid sources into a heated volume (Fig. 1.14 a) precise precursor supply for the chemical reaction process can be obtained. The amount of each injected liquid can be controlled in a very wide range by in-situ injection frequency or digital valve opening time variation. The evaporated precursor is then transported by an inert gas to the reactor unit as shown in Fig. 1.14 b).



Fig. 1.14. a) Injection of precursor and b) more detailed cross section of the vaporizer unit.<sup>135</sup>

Just below the reactor inlet the precursor vapors reach the showerhead, where a consistent mixing of the evaporated precursor and the reactive gases like  $O_2$  or NH<sub>3</sub> occurs. The showerhead concept allows achieving good thickness uniformities (standard deviations <1%) of deposited layers. As reactive intermediates reaches a hot substrate (an example of heated 200 mm Si substrate is given in Fig. 1.15), the decomposition of the precursor takes place and growth of thin film starts, as already described in the CVD case and presented in Fig. 1.12.



Fig. 1.15. Example of heated 200mm wafer

The most important properties (precursor supply mode as a function of time) of AVD technology compared with conventional CVD and ALD are schematically shown in Fig. 1.16. While conventional CVD suffers from low efficiency and poor volatility (as mentioned above) the frequently used ALD mode (a layer-by-layer growth on the atomic scale), based on self-limiting chemistries on limited process regimes and selected chemical elements, provides good efficiencies as well as materials properties. On the other hand, this technique suffers from limited selection of precursor sources, remaining precursor-induced contamination, and is pretty time consuming.

The sandwiched plot represents the AVD mode, which enables a higher throughput thanks to the growths rates up to more than 30 nm per minute, without loosing the properties of materials. It also provides excellent control of the composition of the deposited layer by its use of one precursor per injector. Thus the composition can be tailored by both the injector frequency (i.e. number of pulses per second) and the amount of precursor per pulse allowing growing complex oxides as well as metal electrodes.



Fig. 1.16. Illustration of the differences and common properties of ALD, AVD and conventional CVD.<sup>135</sup>

# Chapter II

# 2. Experimental

# **2.1. Tricent AVD Tool**

Industrial type AVD TRICENT cluster tools were used in this work. The scheme and picture are shown in Fig. 2.1. The cassettes with the 24 wafers were introduced through the cassette holders, and then transported with Brooks wafer handling system to the metallization and oxide chambers in vacuum for further processing. The movement of wafers in the handler was done at room temperature, while both deposition chambers were always kept at 400°C and the pressure at 10 mbar. The exact details of deposition conditions for each oxide and TiN are different and will be noticed in corresponding parts of the result chapters.

Standard 8 inch p-type Si (100) wafers with 2 nm thermal  $SiO_2$  were used as starting wafers. Trenched wafers with an aspect ratio of 2:1 were used for step coverage investigation of HfO<sub>2</sub> as well as of TiN.



Fig. 2.1. A scheme of AVD cluster and picture of AVD oxide module.

# **2.2. Precursors**

As already described in the introduction, one of the biggest issues for any CVD process is to find a suitable precursor. Whatever form of CVD process takes place, the same precursor requirements generally can be applied. The requirements for AVD precursor can be summarized as follows:

- ✓ Adequate volatility to achieve acceptable growth rates at moderate evaporation temperatures;
- ✓ Stability so that decomposition does not occur during evaporation;
- A sufficiently large temperature "window" between evaporation and decomposition for film deposition;
- ✓ High chemical purity;
- ✓ Clean decomposition without the incorporation of residual impurities;
- $\checkmark$  Good compatibility with co-precursors during the growth of complex materials;
- ✓ Long shelf-life with indefinite stability under ambient conditions;
- ✓ Readily manufactured in high yield at low cost;
- ✓ Non-hazardous or low hazard risk.

Commercially available precursors, supplied by Air Liquide, Sigma Aldrich (former Epichem) or Kojundo were used in this work. All the precursors were kept in the stainless steel tanks under 1000 mbar of pressure.

The precursors were purified to minimize the content of moisture (< 100 ppm H<sub>2</sub>O) and other impurities. The solutions of precursors were filtered from the particles of al least >0,3 $\mu$ m.

#### 2.2.1. Tetrakis(diethylamido)Titanium (TDEATi)

The structural drawing of the precursor is shown in Fig. 2.2. It is a dark red liquid which has a vapor pressure of 0.5 mTorr at room temperature and a melting point of -28°C. It is air sensitive. Pure and octane diluted (0.05 M) solution were used to deposit TiN films. The precursor was evaporated at 75°C.



tetrakis(diethylamino)titanium Fig. 2.2. Structure of TDEATi.

### 2.2.2. Tetrakis(ethylmethylamido) Hafnium (TEMAHf)

Pure TEMAHf precursor was used for the depositions of HfO<sub>2</sub> and is depicted in Fig. 2.3. This precursor is a pale yellow liquid and is also moisture sensitive. It has a vapor pressure of 5 mTorr and thermally decomposes at 271°C at atmospheric pressure. A temperature of 140°C was set for the vaporizer.



tetrakis(ethylmethylamino)hafnium

Fig. 2.3. Structure of TEMAHf.

# 2.2.3. Bis[pentakis(ethoxy)methoxyethoxide)tantalum]strontium

 $Sr[Ta(OEt)_5(me)]_2$  precursor (Fig. 2.4) is a pale yellow liquid and was used in 0.05 M dilution with toluene. It fully evaporates at 310°C at atmospheric pressure; therefore the evaporator temperature was set to 200°C since the process pressure was kept in the range of 5–10 mbar.



Bis[pentakis(ethoxy)methoxyethoxide)tantalum]strontium Fig. 2.4. Structure of Sr[Ta(OEt)<sub>5</sub>(me)]<sub>2.</sub>

# 2.2.4. Bis[pentakis(ethoxy)dimethylaminoethoxy)tantalum]strontium

This  $Sr[Ta(OEt)_5(dmae)]_2$  precursor (Fig. 2.5) was also used in this study provided by different supplier. The characteristics and evaporation temperature was kept the same as in the case of  $Sr[Ta(OEt)_5(me)]_2$  0.05 M solution with toluene was used in this work.



Bis[pentakis(ethoxy)dimethylaminoethoxy)tantalum]strontium Fig. 2.5. Structure of Sr[Ta(OEt)<sub>5</sub>(dmae)]<sub>2.</sub>

# 2.2.5. Bis(isopropoxy)bis(1-methoxy-2-methyl-2propoxy)titanium

For obtaining TiTaO films,  $Ti(OPr^i)_2(mmp)_2$  was used as a Ti source. Its structure is shown in Fig. 2.6. It is a white solid which evaporates at 250°C at atmospheric pressure and decomposes at temperatures < 400°C. The evaporator temperature was maintained at 200°C to evaporate the 0.1 M solution with octane.



Bis(isopropoxy)bis(1-methoxy-2-methyl-2-propoxy)titanium Fig. 2.6. Structure of Ti(OPr<sup>i</sup>)<sub>2</sub>(mmp)<sub>2</sub>

# 2.2.6. Tertiarybutylimidtris(diethylamino)tantalum (TBTDET)

For the Ta source in TiTaO films, TBTDET (Fig. 2.7) was used. It is a yellow–orange liquid which has a temperature of evaporation of 260°C at atmospheric pressure and vapor pressure of 6 mTorr at room temperature. The evaporation was done at 200°C which is the same temperature as in the case of Ti precursor.



tertiarybutylimidtris(diethylamino)tantalum Fig. 2.7. Structure of TBTDET.

# 2.3. Structure and thickness characterization

## 2.3.1. Dual Beam Spectroscopy and Ellipsometry

The thickness of the films and their stacks was measured by KLA Tencor Spectra Fx 200 films measurement tool. It encompasses two technologies – Dual Beam Spectrometry (DBS) and Spectroscopic Ellipsometry (SE). As SE alone has limitations to describe a complex multilayer stack correctly<sup>136</sup>, SE was used in combination with DBS to determine the optical constants and thickness of the HfO<sub>2</sub>/TiN/Si stacks. For both DBS and SE, the surface of the wafer is illuminated with a broadband (visible plus ultraviolet) light source, and the reflected light is measured for all wavelengths in this range. However, the illumination and measurement methods are different for these two technologies.

In DBS, a non-polarized beam of polychromatic light ( $\lambda = 190$  to 800 nm) illuminates the wafer at vertical incidence as shown in Fig. 2.8.



Fig. 2.8. DBS optical path schematic.

The intensity, R, of the light reflected by the wafer is measured as a function of the wavelength,  $\lambda$ , using a diffraction grating and a linear diode array. The intensity of the light reflected from the wafer is normalized to the intensity of the light reflected by a reference mirror.

In SE, a linearly polarized beam of polychromatic light ( $\lambda = 240$  nm to 800 nm) illuminates the wafer at the 72° angle of incidence as indicated in Fig. 2.9. A prism separates the reflected light into its different components. The incident light goes through a rotating analyzer and the reflected light – through a fixed analyzer.



Fig. 2.9. Schematic of spectroscopic ellipsometer.

In general, the reflected light is elliptically polarized. It can be represented by a *p*-component,  $R_p$ , with polarization parallel to the plane of incidence and reflected beams, and an *s*-component,  $R_s$ , with the polarization perpendicular to that plane. The fundamental equation of ellipsometry is:

$$\frac{R_p}{R_s} = \frac{|R_p|}{|R_s|} \exp(i\Delta) = \tan \Psi \cdot \exp(i\Delta)$$
(2.1)

Where  $\Delta$  is the phase difference between the *p* and *s* components, and  $tan\Psi$  is the ratio of the *p* and *s* reflected intensities.<sup>137</sup> The standard ellipsometry parameters are  $tan\Psi$  and  $cos\Delta$ , where  $cos\Delta$  is the real part of the complex quantity,  $exp(i\Delta)$ . The SE measures the reflected light intensity as the function of polarization angle of the rotating polarizer, for the whole wavelength range, and obtains the values of the two ellipsometry parameters mentioned above. The thickness average was taken from 49 point mapping measurements.

#### **2.3.2.** X – Ray Photoelectron spectroscopy (XPS)

Of all the contemporary surface characterization methods, X-ray Photoelectron Spectroscopy (XPS) is the most widely used. A PHI Electronics XPS analysis machine, equipped with Al K<sub> $\alpha$ </sub> (1486.6 eV) radiation and hemispherical analyzer was employed to determine the composition of TiN, HfO<sub>2</sub>, Sr-Ta-O and Ti-Ta-O surfaces. The profiles of the mentioned films were investigated after sputtering with Ar<sup>+</sup> (1 keV) ions.

XPS method is based on the photoemission process<sup>138,139</sup> which can be described as following: Surface of the sample is irradiated with photons and the atoms comprising the surface emit electrons (photoelectrons) after direct transfer of energy from the photon to the core level electron. These emitted photoelectrons are then collected under an angle  $\varphi$ and analyzed with respect to their kinetic energy as illustrated in Fig. 2.10.



Fig. 2.10. The principle of XPS measurement setup.

The basic physics behind this process can be described by the Einstein equation:<sup>140</sup>

$$E_B = h\upsilon - KE \tag{2.2}$$

where  $E_B$  is the binding energy of the electron in the atom, hv is the energy of X-ray source and *KE* is the kinetic energy of the emitted electron that is measured in the XPS spectrometer. Because each core level state has a unique set of binding energies, XPS can be used to identify and determine the concentration of the elements of the surface.

While X-rays can readily travel through solids, electrons exhibit significantly less ability to do so. Only those electrons that originate within tens of angstroms below the solid surface can leave the surface without energy loss and reach the detector. This effect results form the inelastic mean free path (IMFP)  $\lambda$  of the photoelectrons.<sup>141</sup> The intensity attenuation *I* of electrons escaping from depth *d* under an angle  $\varphi$  is described by Beer-Lambert law:<sup>142</sup>

$$I(d) = I_0 \exp(-d / \lambda \cos \varphi)$$
(2.3)

Since  $\lambda$  of low energy electrons in solids corresponds to only few atomic layers, XPS is surface sensitive technique and gives information depths up to 5 nm.

#### **2.3.3.** X – Ray diffraction and X – Ray Reflectivity

X-ray diffraction is a versatile, non destructive technique that reveals detailed information about the phase composition and crystallographic structure of materials<sup>143</sup>. A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes from one another by a distance *d*, which varies according to the nature of the material. When a monochromatic X-ray beam with a wavelength  $\lambda$  is projected onto a crystalline material at an angle  $\theta$ , diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number *n* of the wavelengths. This is mathematically expressed in Bragg's Law:<sup>144</sup>

$$n\lambda = 2d\sin\theta \qquad (2.4)$$

According to this equation, we can see that if there is an absence of periodic lattice spacings d, characteristic diffraction pattern of the material can not be produced. This is the case of amorphous materials, where atoms are arranged in a random way.

Crystallization of the films was studied in Bragg-Brentano geometry (Fig. 2.11) using RIGAKU DMAX 1500 diffractometer.



Fig. 2.11. Bragg-Brentano diffractometer arrangement in XRD and XRR experiments.

In the so called specular  $\theta$ - $2\theta$  geometry to study the vertical growth orientation of the films, samples were mounted on the holder and irradiated with monochromatic CuK<sub>a</sub> radiation ( $\lambda = 0.154$  nm) under an incident angle  $\omega$ , and the reflected intensity was measured at an angle  $2\theta$ . A typical spectrum consists of a plot of the intensity versus the detector angle, which was typically 20–60° in  $2\theta$  used in this study. For the measurement of X-ray reflecticity (XRR), the same setup as described for the XRD measurements was used, but the measured angular range for  $2\theta$  was between 0° and 8° degrees. XRR was used in this work to confirm the thickness of the layers measured by ellipsometry.

#### **2.3.4. Scanning Electron Microscopy**

Cross-sections of integrated TiN/HfO<sub>2</sub>/TiN stacks and step coverage of HfO<sub>2</sub> and TiN were investigated by Scanning Electron Microscopy (SEM)<sup>145</sup>. During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal. A Hitachi S 4500 SEM tool was used for investigations of cross sections in this work.

#### **2.3.5.** Transmission Electron Spectroscopy

In Transmission Electron Microscopy (TEM) a well focused high energy beam (100–400 keV) of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through.<sup>146</sup> It exploits the very small wavelengths of high–energy electrons to probe solids at the atomic scale. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device.

Philips CM 200 was used in this study for investigation of  $HfO_2/TiN$  interfaces. The samples were prepared by mechanical polishing perpendicular to the film. The final thinning was performed by  $Ar^+$  ion polishing with 2 keV for 20 minutes. The electron beam energy of 200 keV was used in this case.

# 2.4. Structuring of MIM capacitors

#### 2.4.1. Reactive Ion Etching

Reactive Ion etching (RIE)<sup>147,148</sup> is a plasma-based dry etching technique characterized by the combination of physical sputtering with the chemical activity of reactive species. This enables the achievement of material selective etch anisotropy.

The plasma etching of TiN/HfO<sub>2</sub>TiN structures was made in a magnetically enhanced RIE tool (Applied Materials, P5000). A conventional cathode and wall temperature was kept at 60°C. TiN layer was selectively etched with HBr plasma, while HfO<sub>2</sub> film was etched by applying BCl<sub>3</sub> plasma. More details concerning the exact procedure of this etching procedure can be found in the Diploma Work of M. Fraschke.<sup>149</sup>

#### 2.4.2. Metallization by resistive thermal evaporation

Resistive thermal evaporation is one of the most commonly used metal deposition techniques.<sup>150</sup> It consists of vaporizing a solid material (pure metal, eutectic or compound) by heating it to sufficiently high temperatures and recondensing it onto a cooler substrate to form a thin film. The heating is carried out by passing a large current through a filament

container (usually in the shape of a basket, boat or crucible) which has a finite electrical resistance.

In this work, to form simple MIM test structures, pure (99,999%) Gold (Au) and Aluminium (Al) were deposited through a shadow mask. The evaporation occurred after conducting a Tungsten boat with 90 A and at the pressure of  $1 \cdot 10^{-2}$  Pa. The thickness of the electrode was ~ 150 nm and the area about  $3 \cdot 10^{-3}$  cm<sup>2</sup>.

# 2.5. Electrical characterizations

#### 2.5.1. Sheet Resistance

Resistivity is a particularly important parameter of TiN and it was extracted from sheet resistance measurements. Sheet resistance was metered by a  $R_s$  Omni map 75 wafer mapping tool in 4-point probe configuration,<sup>151</sup> which is schematically depicted in Fig. 2.12.



Fig. 2.12. Schematic of 4-point probe measurement technique.

S is the spacing of the probe in cm; l is the distance from any probe to the nearest boundary, I the test current, and V the measured voltage. It contains four thin collinearly placed tungsten wires which are made to contact the sample under test. Current I is made

to flow between the outer probes, and voltage V is measured between the two inner probes. If the sample is of semi-infinite volume and if the interprobe spacings are s1 = s2 = s3 = s, then the differential resistance can be given by:

$$\Delta R = \rho \left(\frac{dx}{A}\right) \tag{2.5}$$

Where  $\rho$  is resistivity, x is voltage between two inner tips, and A is area.

The integration between the inner probe tips (where the voltage is measured):

$$R = \int_{x_1}^{x_2} \rho \, \frac{dx}{2\pi x^2} = \frac{\rho}{2\pi} \left( -\frac{1}{x} \right) = \frac{1}{2s} \frac{\rho}{2\pi}$$
(2.6)

Due to the superposition of current at the outer two tips, R = V/2I, bulk resistivity (when thickness d >> distance *s* between probes) is defined as:

$$\rho = 2 \pi s \left(\frac{V}{I}\right) \tag{2.7}$$

Practical samples (very thin layers), of course, are of finite size, (thickness  $d \ll s$ ) and therefore correction factor a = 0.72 d/s has to be included. When substituted in equation (2.7) we get:

$$\rho = a \, 2 \, \pi s \, \frac{V}{I} = 4.53 \, d \, \frac{V}{I} \tag{2.8}$$

If both sides of Equation (2.8) are divided by d we get:

$$R_{s} = \frac{\rho}{d} = 4.53 \frac{V}{I}$$
(2.9)

where  $R_s$  is referred as sheet resistance.  $R_s$  is independent of any geometrical dimension and is therefore a function of the material alone. The significance of the sheet resistance can be more easily seen if we refer to the end-to-end resistance of a rectangular sample. From the regular three-dimensional conductor, resistance can be written as

$$R = \rho \, \frac{l}{wd} \tag{2.10}$$

(where *l* is length and *w* is width) we see that if w = l (a square) we get

$$R = \frac{\rho}{d} = Rs \tag{2.11}$$

Therefore,  $R_s$  may be interpreted as the resistance of a square sample, and for this reason the units of  $R_s$  are taken to be Ohms per square.

#### 2.5.2. Capacitance–Voltage measurements (C–V)

Capacitance versus voltage, referred to as C-V, measurements can be used to study the most basic properties of MIM capacitors. It allows obtaining capacitance values at a given bias, important parameters such as k value and capacitance–voltage nonlinearity coefficient  $\alpha$ .

C-V measurements were performed in serial mode using Agilent 4294A precision impedance analyzer. Schematically the simplified setup can be illustrated in Fig. 2.13. Characteristics were measured at a frequency of 100 KHz with AC-amplitude of 0.1 V. The bias was varied in the range from -3 V to 3 V.



Fig. 2.13. Simplified schematics of *C*–*V* measurement setup.

### 2.5.3. Current – Voltage Measurements (I–V)

Leakage currents were extracted from Current-Voltage measurements, as schematically shown in Fig. 2.14. In this study, data was collected at a probe station with a HP 4140 ampermeter, which can measure direct current (DC) currents down to picoampere (pA) range. The DC leakage current was measured at room temperature while sweeping the applied voltage typically from - 3V to 3 V.

Breakdown strengths were also obtained from (I-V) measurements by applying the most widely used technique, namely the voltage ramp. The voltage is ramped with a

constant ramp rate dV/dt, which was 0.1V/s in this work. While the current through the oxide is being measured, it increases towards higher voltage levels. When there is a breakdown, the current jumps to a high level and pass a pre-set current limit. The value of the voltage at which this happens is defined as breakdown voltage. By dividing it by the thickness of oxide we the breakdown strength in MV/cm of a particular dielectric can be calculated.



Fig. 2.14. Simplified sketch of I–V measurement circuit.

#### 2.5.4. Reliability measurements

Another technique which consists of the application of a constant voltage and measuring the time to breakdown is TDDB. In this case, a voltage, close to the breakdown voltage is selected, applied to the MIM stack and the time to breakdown is measured. The extrapolation to 10 years lifetime shows the operating voltage of the device. These measurements were also done in the HP 4140 probe station.

# Chapter III

# 3. Results and discussion of AVD TiN

# 3.1. Deposition conditions

The main part of this chapter is focused on the optimization of deposition conditions of TiN films, while up to now there are no literature reports concerning the results of pulsed injection MOCVD TiN thin films. The influence of process temperature and concentration of the TDEATi precursor on TiN layer properties such as resistivity, roughness, morphology and stoichiometry is investigated.

A standard Si(001) with 2 nm thermal oxide substrates were used for the depositions of 20 nm TiN. A process flow is depicted in Fig. 3.1 and the deposition conditions are presented in Table III. The typical thickness standard deviation for a 200 mm wafer was between 1 to 2 %.



Fig.3.1. Process of TiN preparation

	Pure TDEATi	0.05 M TDEATi
Substrate	2nm SiO <sub>2</sub> /Si	2nm SiO <sub>2</sub> /Si
Deposition Temperature [°C]	400–600	400–500
Pressure [mbar]	3	10
Evaporation Temperature [°C]	70	70
Carrier Gas	N <sub>2</sub>	$N_2$
Total Gas Flow [sccm]	2000	2000
NH <sub>3</sub> flow [sccm]	45	45
Injection frequency [Hz]	5	5

Table III. Deposition conditions of TiN

# **<u>3.2. Influence of the deposition temperature on the growth rate</u> <u>and resistivity of TiN</u>**

The effects of deposition temperature and concentration of TDEAT precursor on growth rate and TiN film resistivity were studied in the temperature range between 400°C and 600°C. Fig. 3.2 presents the deposition kinetics of TiN films obtained from pure and 0.05 M diluted (in octane) TDEAT precursors. Generally, these growth rates versus temperature curves are not very typical for standard CVD processes, where growth rate is increasing with increasing temperature (kinetic controlled region) and stabilizes at a certain temperature to enter a diffusion controlled region. In our case of TiN, the growth rates slightly decreases and have minimum growth rates at different temperatures depending on the concentration of TDEAT precursor. As can be seen, the lowest growth rate of 4.5 nm/min is achieved at 425°C for a diluted precursor, and 4.8 nm/min for the pure one at 500°C. The reason of such behaviour is probably related to the deposition temperature for TiN. Probably, the amount of TiN in the films grown at 400–500°C is almost equal, but at the optimum growth temperature the purity (and therefore the density) of the films is the highest. This is recognised by ellipsometry as the decrease of thickness. Higher amount of contaminants (C, O) at higher and lower temperatures from optimum decrease the density, increase the film porosity and therefore increase the observed thickness. Lower than

optimum temperatures result in incomplete precursor decomposition and presence of precursor organic groups in the film. Too high temperatures, due to a very high reactivity with NH<sub>3</sub>, result in such modification of ligands in precursor molecules that result again in higher C incorporation and therefore higher porosity. This explanation is confirmed the amount of Carbon detected by XPS analysis. It was found that the amount of carbon has a relation to the minimum values of resistivity. For the diluted precursor the minimum amount of carbon in TiN is 4% at 425°C. With increasing as well as with decreasing temperature, the carbon content increases to 5 % at 400°C and to 8 % at 500°C respectively. The same tendency is obtained with the pure TDEAT precursor. The contamination content of carbon (4 %) is the lowest at 500°C and the highest (6%) at 600°C.



Fig. 3.2. Growth rate vs. deposition temperature of TiN obtained from 0.05 M in octane diluted (•) and pure ( $\circ$ ) (Ti[N(Et)<sub>2</sub>]<sub>4</sub> precursors.

As shown in Fig. 3.3, the resistivity of TiN films, deposited at 400°C, is about 400  $\mu\Omega$ ·cm and is not really affected by the type of precursor. The observed value is comparable to that of 500  $\mu\Omega$ ·cm reported by Bulger et al.<sup>152</sup>, obtained by MOCVD at 340°C from a TDEAT precursor, while Kim et al. published a resistance of ~5000  $\mu\Omega$ ·cm for MOCVD TiN films from the same TDEAT precursor at 400°C.<sup>109</sup>



Fig. 3.3. Resistivity vs. process temperature of TiN films obtained from 0.05 M in octane diluted ( $\bullet$ ) and pure ( $\circ$ ) (Ti[N(Et)<sub>2</sub>]<sub>4</sub> precursors.

The separation of resistivities starts at 450°C and is very significant at a deposition temperature of 500°C. In the case of pure Ti[N(Et)<sub>2</sub>]<sub>4</sub> precursor, the raise of process temperature up to 500°C results in a significant reduction of resistivity by a factor of 2. The minimum TiN resistivity of 220  $\mu\Omega$  cm with pure Ti[N(Et)<sub>2</sub>]<sub>4</sub> precursor was achieved at 500°C. The lowest observed CVD–produced TiN resistivity value is around 85  $\mu\Omega$ ·cm as found by Ramanuja et al.<sup>153</sup> and by Yokoyama et al.<sup>154</sup> using TiCl<sub>4</sub> precursors at 700°C, but it is still approximately a factor of 2 higher than 39  $\mu\Omega$ ·cm reported for physical vapor deposited TiN films.<sup>155</sup>

### **3.3.** Oxygen incorporation in TiN films: influence on resistivity

In order to understand the difference between the minimum resistance values at different temperatures of our TiN layers, obtained from different precursor concentration, X-ray diffraction, X-ray reflectivity and X-ray photoelectron spectroscopy measurements were performed.

To check whether the films crystallize at these deposition temperatures, XRD analysis was performed for the samples deposited from pure and diluted precursors. The XRD data is shown in Fig. 3.4.



Fig. 3.4. XRD pattern of TiN grown at various temperatures from pure and 0.05 M in octane diluted precursors.

As can be seen from the figure, TiN layers deposited at 400°C from both pure and diluted precursors were amorphous according to X-ray analysis. Partial crystallization from diluted TDEAT was observed at deposition temperature of 500°C, while TiN from pure TDEAT starts to crystallize at 600°C. On the contrary, Shin et al. reported MOCVD-obtained microcrystalline TiN films deposited at 350°C from TEMAT as precursor.<sup>116</sup> Typically, TiN is produced by PVD and the films are already polycrystalline even after the deposition at lower than 200°C or even at room temperature.

The changes in structures of TiN observed by XRD were confirmed by XRR measurements, which indicated that the roughness of TiN films is continuously increasing when the higher deposition temperatures are used as shown in Fig. 3.5. The raising roughness could be explained by the starting crystallization of the TiN films. In addition, the roughness of titanium nitride layers deposited from diluted TDEAT is higher compared to those obtained from the pure precursor.



Fig. 3.5. Roughness vs. process temperature of TiN films obtained from 0.05 M in octane diluted ( $\bullet$ ) and pure ( $\circ$ ) (Ti[N(Et)<sub>2</sub>]<sub>4</sub> precursors.

It is also well known that resistivity of TiN depends of the ratio of Ti to N. To check the stoichiometry of the layers, deposited in this work, XPS analysis was applied. The atomic concentrations of Titanium, Nitrogen, Carbon and Oxygen were extracted from the bulk TiN after sputtering the samples with 1 keV. The measured Ti and N concentrations in all the samples were almost unaffected by the deposition temperature and the ratio was  $\sim 1:1$ , but the concentration, which was changing a lot, was the one of Oxygen. As indicated in Fig. 3.6a), there is a correlation between oxygen amount in the films and the process temperature. The graph shows the same tendency as resistivity vs. process temperature and gives us a hint of the resistivity dependence of the oxygen amount. This dependence of resistivities as a function of oxygen content in all the TiN films.



Fig. 3.6. a) Oxygen amount in TIN films deposited from 0.05 M in octane diluted ( $\bullet$ ) and pure ( $\circ$ ) precursors vs. process temperature. b) Resistivity as a function of oxygen content in the TiN layers deposited from pure and diluted precursors.

Combining XRD, XRR and XPS analysis, we can explain the fact that TiN layers deposited with different precursor concentrations have the minimum resistivity values at different temperatures. The microscopic structure of the films seems to have the highest impact for the variation of resistivity. Schematically it can be illustrated in Fig. 3.7. With increasing deposition temperature the crystallinity of TiN is more pronounced, therefore the diffusion of oxygen at grain boundaries is intensified and the absorption of oxygen in polycrystalline films is enhanced.<sup>156,102,157</sup> As a consequence from all the results, optimized films should remain in the amorphous state in order to prevent oxygen diffusion into the TiN films.



Fig. 3.7. A possible oxygen incorporation mechanisms in TiN thin films in the case of a) amorphous TiN, b) polycrystalline layers.

# 3.4. Thickness influence on resistivity of TiN

Due to the thermal budget of BEOL process, a temperature of 400°C was selected for further investigation of TiN thin films. Therefore, the series of different thicknesses at 400°C were deposited to investigate the resistivity dependence on film thickness. Resistivity of TiN films as a function of thickness is presented in Fig. 3.8.



Fig. 3.8. Resistivity vs. TiN thickness. The black line represents the Eq. 3.1.

As can be seen, at values lower than 20 nm, the resistivity starts to increase. The origin of this behaviour was explained by Daydal et. al, who claimed that the scattering of the conduction electrons at the surface of the film causes a reduction of the conductivity<sup>158</sup>. This effect is getting more pronounced with decreasing film thickness. According to this theory, the electrical resistivity of a film  $\rho$  can be calculated by:

$$\frac{\rho}{\rho_0} = 1 + \frac{3}{8} \frac{l_0}{d} (1 - p)$$
(3.1)

where  $\rho_0$  represents the resistivity of the bulk with the same content of impurities as the film,  $l_0$  is the mean free path of the electrons, d is the film thickness and p is the elastic scattering factor at the film surface. The electrons in amorphous films are considered to be scattered diffusely, therefore p can be neglected (p = 0). The fitted curve is shown as the solid line in Fig. 3.8, whereby the bulk resistivity is 380  $\mu\Omega$ ·cm and the mean free path is calculated as 21 nm. This mean free path value is in a good agreement with the reported by other authors.<sup>105</sup>

#### **3.5. Work function of TiN**

Another important parameter of metal electrodes is a work function. The work function of AVD TiN was extracted from high-frequency C-V measurements of metaloxide-semiconductor structures, including HfO<sub>2</sub> layers with different thicknesses as dielectric. The preparation of the samples was different from the preparation of MIM capacitors. In this case, HfO<sub>2</sub> was directly deposited on Si wafers and then transferred to nitride the chamber to be covered with TiN to form the MOS structures. Later Aluminium dots were sputtered through the hard mask at room temperature to thicken the electrode. Finally, TiN was etched with HBr to reach HfO<sub>2</sub>. The final picture of the MOS structure is shown in Fig. 3.9.



Fig. 3.9. MOS structure for determination of TiN work function.

For the calculations of the work function of TiN, flatband voltages ( $V_{FB}$ ) have to be extracted for each thickness of HfO<sub>2</sub>. The Flatband voltages were taken from all of the C-V curves (at half of the capacitance value) as shown in the example of 6 nm HfO<sub>2</sub> film in Fig. 3.10.



Fig. 3.10. An example of C-V curve of 6 nm HfO<sub>2</sub> MOS stack. The red arrow indicates the flatband voltage.

Without charges in the oxide or at the oxide-semiconductor interface, the flat band voltage simply equals the difference between the gate metal work function ( $\Phi_M$ ) and the semiconductor work function ( $\Phi_{Si}$ ). In real MOS structures,  $V_{FB}$  is further affected by fixed charges  $Q_f$  in the oxide or at the oxide-semiconductor interface and is given by:

$$V_{FB} = \Phi_{M} - \Phi_{Si} - \frac{Q_{f}}{\varepsilon_{0}k} EOT$$
(3.2)

where EOT is defined as an equivalent oxide thickness and was calculated for each MOS stack with different thicknesses of HfO<sub>2</sub> by using the following equation:

$$EOT = \frac{\varepsilon_0 k_{SiO_2}}{C}$$
(3.3)

The work function of Si is strongly dependent on the doping concentration of the substrate. In this study, doping level with boron for standard p–type silicon is in the level of  $10^{19}$  atoms/cm<sup>3</sup>. The calculated ( $\Phi_{Si}$ ) value for such doping concentration is 4.9 eV.

If the  $V_{FB}$  of a single *C*–*V* measurement is plotted versus the EOT (as shown in Fig. 3.11), the intersection with the Y axis gives the value of the flatband voltage when EOT is 0. With the knowledge of the work function of silicon and flatband voltage, the work function of TiN can be calculated by using Eq. 3.2. The determined work function of AVD TiN is 4.7 eV, which is in agreement with published values.<sup>159</sup>



Fig. 3.11. Flatband voltage versus equivalent oxide thickness (EOT) for TiN/HfO<sub>2</sub>/SiO<sub>2</sub> MOS structures.

#### **3.6.** Conclusions

The influence of various deposition conditions (process temperature, concentration of TDEATi precursor and deposition pressure) was examined for the growth of TiN films on SiO<sub>2</sub>/Si substrates by Atomic Vapor Deposition.

Resistivity values of 370–440  $\mu\Omega$ ·cm were obtained for TiN films at the deposition temperature of 400°C from pure and diluted precursors, but it varies with the temperature of deposition. The resistivity of the films could be reduced to 210  $\mu\Omega$ ·cm (when pure TDEATi is used) if the process temperature is increased to 500°C, but resistivity increases to the value of ~1300  $\mu\Omega$ ·cm if the temperature is increased to 600°C. In addition, the roughness of the films strongly increases with raising the temperature, which can be attributed to the starting crystallization of TiN. The crystallization creates grain boundaries through which oxygen can diffuse into the TiN layers. Oxygen incorporation in the films was found to be the dominant factor which affects the resistivity of TiN. In order to prevent or to minimize the diffusion of oxygen, TiN should stay in amorphous state; therefore a deposition temperature of 400°C was used. This temperature fits very well the thermal budget of BEOL. The determined minimum thickness of 20 nm and a work function of 4.7 eV make AVD–grown TiN suitable as an electrode material for MIM applications.

# Chapter IV

# 4. Results and discussion of AVD HfO<sub>2</sub>

# **4.1. Optimization AVD HfO2 deposition process**

## 4.1.1. Deposition conditions and process flow

20 nm AVD–deposited TiN films were used as substrates for further processing of MIM capacitors. Schematically it is shown in Fig. 4.1. The deposition conditions of  $HfO_2$  are summarized in Table IV.



Fig. 4.1. Process of MIM preparation with HfO<sub>2</sub> as dielectric.

Precursor	Pure TEMAHf	
Substrate	20nmTiN/SiO <sub>2</sub> /Si	
Deposition Temperature [°C]	320-425	
Pressure [mbar]	2–10	
Evaporator Temperature [°C]	140	
Carrier Gas	Ar	
Total Gas Flow [sccm]	2000	
O <sub>2</sub> flow [sccm]	1000	
Injection frequency [Hz]	5	

Table IV. Deposition conditions of HfO<sub>2</sub>

# 4.1.2. Influence of deposition temperature on growth rate and crystallinity

Growth rate dependence on the deposition temperature is given on Fig. 4.2, where two regions can be clearly observed. In the temperature range of 320–375°C, the kinetic growth regime dominates.



Fig. 4.2. HfO<sub>2</sub> growth rate variation as a function of the temperature of the process.

In this region, the growth rate of  $HfO_2$  films is controlled by the kinetics of chemical reactions either in the gas phase or on the substrate. At higher temperatures (>380°C) the growth rate becomes nearly independent of the temperature and is defined by the diffusion of reagents to the surface of the substrate. As can be seen,  $HfO_2$  layers can be deposited with ~ 12 nm/min at 320°C (kinetic region); while at 400°C, (diffusion region) films tend to grow at ~ 25 nm/min. As these two deposition temperatures, 320°C and 400°C, are suitable for BEOL applications, they were chosen for further investigation and a comparison of differences between kinetic and diffusion controlled regions.

In order to determine the microstructure of deposited  $HfO_2$  films, XRD analysis was performed. As can be seen in Fig. 4.3,  $HfO_2$  films grown at 320°C (black line) are amorphous, while the increase of the deposition temperature to 360°C (blue line) leads to the crystallization of the grown  $HfO_2$  layers. Films deposited at 400°C (red line) are also polycrystalline. The signals refer to the (111), (200) and (220) Bragg peaks of the cubic  $HfO_2$  phase. It has to be noted that for this investigation  $HfO_2$  films were obtained at the process pressure of 4 mbar.



Fig. 4.3. XRD patterns of  $HfO_2$  as a function of deposition temperature: black line –  $320^{\circ}C$ , blue –  $360^{\circ}C$  and red –  $400^{\circ}C$ .
Influence of process pressure on the microstructure of deposited HfO<sub>2</sub> films was also investigated and is shown in Fig. 4.4. In this case, the temperature of deposition was fixed to 400°C and the process pressure was varied form 2 to 10 mbar. As can be seen, the degree of crystallization of the films, deposited at 400°C, increases, when process pressure is reduced from 10 to 2 mbar. This phenomenon is not clearly understood but it could be related to the different growth mechanisms that occur at different pressures. Process pressure is an important parameter that could influence the growth mode. Probably, at lower pressure (2 mbar), the growth is more defined by surface reactions and HfO<sub>2</sub> grows polycrystalline. When the pressure is increased to 10 mbar, gas phase reactions become more dominant and we get less crystalline HfO<sub>2</sub> layers compared to the ones obtained at 2 mbar and the degree of crystallization decreases. In addition, a longer residence time of precursor at the substrate at a process pressure of 10 mbar compared to 2 mbar could also influence the growth mode and therefore affect the crystallinity.



Fig. 4.4. XRD patterns of HfO<sub>2</sub> deposited at 10 mbar (black line), 4 mbar (red line) and 2 mbar (blue line).

## 4.1.3. Influence of the crystallinity on the electrical properties of MIM capacitors

In order to characterize electrical properties of crystalline and amorphous phases of HfO<sub>2</sub> films, two different sets of deposition conditions (process temperature and pressure) are selected: 320°C and 4 mbar for getting amorphous HfO<sub>2</sub> films and 400°C and 10 mbar for polycrystalline layers. Electrical measurements, performed on the TiN\HfO<sub>2</sub>\Au MIM capacitors, revealed that the dielectric constant *k* is influenced by the process pressure and temperature. This can be seen from the plot of equivalent oxide thickness versus physical thickness which is presented in Fig. 4.5. The extracted *k* values are 18 for amorphous and 22 for polycrystalline phases, which are typical for amorphous HfO<sub>2</sub> films<sup>40,43</sup> and the cubic HfO<sub>2</sub> phase.<sup>160</sup> In addition, thin, less than 1 nm, interfacial layers are also observed by the intercept of the linear extrapolation with the Y–axis.



Fig. 4.5. EOT dependence of HfO<sub>2</sub> films, deposited at 400°C ( $\circ$ ) and 320°C ( $\bullet$ ). The solid and dotted lines represent Eq. 3.3.

As already mentioned, the fundamental parameter for the applications of MIM capacitors in mixed signal ICs is capacitance voltage linearity, which is strictly defined and must be smaller than 100 ppm/V<sup>2</sup>. The variation of  $\alpha$  as a function of HfO<sub>2</sub> film

thicknesses is shown in Fig. 4.6. Setting an  $\alpha$  value of 100 ppm/V<sup>2</sup> as upper limit (solid line in Fig. 4.6); we can extract the minimum thickness and maximum capacitance densities for amorphous and crystalline HfO<sub>2</sub> based MIM capacitors. Using the determined dielectric constants k of 18 (320°C) and 22 (400°C), we calculated capacitance densities according to equation 2. HfO<sub>2</sub> films deposited at 320°C provide capacitance density of 4.4 fF/µm<sup>2</sup> for 36 nm thickness, while 47 nm HfO<sub>2</sub> layers deposited at 400°C permit a capacitance of 4.2 fF/µm<sup>2</sup>.



Fig. 4.6. Quadratic capacitance voltage coefficient α as a function of HfO<sub>2</sub> films thickness.
The dielectric layers were grown at 400°C (○) and 320°C (●). The doted lines represent equation 1.3 and solid line the upper limit of the alpha value.

According to the requirements of ITRS, leakage current is another crucial parameter for MIM applications, particularly at higher voltages. Fig. 4.7 shows leakage current densities at 2V of HfO<sub>2</sub> MIM capacitors, processed at 320°C and 400°C. As can be seen, HfO<sub>2</sub> films, deposited at 320°C are better insulators than the ones obtained at 400°C.



Fig. 4.7. Leakage current densities at 2V in MIM capacitors versus HfO₂ film thickness. The dielectric layers were grown at 400°C (○) and 320°C (●).The dotted lines represent equation 4.1.

Due to the characteristics of metalorganic precursors, atomic vapor deposited HfO<sub>2</sub> films, grown within the thermal budget of BEOL processes ( $T_{dep} < 400^{\circ}$ C), contain hydrogen, nitrogen and carbon based defects<sup>161</sup>. These defects cause additional energy states within the band gap of HfO<sub>2</sub>. Interstitial hydrogen is calculated to act as a shallow donor in HfO<sub>2</sub>, about 0.3 eV below the conduction band edge.<sup>162</sup> Oxygen vacancies are also known to form defect levels in the band gap of HfO<sub>2</sub>. Carbon, which is presented interstitially in HfO<sub>2</sub>, forms trap levels at 0.8 eV below the conduction band edge.<sup>163</sup> Gavartin et al. calculated the energy level of nitrogen containing defects.<sup>164</sup> N as well as N<sub>2</sub> interstitial and substitutional defects form deep levels of 3 to 4 eV below the conduction band.

Due to the thermal emission process of charge carriers, Poole-Frenkel emission is becoming the dominant current mechanism. The current  $J_{PF}$  is described by:<sup>25</sup>

$$j_{PF} = j_0 \exp\left(\frac{\beta_{PF} E^{1/2} - \Phi_{PF}}{k_B T}\right)$$
 (4.1)

where  $j_0$  is the low-field current density,  $\beta_{PF} = (q^3/\pi\epsilon_0 n)^{1/2}$ , q is the electronic charge,  $\epsilon_0$  is the dielectric constant of free space, n is the refractive index, T is the temperature,  $k_B$  is the Boltzmann constant and  $\Phi_{PF}$  is the trap energy level with respect to the conduction band. The dotted lines are the fitted Poole-Frenkel currents in equation 4.1. The extracted trap energy levels are 0.35 eV (T<sub>dep</sub> = 400°C) and 0.40 eV (T<sub>dep</sub> = 320°C), indicating a slightly higher Poole-Frenkel barrier height for the HfO<sub>2</sub> layer, deposited at 320°C. However, we stress that the complete conduction mechanism is not identified yet.

Dielectric breakdown is a phenomenon when a critical electrical field applied to the layer is exceeded, resulting in the growth of conduction paths and leading to destructive breakdown. The dielectric breakdown voltages ( $V_b$ ), determined form I-V curves, are presented in Fig. 4.8. Breakdown strengths can be extracted form the slopes of the fits, presented in solid and dotted lines in Fig. 4.8. The value of 5.3 MV/cm is obtained for the HfO<sub>2</sub> films deposited at 320°C and is higher compared to the one of 4.4 MV/cm for the layers grown at 400°C.



Fig. 4.8. Breakdown voltages of MIM capacitors as a function of thickness of  $HfO_2$ , deposited at 400°C ( $\circ$ ) and 320°C ( $\bullet$ ).

As already mentioned in the introduction, no dielectric is perfect and has some losses. The parameter which shows how good is the dielectric is the quality factor, which has to be higher than 50 at 5 GHz. In this study, due to the limitations of measurement equipment, the quality factor was measured up to 1 MHz.

The comparison of quality factors of  $HfO_2$  based MIMs of two selected temperatures (320°C and 400°C) is shown in Fig. 4.9. As can be seen, there is a strong impact of the deposition temperature on the quality of the films. MIM capacitors with  $HfO_2$ , deposited at 320°C (full circles) have a quality factor of 50 and are better insulators than the ones obtained at 400°C (open circles). This difference in quality factors seems to be related to the crystallinity and therefore to the leakage of MIM capacitors. As can be seen from XRD (Fig. 4.3) and *I–V* measurements (Fig. 4.7), films deposited at 400°C are polycrystalline and more leaky than the ones at 320°C which are amorphous. Indeed, the quality factor at lower frequencies is mainly impacted by the resistance of the dielectric and if the leakage current is higher, the resistance of dielectric is also lowered.



Fig. 4.9. Quality factor of  $HfO_2$  based MIM, deposited at 400°C ( $\circ$ ) and 320°C ( $\bullet$ ) as a function of frequency.

## <u>4.1.4. Effect of TiN thickness on the quality factor of HfO<sub>2</sub></u> <u>based MIMs</u>

The quality factor of  $HfO_2$  based MIM capacitors is not only affected by the dielectric. In addition, the thickness of bottom electrode has an in influence on it. As already described in Fig. 1.8, quality factor is mainly influenced by the resistance of the electrode at higher frequencies. For this investigation, a series of TiN bottom electrode with different thicknesses were deposited and then covered each time by 50 nm  $HfO_2$  on top. Finally, Gold dots were evaporated through a shadow mask to form MIM structures.

The effect of the TiN electrodes on the quality of HfO<sub>2</sub> based MIM capacitors are studied at frequencies up to 1 MHz. The quality reduction due to finite electrode resistance can be evaluated in a simple way. The total equivalent circuit of MIM capacitors is shown in the insert of Fig. 4.10 where  $C_p$  represents the capacitance and  $R_p$  the resistance of the dielectric film.  $R_S$  represents the serial resistance and is the sum of the finite resistances of electrodes. The resistivity of the top electrode material gold is 2  $\mu\Omega$ ·cm,<sup>165</sup> and can be neglected compared to the resistivity of TiN (~400  $\mu\Omega$ ·cm).



Fig. 4.10.Quality factor vs. frequency curves of MIM capacitors with various TiN thicknesses (▼-8nm, Δ-18nm, ●-53m, □-90nm). Total equivalent circuit of MIM capacitors is shown in the inset graph.

At frequencies f above 100 kHz, the quality factor Q is dominated by the TiN:<sup>166</sup>

$$Q \approx \frac{1}{2\pi f R_s C_p}$$
(4.2)

The quality of the MIM capacitors was measured without bias voltage. As shown in Fig. 4.10, the quality curves are strongly influenced by the thickness of the TiN bottom electrode, while the capacitance value  $C_p$  is unique for all capacitors with unique HfO<sub>2</sub> thickness of 50 nm. The electrical measurements were performed by using two neighboured gold dots. As a consequence of the used set up, the determined electrode resistance can be estimated as:

$$R_s \sim \frac{\rho_{TiN}}{d} \tag{4.3}$$

whereby  $\rho_{\text{TiN}}$  represents the resistivity of the TiN bottom electrode, and *d* is the thickness of the bottom electrode.

The reduction of quality factor of MIM capacitors caused by TiN electrode resistances can be simulated by an equivalent circuit and also experimentally evaluated. The correct choice of electrode thickness as well as the conductivity is required to optimize the quality of MIM devices for high frequency applications.

#### 4.1.4. Comparison of different electrodes: TiN vs. TaN

The electrical properties of MIM capacitors are not only influenced by the dielectric itself, but also by the bottom electrode. It was reported that an interfacial reactions between the high–k material and the bottom electrode during the MIM device processing could reduce the capacitance and increase the leakage current.<sup>167</sup> Therefore, the correct choice of bottom electrode is a critical issue. In this section, TiN is compared to the TaN and the influence of different electrode material on the electrical properties such as leakage current, breakdown voltage, and quadratic voltage capacitance coefficient  $\alpha$  of HfO<sub>2</sub> based MIM capacitors will be shown. For this investigation, sputtered TiN/Ti/Si and TaN/TiN/Ti/Si wafers were used as bottom electrodes for MIM capacitors. Dielectric HfO<sub>2</sub>

was deposited by AVD at the best found conditions, namely 320°C and 4 mbar. Finally gold dots were evaporated to form MIM structures.

The X-ray diffraction pattern indicates an amorphous structure of the  $HfO_2$  layers. As shown in Fig. 4.11 just the Bragg peaks of the silicon substrate and the TiN/Ti and TaN/TiN/Ti electrodes are visible in the XRD pattern.



Fig. 4.11. XRD pattern of HfO<sub>2</sub> deposited on TaN (black line) and on TiN (red line).

The leakage current densities can be reduced by using TaN bottom electrodes, as shown in Fig. 4.12. The current mechanism seems to be determined by the contact barrier potential, but the identification of the mechanism is still in progress. The breakdown strength is also affected by the type of electrode material and the extracted value of 6.4 MV/cm for the HfO<sub>2</sub>/TaN stack is higher than that for the HfO<sub>2</sub>/TiN (4.4 MV/cm) ones.



Fig. 4.12. *I–V* curves of HfO<sub>2</sub>/TaN (black line) and HfO<sub>2</sub>/TiN (red line).

Experimental Capacitance–Voltage measurements were performed at 100 kHz in the range from -3 V to +3 V. The capacitance variations of 50 nm  $HfO_2$  on TaN and on TiN are presented in Figs. 4.13 and 4.14 respectively.



Fig. 4.13. Capacitance dependence of voltage of HfO<sub>2</sub>/TaN MIMs, monitored at 100 kHz.



Fig. 4.14. Capacitance dependence of the voltage of HfO<sub>2</sub>/TiN MIM capacitors, monitored at 100 kHz.

As can be seen, capacitors with TaN as bottom electrode are better than the ones of TiN. The capacitance density at zero bias voltage of HfO<sub>2</sub>/TiN ( $C_0 = 3.1 \text{ fF}/\mu\text{m}^2$ ) is slightly higher compared to the value of HfO<sub>2</sub>/TaN ( $C_0 = 2.8 \text{ fF}/\mu\text{m}^2$ ) and the determined  $\alpha$  value of HfO<sub>2</sub>/TaN based capacitors is 30 ppm/V<sup>2</sup> and is three times lower than  $\alpha$  of HfO<sub>2</sub>/TiN based devices (90 ppm/V<sup>2</sup>). This difference gives us a hint that the interface between the bottom electrode and the dielectric layer also plays a role on the total capacitance of the stacks.

To investigate this difference of capacitance and nonlinearities, the oxidation of both electrode materials has to be evaluated. It is well known, that TiN and TaN tend to form native surface oxides at room temperature. The thickness of native oxides on TiN and TaN surfaces is in the rage of a few nanometers, depending on the growth method and measurement technique<sup>102,103</sup>, but the oxidation mechanisms of TiN and TaN are different at higher temperatures. Oxidation kinetics of TiN surfaces is controlled by the diffusion of oxygen through the already grown surface layer.<sup>97</sup> Therefore, the oxidation mechanism of TiN follows a parabolic behaviour.

According to Tompkins et al., the growth of the oxide layer  $\Delta d_{TiN}$  can be described by:

$$\Delta d_{\text{TIN}} = \sqrt{k_{\text{TIN}} \left( t - t_0 \right)}$$
(4.4)

where  $k_{TiN}$  is the rate constant (6.6 nm<sup>2</sup>/min at 350°C) and  $t_0$  is an initiation rate (357 min at 350°C).<sup>168</sup> The time which is needed to fill the grain boundaries before starting the surface oxidation could be the reason for the initiation delay.

The oxidation of TaN at temperatures below 400°C follows a quartic time law without any initiation time. The quartic behaviour indicates that the dissolution of oxygen is the limiting process in the relevant temperature regime.<sup>169</sup> The growth of the oxide layer  $\Delta d_{TaN}$  is given by:

$$\Delta d_{TaN} = \left(k_{TaN} t\right)^{1/4} \tag{4.5}$$

where  $k_{TaN}$  is 63.3 nm<sup>4</sup>/min at 350°C.

The differences of both oxidations and the growths of oxide layers were calculated by Wenger<sup>170</sup>, and are illustrated in fig. 4.15.



Fig. 4.15. Thickness of  $TaN_xO_y$  (black line) and  $TiN_xO_y$  (red line) surface layer as a function of annealing time at 350°C.

In our study, the films of  $HfO_2$  were grown at 320°C with a constant pressure of 4 mbar. The deposition time of  $HfO_2$  was 5 min. Assuming that the calculated surface layer growth of TiN and TaN at 350°C is adaptable to the deposition temperature of 320°C, an interfacial layer of  $TaN_xO_y$  can be calculated by using Eq. 4.5. The estimated interfacial oxide thickness was around 3 nm. On the contrary, due to the initiation time of TiN, the thickness of the native surface  $TiN_xO_y$  is not affected by the growth of  $HfO_2$  and remains constant (~1.5 nm).

With the knowledge of the thicknesses of both interfaces, the corresponding capacitances of these interfaces can be calculated according to the single plate capacitor shown in Eq. 1.1, but additionally the dielectric constants are also required. Schroeder et. al. have studied the electrical properties of oxynitride interface layers and reported the dielectric constant of  $TiN_xO_y$  to be around 7.<sup>171</sup> By knowing the thickness of interfacial layers and dielectric constants, the total capacitance (without any bias at V = 0) of two capacitors connected in series can be calculated in a simple way:

$$C_{total}(V_0) = \frac{C_1 C_2}{C_1 + C_2}$$
(4.6)

where  $C_1$  characterize the HfO<sub>2</sub> layer and  $C_2$  the interfacial film.

Using a dielectric constant of 18 for HfO<sub>2</sub>, and 7 for TiN<sub>x</sub>O<sub>y</sub>, and an interfacial layer thickness of 1 nm, the theoretically calculated  $C_0$  of the dielectric HfO<sub>2</sub>/TiN<sub>x</sub>O<sub>y</sub> stack is 3.1 fF/µm<sup>2</sup>. As shown in Fig. 4.14, the calculated capacitance density is in agreement with the experimental value. Assuming the same dielectric constant for TaN<sub>x</sub>O<sub>y</sub>, and a thickness of the interfacial layer of 3 nm, a capacitance density of 2.75 fF/µm<sup>2</sup> is calculated, which is also in a very good agreement with the experimental value shown in Fig. 4.13. This correlation of the experimental and theoretical values of capacitance shows that the oxidation of both electrodes takes place and has an influence on the capacitance density as well as on the alpha value.

Since capacitance of MIMs is influenced by the interfaces, the difference in  $\alpha$  values of TiN and TaN based capacitors is caused by different thicknesses of interfacial layers. More detailed investigation will be given in the following section where the correlation between the alpha value and interfacial layer thickness will be demonstrated.

#### 4.1.5. Oxidation of TiN

As shown in the previous section that the interface between the electrode and dielectric has an influence on the electrical properties of MIM capacitors, in this part more detailed investigation will be addressed on the role of the TiN/HfO<sub>2</sub> interface with respect to Capacitance–Voltage curves of Au/HfO<sub>2</sub>/TiN MIM capacitors.

As TiN oxidises and forms an interfacial layer of TiO<sub>x</sub>N<sub>y</sub>, this interfacial layer has also its own  $\alpha$  value which affects the total nonlinearity of the stack. By using equation 1.3, the quadratic voltage capacitance coefficient  $\alpha$  can be simulated if all parameters ( $n_0$ ,  $n_2$ and  $k_0$ ) for TiO<sub>x</sub>N<sub>y</sub> are known. As the nonlinear refractive index  $n_2$  is a function of the dielectric constant and Young's modulus, it can be calculated if this Young's modulus is known. Indeed, Chappe<sup>172</sup> studied the mechanical properties of TiO<sub>x</sub>N<sub>y</sub> and reported Young's modulus to be 240 GN/m<sup>2</sup>. The linear refractive index was 2.2 as measured by ellipsometry. Dielectric constant of 7 was already introduced in the previous section. With the knowledge of  $n_0$ ,  $n_2$  and  $k_0$  for TiO<sub>x</sub>N<sub>y</sub>, the alpha value can be calculated and is illustrated in Fig. 4.16.



Fig. 4.16. Quadratic voltage capacitance coefficient  $\alpha$  as function of TiO<sub>x</sub>N<sub>y</sub> layer thickness according to Eq. 1.3.

As can be seen from this plot, to minimize the value of alpha, either the interfacial  $TiO_xN_y$  layer has to be removed or its thickness has to be increased by an additional process. As the removing of this interfacial layer is impossible because the wafers have to be heated to 320°C for the deposition of HfO<sub>2</sub>, the approach of growing TiO<sub>x</sub>N<sub>y</sub> by thermal annealing was chosen. TiN bottom electrode layers were oxidized in pure oxygen ambient and a pressure of 10 mbar at three different temperatures: 450°C, 500°C and 600°C. After this step, the temperature was set to 320°C, and standard 50 nm HfO<sub>2</sub> layers were deposited.

The increased thicknesses of the interfacial layers were confirmed by TEM and XPS analysis. TEM pictures of layers annealed at 450°C and 500°C and the as deposited film are shown in Fig. 4.17. Compared to the as deposited sample, the growth of the initial 20 nm thick TiN layer is visible when the temperature of annealing increases. Nevertheless, the TEM contrast between  $TiO_xN_y$  and TiN is too weak to distinguish between both materials.



Fig. 4.17. TEM pictures of: a) standard TiN and layers annealed at b) 450°C and c) 500°C

The increased interface can also be seen in the XPS depth profiles. Although it is very difficult to extract the thickness of interface from XPS depth profiles, the tendency shown in the Fig. 4.18 is obvious. It is clearly visible that when the annealing temperature of TiN increases, the oxygen signal is more incorporated in the profile of TiN. The slope

of the oxygen signal (full triangles in Fig. 4.18) at the oxide/electrode interface decreases, indicating the formation of a thicker interface.



Fig. 4.18. XPS depth profiles of as deposited a) and annealed TiN films at b) 450°C and at
c) 500°C. Hf (□), O (▲), Ti (○) and N (∇) content are illustrated.

In the following the effect of this increased interface on the electrical properties is investigated. Therefore, standard MIM structures were constructed and C-V measurements were performed.

As already expected, the C-V measurements revealed that the  $\alpha$  value of the total MIM stack is suppressed when the thickness of interfacial Titanium Oxynitride is increased after annealing. This effect is illustrated in Fig. 4.19, were alpha is plotted as a function of thickness of TiO<sub>x</sub>N<sub>y</sub>. In this case, the thicknesses of interfacial layers were measured by XRR. As can be seen from the figure, alpha can be reduced from 60 ppm/V<sup>2</sup> to 20 ppm/V<sup>2</sup> when the interfacial TiO<sub>x</sub>N<sub>y</sub> layer thickness increases from 2 nm to 6 nm. This result is a positive result since the alpha value should be kept as low as possible.



Fig. 4.19. Quadratic voltage capacitance coefficient  $\alpha$  versus the thickness of TiO<sub>x</sub>N<sub>y</sub>.

Unfortunately, the total capacitance density of the stack is reduced from 3  $fF/\mu m^2$  to the value of below 1  $fF/\mu m^2$  if the annealing steps are included in the processing. This tendency is shown in Fig. 4.20. The reason for such behaviour is related to the dielectric constant of the interfacial layer. The total capacitance of the MIM stack is defined by the smallest capacitance in the stack. Since the dielectric constant of TiO<sub>x</sub>N<sub>y</sub> is low, the total capacitance is dramatically reduced with increasing interface layer thickness.



Fig. 4.20. Capacitance density versus TiO<sub>x</sub>N<sub>y</sub> interface thickness.

## **4.2. Integration of HfO<sub>2</sub>**

## **4.2.1.** Process flow of integrating HfO<sub>2</sub> in BiCMOS.

In order to verify the suitability of AVD grown  $HfO_2$  as dielectric for MIM applications, 50 nm thick  $HfO_2$  films were integrated between 75 nm bottom TiN electrode and 150 nm top TiN in metallization layers. The process flow of forming MIM capacitors in 0.25 µm BiCMOS technology is illustrated in Fig. 4.21–4.24.

The complete FEOL and the first metal layer are already prepared in the previous steps. The second metal (metal 2) layer consists of TiN/Ti/AlCu/Ti/TiN stack with the thickness of 75 nm of TiN.



Fig. 4. 21. Cross section after deposition of second metal layer.

On the top of the TiN bottom electrode 50 nm  $HfO_2$  is deposited by AVD, as indicated by the red layer in Fig. 4.22.



Fig. 4. 22. Cross section after deposition of HfO2.

Then, a 20 nm AVD TiN is deposited on  $HfO_2$  to cover it. Later, a standard IHP PVD TiN is deposited to increase the thickness of the electrode to 150 nm. The structure of the MIM stack after this process is illustrated in Fig. 4.23.

TiN		
HfO <sub>2</sub>		
Metal 2		

Fig. 4. 23. Cross section of the stack after deposition of TiN.

At the last step, for contacting the bottom TiN electrode, a two step selective plasma etching procedure was applied. In the first stage, top TiN layer was selectively (15:1) etched until HfO<sub>2</sub> was reached using HBr plasma. The etching rate of ~ 100 nm/min was achieved. In the second step, the remaining HfO<sub>2</sub> film was etched by applying BCl<sub>3</sub> plasma. In this case, a selectivity of 4:1 and an etch rate of ~60 nm/min are achieved. The cross section after the etching step is shown is Fig. 4. 24.



Fig. 4. 24. Cross section after structuring the MIM capacitor.

The following steps included the passivation of structured MIM, deposition of tungsten plugs, formation of metal 3 layer, and creation of bond pads for electrical measurements. The final sketch and SEM cross–section pictures of the processed MIM capacitors with  $HfO_2$  are shown is Fig. 4.25 and Fig. 4.26.



Fig. 4. 25. Schematic of finished HfO<sub>2</sub> based MIM integration.



Fig. 4.26. SEM cross sections of HfO<sub>2</sub> MIM capacitors.

## **4.2.2. Electrical properties of integrated HfO<sub>2</sub> based MIM**

The key electrical parameter, the capacitance density, extracted from C-V measurements revealed that TiN/ 50 nm HfO<sub>2</sub>/TiN stacks possessed a capacitance density of 3 fF/µm<sup>2</sup> which is 3 a times higher value compared to standard TiN/ 50 nm SiO<sub>2</sub>/TiN capacitors with 1 fF/µm<sup>2</sup> without any changes in the thickness. The standard C-V measurement of integrated MIM with HfO<sub>2</sub> is presented in Fig. 4.27, where the capacitance of 3 fF/µm<sup>2</sup> and the voltage nonlinearity coefficient  $\alpha$  of 100 ppm/V<sup>2</sup> can be extracted.



Fig. 4.27. Capacitance dependence on voltage of integrated TiN/HfO<sub>2</sub>/TiN MIM stack. Red line represents Eq. 1.2.

Integrated MIM capacitors should also satisfy the requirement of leakage currents  $(<10^{-7} \text{ A/cm}^2)$  particularly at higher voltages and at a different operating temperatures for BiCMOS applications. Leakage current densities of HfO<sub>2</sub> based MIMs measured at 25°C (black line in Fig. 4.28) fulfil the requirements at 5 V, but leakage currents are slightly too high after the increasing the temperature to 125°C (red line in Fig. 4.28). This reason of this increase of leakage currents is related to the leakage mechanism of the dielectric. As already described in 4.1.3 section, the leakage mechanism in this case is Poole–Frenkel, which is strongly temperature dependent as can be seen from Eq. 4.1. If the temperature is increased, the electrons gain more energy to overcome the barrier height.

Reliability tests of integrated MIMs with  $HfO_2$  as dielectric were done after cutting the wafers and packaging them into single chips. The tests, performed at 100°C, revealed that 70 % of MIMs could operate for 10 years at the voltage of 9V.



Fig. 4.28. *I–V* characteristics of integrated MIM with HfO<sub>2</sub> measured at 25°C (black line) and 125°C (red line).

## 4.3. Conclusions

Uniform HfO<sub>2</sub> films were deposited by Atomic Vapor Deposition technique from an amide Hf(NEtMe)<sub>4</sub> precursor on TiN/Si substrates within a thermal budget of back-end of line (320–400°C). The best results were achieved at the deposition temperature of 320°C and process pressure of 4 mbar. Optimized MIM capacitors with 50 nm HfO<sub>2</sub> have leakages as low as  $3 \cdot 10^{-9}$  A/cm<sup>2</sup> at 2 V and a breakdown strength of 5.3 MV/cm and posses high capacitive density of 2.9 fF/µm<sup>2</sup> (k = 18) in combination with the required linearity coefficient of <100 ppm/V<sup>2</sup>. The quality factor of HfO<sub>2</sub> based MIMs is strongly affected by the thickness of bottom TiN electrode, caused by TiN resistances. This effect was presented in equivalent circuit and experimentally evaluated. To fulfil the requirement of a quality factor of 50, a thickness of 20 nm of TiN for MIM applications is needed.

Since the electrical properties of MIM capacitors are also influenced by the bottom electrode and the interface between them, the effect of different bottom electrode materials on electrical properties was evaluated in Au/HfO<sub>2</sub>/TaN and Au/HfO<sub>2</sub>/TiN MIM capacitors. Due to the interfacial TaN<sub>x</sub>O<sub>y</sub> layer growth during the HfO<sub>2</sub> deposition, TaN

based capacitors possess lower quadratic voltage capacitance coefficient  $\alpha$  as well as lower capacitance density. The leakage current densities can also be reduced by using TaN as bottom electrode. The breakdown strength is also affected by the type of electrode material. The extracted value of 6.4 MV/cm for the HfO<sub>2</sub>/TaN stack is higher than that for HfO<sub>2</sub>/TiN (4.4MV/cm).

The correlation between the quadratic capacitance–voltage variation and the interfacial layer thickness was demonstrated using  $HfO_2$  as high-*k* dielectric and TiN as bottom electrode. With increasing thickness of interfacial  $TiO_xN_y$  layer thickness the quadratic voltage coefficient of the dielectric stack can be reduced by a factor of 3. Due to the low k value of  $TiO_xN_y$  the total capacitance density of the stacked MIM capacitor is also strongly reduced.

Finally, we demonstrated the integration of a complete MIM stack (75 nm TiN/50nm HfO<sub>2</sub> / 150nm TiN) into the back–end of line process. Extracted capacitance density possess a 3 times higher capacitance density compared to SiO<sub>2</sub> based MIM capacitors. Capacitance voltage nonlinearity of integrated HfO<sub>2</sub> MIMs also satisfy the requirement of  $< 100 \text{ ppm/V}^2$ , but leakages currents (especially at 125°C) and reliability need to be improved in future studies.

## Chapter V

# 5. Alternative high–k dielectrics and 3D MIM structures

## 5.1. Sr-Ta-O (STA) system

## 5.1.1. Deposition conditions of STA

Thin films of Sr-Ta-O with thicknesses between 10 and 50 nm were deposited on TiN/Si (100) substrates at 400°C to form a MIM structure in the same way as already shown in the case of  $HfO_2$  (Fig. 4.1). But the depositions conditions, due to the characteristics of precursors were different and are presented in Table V. The typical thickness standard deviation was between 2 to 3%.

Precursors	0.05 M Sr[Ta(OEt) <sub>5</sub> (me)] <sub>2</sub> 0.05 M Sr[Ta(OEt) <sub>5</sub> (dmae)] <sub>2</sub>	
Substrate	20nmTiN/SiO <sub>2</sub> /Si	
Deposition Temperature [°C]	400	
Pressure [mbar]	2–10	
Evaporator Temperature [°C]	200	
Carrier Gas	Ar	
Total Gas Flow [sccm]	2000	
O <sub>2</sub> flow [sccm]	500	

Table V. Deposition conditions of Sr-Ta-O films.

#### 5.1.2. Optimization of SrTaO process

As the deposition temperature of BEOL is limited to 400°C, another important parameter which could be varied is the process pressure. In order to evaluate its influence on electrical parameters of STA MIMs, the process pressure was varied between 2 and 10 mbar. The stoichiometry of the Sr-Ta-O films was studied by XPS after calibrating the machine with the single  $Sr_2Ta_2O_7$  crystal. According to measurements, the range of the Sr/Ta ratio at 400°C is between 1.0 and 1.6, whereby the raise of process pressure results in a reduction of the Sr/Ta ratio, as shown in Fig. 5.1.



Fig. 5.1. Sr/Ta ratio, defined by XPS, as a function of process pressure. Depositions were done at 400°C.

The reason for this behaviour might be explained by the raised precursor residence time in the reactor with increasing process pressure. This effect allows the compensation of the higher reactivity of the Sr component. Therefore, the precursor probably dissociates to separate components near the substrate surface. It has to be mentioned that two slightly different precursors from separate suppliers have been tested for depositions of STA films, but no significant difference was noticed. Attempts to increase the content of Ta in the films have been done by introducing more Ta from an additional TBTDET precursor. Nevertheless, the increase of Ta concentration was observed neither in XPS analysis, nor in the electrical data of MIM capacitors.

The XPS studies of all Sr-Ta-O films showed an excess of Sr content compared to the initial stoichiometry of the precursor. At the pressure of 10 mbar, the Sr/Ta ratio is about 1, therefore the composition of films is identified as  $Sr_2Ta_2O_{7-\delta}$ . At 5 mbar deposited Sr-Ta-O films exhibit a Sr/Ta ratio of 1.37, which could be compared to the  $Sr_5Ta_4O_{15-\delta}$  phase. At both of these deposition conditions (5 and 10 mbar) Sr-Ta-O films were X-ray amorphous, as shown in Fig. 5.2. Compared to the  $Sr_2Ta_2O_7$  calibration crystal, the as deposited Sr-Ta-O films are slightly oxygen-deficient. A carbon content of about 5 % was observed on the surface, while the bulk value was below 1%.



Fig. 5.2. XRD pattern of STA films deposited at 10 mbar (black line) and 5 mbar (red line).

The amorphous character of the Sr-Ta-O films is also confirmed by XTEM images. The  $SiO_2$  based interfacial layer between the Si substrate and the TiN film is also clearly visible in Fig. 5.3 for the films deposited at 10 mbar. Besides, we obtain comparable XTEM image for the films, grown at 5 mbar.



Fig. 5.3. XTEM picture of STA/TiN stack.

### 5.1.3. Electrical characteristics of STA MIMs

In order to characterize the electrical properties of different stoichiometries, process pressures of 5 and 10 mbar are selected. The extracted  $\alpha$  and capacitance values as a function of thickness are shown in Fig. 5.4.



Fig. 5.4. Quadratic voltage coefficient  $\alpha$  and capacitance density as a function of STA films deposited at 10 mbar (•) and 5 mbar (°).

As can be seen from the plot, the nonlinear curves are quite similar for both MIM capacitors and are not dependent on the pressure at which they were processed. Another important thing that is visible is that the non–linear characteristics of SrTaO films are dependent on the thickness and fit quite well (solid line) Eq. 1.3. This is in agreement with literature reports, where this inverse quadratic relation of  $\alpha$  and d was also observed for several dielectrics<sup>173</sup>.

Capacitance dependence of the physical thickness is also presented in Fig. 5.4. The capacitance of STA based MIMs is also not affected by the deposition pressure. The dashed line represents Eq. 1.1. As visible in Fig. 5.4, the capacitance values of MIM capacitors with thin Sr-Ta-O films fit quite well at higher thicknesses of STA, but strongly deviate from the parallel plate capacitor curve for the thin layers of STA. This behaviour indicates the presence of low–k interfacial layers, which are not apparent in the TEM images.

By plotting the alpha values and the capacitance of STA based capacitors versus the physical thickness, the maximum capacitance can be extracted for the given thickness with the requirement of nonlinearity defined by ITRS. Keeping this requirement of alpha lower than <100 ppm/V<sup>2</sup> (indicated as dotted line in Fig. 5.4); a capacitance density of 5.5 fF/ $\mu$ m<sup>2</sup> for 30 nm thick STA MIM capacitors can be achieved. This value is about 5 times higher than the one of standard SiO<sub>2</sub> based MIMs.

Additionally, a dielectric constant can be extracted form this plot. The determined dielectric constant is 20. Dielectric permittivities in the range of 18–25 are typical for amorphous Sr-Ta-O films.<sup>174</sup> The dielectric constant of  $Sr_2Ta_2O_7$  crystals is 85<sup>69</sup> while the dielectric constant of  $Sr_5Ta_4O_{15}$  crystals is 41.<sup>67</sup> Our observed values are distinctly smaller compared to the values of crystals from literature because of the amorphous state of the films.

According to the ITRS requirements, the leakage current is a crucial parameter for MIM applications, especially at higher operating voltages. Fig. 5.5 shows the leakage current densities of Sr-Ta-O MIM capacitors, obtained at the pressures of 5 and 10 mbar, determined at a voltage of 2 V. Generally, Sr-Ta-O layers with thicknesses above 10 nm are excellent insulators, but the films deposited at two selected pressures behave differently when the voltage is applied. It is clearly visible that the MIMs with STA deposited at 10 mbar are better insulators than the ones obtained at 5 mbar and values as low as  $3 \cdot 10^{-9}$  A/cm<sup>2</sup> for 50 nm films can be reached.



Fig.5.5. Leakage current densities determined at 2V versus layer thickness deposited at 10 mbar (•) and 5 mbar (°).

These values of leakage currents can not be directly correlated to the band gaps of the STA oxides. The band gap of  $Sr_2Ta_2O_7$  crystals is 4.5 eV<sup>175</sup> and the value of a  $Sr_5Ta_4O_{15}$  crystal is 4.75 eV<sup>66</sup>. Although the band gap of  $Sr_5Ta_4O_{15}$  is 0.25 eV bigger than the value of  $Sr_2Ta_2O_7$ , our amorphous  $Sr_2Ta_2O_{7-\delta}$  layers exhibit even lower leakage current values than amorphous  $Sr_5Ta_4O_{15-\delta}$  films. However, we stress that the conduction mechanism in Sr-Ta-O films has not been yet identified.

The maximum quality factors, determined at 10 kHz, are plotted in Fig. 5.6. The  $Sr_2Ta_2O_{7-\delta}$  based MIM capacitors show suitable quality factors of 50 and this value is higher than the one of 37 of the STA films deposited at 5 mbar. This difference of quality factors is related to the resistance values of both stoichiometries. As can be seen in Fig. 5.5, films deposited at 10 mbar are better insulators and therefore have higher resistances at 2V. This directly affects the quality factor of the MIM capacitors since, as shown in Fig. 1.8, quality factor is mainly influenced by the resistance and dielectric constant of oxide layers at lower frequencies. As the *k* value is equal for the both MIMs deposited at different pressures, the main parameter that affects the quality is the resistance of the dielectric oxide.



Fig. 5.6. Quality factor at 10 kHz of MIMs based with STA as a dielectrics, obtained at 10 mbar (•) and 5 mbar (°).

The dielectric breakdown voltages, determined from I-V curves, are shown in Fig. 5.7.



Fig. 5.7. Breakdown voltages of STA MIM capacitors proceeded at 10 mbar (•) and 5 mbar (•) as a function of oxide thickness.

As can be seen for the plot, breakdown strengths of STA films deposited at 5 and 10 mbar are determined by linear fits in the thickness range between 10 and 40 nm. The breakdown strength of layers deposited at 5 mbar is 3.3 MV/cm and therefore slightly higher than the determined value 2.9 MV/cm for the ones deposited at 10 mbar. The important thing that can be seen from this plot is that a clear deviation from the linear curve of breakdown strength at thicknesses above 40 nm is visible. This effect could be caused by low-breaking interfacial layer presence between TiN and Sr-Ta-O, its influence is reduced with increasing Sr-Ta-O layer thicknesses. The compositions, determined by XPS, through the films are the same and are not dependent on the thickness of the Sr-Ta-O layers; therefore, the actual mechanism of the destructive oxide breakdown is rather complicated and not fully understood. The reported breakdown strength of Sr-Ta-O films without interfacial layer, grown on Pt-electrode is 6.0 MV/cm.<sup>77</sup>

The reliability of STA based MIMs was studied by applying the Time Dependent Dielectric Breakdown (TDDB) tests at room temperature and then compared to the MIMs of HfO<sub>2</sub>. From the analysis of breakdown data, mean time to failure is calculated. The extracted mean time to breakdown values of layered MIM capacitors are shown in Fig 5.8. The extrapolated operating voltages for 10 years lifetime of MIMs with HfO<sub>2</sub> ( $3.5 \text{ fF}/\mu\text{m}^2$ ) and STA ( $4.5 \text{ fF}/\mu\text{m}^2$ ) are 9 V and 3 V, respectively.



Fig. 5.8. Time to breakdown characteristics of  $HfO_2(\circ)$  and STA (•) MIM capacitors. Operating voltages for 10 years lifetime were extracted after the extrapolation of the linear fit of the experimental results.

#### 5.1.4. Conclusions

Sr-Ta-O films were deposited by Atomic Vapor Deposition technique from singlesource Sr[Ta(OEt)<sub>5</sub>(me)]<sub>2</sub> and Sr[Ta(OEt)<sub>5</sub>(dmae)]<sub>2</sub> precursors on TiN substrates within a thermal budget of back-end-of-line (400°C). The Sr/Ta ratio was altered by varying the process pressure. Two stoichiometries, obtained at 10 and 5 mbar, namely Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7- $\delta$ </sub> and Sr<sub>5</sub>Ta<sub>4</sub>O<sub>15- $\delta$ </sub>, were intensively characterized, whereby Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7- $\delta$ </sub> based MIM capacitors offer better electrical performance. The best results, achieved at a Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7- $\delta$ </sub> layer thickness of 30 nm, have a capacitive density of 5.5 fF/µm<sup>2</sup> in combination with a linearity coefficient of 80 ppm/V<sup>2</sup> and a quality factor of 52 at 10 kHz. The corresponding leakage current density at 2 V is 7·10<sup>-9</sup> A/cm<sup>2</sup> and the determined breakdown strength is 3.2 V/cm. The operating voltages for 10 years lifetime of STA based MIMs were compared to the ones with HfO<sub>2</sub>. The extrapolated values were 3V for STA films and 9 V for HfO<sub>2</sub>.

In general, it could be concluded that Sr-Ta-O MIMs fulfil almost all the requirements for ITRS and are very promising alternative insulators, but reliability, contamination tests and other specific requirements for different applications have to be satisfied before integration of the films into technology.

## 5.2. Ti-Ta-O (TTO) system

## <u>5.2.1. Deposition conditions and main properties of $TiO_2$ </u> and $Ta_2O_5$

At first, the growth and crystallization behaviour of single  $TiO_2$  and  $Ta_2O_5$  oxides was investigated using the precursors and the optimized deposition conditions presented in Table VI. Two separate Ti and Ta precursors were used since no single source precursor, which contains both metals, is yet available.

	Ti(OPr <sup>i</sup> ) <sub>2</sub> (mmp) <sub>2</sub>	TBTDET
Concentration [mol/l]	0.1 in octane	0.2 in octane
Substrate	20nmTiN/SiO <sub>2</sub> /Si	20nmTiN/SiO <sub>2</sub> /Si
Deposition Temperature [°C]	400	400
Pressure [mbar]	10	10
Evaporation Temperature [°C]	200	200
Carrier Gas	Ar	Ar
Total Gas Flow [sccm]	2000	2000
O <sub>2</sub> flow [sccm]	500	500
Injection frequency [Hz]	1	2

Table VI. Depositions conditions of TiTaO films.

In order to investigate the crystallinity of both  $TiO_2$  and  $Ta_2O_5$  thin films, XRD measurements were done after the depositions of oxides at 400°C on TiN. As indicated in Fig. 5.9, layers of  $Ta_2O_5$  were amorphous and this result is expected since it crystallizes in the temperature range of 600–700°C. On the contrary, Fig. 5.10 shows that  $TiO_2$  films grown at the same temperature were polycrystalline and the reflections indicate the anatase structure of the layers. This crystallization temperature is also typical for  $TiO_2$  thin films.



Fig. 5.9. XRD pattern of Ta<sub>2</sub>O<sub>5</sub> layer deposited on TiN.



Fig. 5.10. XRD pattern of anatase phase of TiO<sub>2</sub> (black line) deposited on TiN. The red line indicates the dominant peaks of anatase phase.

#### 5.2.2. Composition and thermal stability of Ti-Ta-O

As both oxides can be grown at the temperature of 400°C and this temperature fits very well the thermal budget of the BEOL process, both oxides are now mixed to get TiTaO films in the next step. The samples were deposited from both precursors at the conditions given in Table VI.

In order to investigate the thermal stability and whether it is possible to get a crystalline TiTaO phase, a series of samples were deposited on Si substrates and then annealed at different temperatures. Characterization of samples by XRD showed in Fig. 5.11.



Fig. 5.11. XRD plots of TiTaO films: red line – as deposited, and annealed in 700°C (green), 800°C (blue), 900°C (cyan) and 1000°C (magenta). Black line represents the main reflections of orthorhombic Ta<sub>2</sub>O<sub>5</sub> phase.

Firstly, it can be seen that as deposited TiTaO films (red line in Fig. 5.11) are amorphous. On, the contrary, pure  $TiO_2$  films, as already shown in Fig. 5.10, were crystalline. This gives as an indication that  $Ta_2O_5$  mixes with  $TiO_2$  at 400°C and forms compound, which is amorphous. This phenomenon can be related to the addition of Ta–O inside the Ti–O matrix and block the crystallization of  $TiO_2$ .

As can also be seen from the XRD pattern, Ti-Ta-O films remain amorphous until 700°C (green line in Fig. 5.11) and start to crystallize at 800°C in the phase which is closest to the orthorhombic  $Ta_2O_5$  phase. Similar XRD results were observed by Gan et. al.<sup>80</sup>. The authors noticed that films, produced by rf sputtering, remained amorphous for the annealing temperatures below 700°C. Crystalline structure which was identified to be the metastable monoclinic phase of TiTaO appeared at the annealing temperatures higher than 800°C. The amorphous state of TiTaO films deposited by CVD at 500°C was also observed by Jimenez et al.<sup>81</sup>

According to XRD powder database, several TiTaO phases such as TiTaO<sub>4</sub>,  $TiTa_2O_6$  exist, but none of their diffraction peaks matched the reflections of our samples. Probably, at higher temperatures, the Ta–O and Ti–O phases start to separate and Ti-O remains amorphous. On the other hand, literature reports that Ti is incorporated into the Ta–O matrix and therefore only diffraction peaks of Ta<sub>2</sub>O<sub>5</sub> are visible.<sup>176</sup>

The composition of TiTaO films were investigated by XPS. The analysis showed that the Ta/Ti ratio was 1.5. According to the  $(Ta_2O_5)_{1-x}(TiO_2)_x$  formula, the Ta/Ti ratio of 23 should be achieved if 8% additional TiO<sub>2</sub> is incorporated in Ta<sub>2</sub>O<sub>5</sub> phase. As already described in the introduction, this addition should stabilize the phase which has the highest dielectric constant value of ~ 125.

#### 5.2.3. Electrical characterization of Ti-Ta-O MIMs

Since the temperature of final applications can not exceed 400°C, TiTaO films with different thicknesses were deposited on the standard 20 nm TiN wafers at this temperature to form MIM structures. One of the most important parameter of MIM capacitor is capacitance density. Its dependence as the function of the thickness of TiTaO films is presented in Fig. 5.12.



Fig. 5.12. Capacitance density of TiTaO as a function of oxide thickness. The dotted line represents Eq.1.1.
From this plot (dotted line in Fig. 5.12) a dielectric constant of 50 can be extracted. This value is relatively high for the amorphous phase and is higher compared to values of thin films in the literature. The k value of 39–45 is reported by Chiang <sup>82</sup> and 30 in the work of Gan et. al. who found that dielectric constants critically depend on whether the crystalline phase was formed. They observed the increase of dielectric constants from 30 to 55 after annealing it at 800°C, which is the crystallization temperature detected by XRD. The dielectric constant values, extracted for C-V measurements, were 45 for Ta<sub>2</sub>O<sub>5</sub> and around 120 for TiO<sub>2</sub>. These electrical characteristics combined with the XPS data suggests that the composition is still not optimal to increase the dielectric constant to the value reported by Cava. Therefore, further investigation and process optimization to obtain the desired phase is in progress.

The capacitance voltage linearity coefficient  $\alpha$  versus the thickness of TiTaO is illustrated in Fig. 5.13. Setting the alpha value of 100 ppm/V<sup>2</sup> as upper limit (solid line in Fig. 5.13), a minimum thickness and the corresponding capacitance of the MIM stack can be extracted. TiTaO based MIM capacitors, deposited at 400°C, permit a high capacitance density of 11 fF/µm<sup>2</sup> for the 37 nm thick dielectric. This value is much higher than the ones obtained for SrTaO and HfO<sub>2</sub> MIM capacitors which make this material quite promising as possible dielectric for MIM applications.



Fig. 5.13. Quadratic capacitance voltage coefficient as a function of TiTaO thickness. The dotted line represents Eq. 1.2.

Leakage current densities for different thicknesses of TiTaO capacitors are shown in Fig. 5.14. As can be seen, TiTaO films are good insulators with currents up to  $1\cdot10^{-7}$  A/cm<sup>2</sup> at -3V for gold injection and  $1\cdot10^{-5}$  A/cm<sup>2</sup> at +3V for TiN injection. This difference could be related either to the differences in work functions ( $\Phi_{Au}$ = 5.1 eV and  $\Phi_{TiN}$ = 4.7 eV) or to interface interactions between oxide and metal. For comparison, MIM capacitors with only TiO<sub>2</sub> were almost leaky while the ones with Ta<sub>2</sub>O<sub>5</sub> had leakage currents in the range of 10<sup>-4</sup> A/cm<sup>2</sup> at 1V.



Fig.5.14. Leakage current densities of TiTaO capacitors for different dielectric thickness.

#### 5.2.4. Conclusions

In conclusion, thin films TiTaO were successfully deposited for the first time by Atomic Vapor Deposition on TiN electrodes as well as on Si substrates. Amorphous films of TiTaO, with Ta/Ti ratio of 1.5/1, were obtained at 400°C using TBTDET and Ti( $OPr^i$ )<sub>2</sub>(mmp)<sub>2</sub> precursors. The dielectric layers remain amorphous until the annealing temperature of 700°C and crystallize in an orthorhombic Ta<sub>2</sub>O<sub>5</sub> phase at 800°C. The *C*–*V* analysis of TiTaO based MIMs showed that amorphous TTO films have a very high dielectric constant of 50. In addition, the voltage linearity coefficient was below the limit

of 100 ppm/V<sup>2</sup> for the MIM capacitors with TiTaO layer thickness higher than 37 nm. MIMs with such thickness of TTO possess very high capacitance density of 11 fF/ $\mu$ m<sup>2</sup> and relatively low leakage currents in the range of 10<sup>-7</sup> A/cm<sup>2</sup> at 1V. All these properties make TiTaO dielectric to be a very promising alternative high–*k* material for further investigations and applications.

# 5.3. 3D MIM structures

Capacitance density, as defined by ITRS, has to be higher than 5  $fF/\mu m^2$  for future applications. Although capacitance density can be increased by reducing the thickness of the dielectric, other electrical parameters such as leakage currents or breakdown voltages become too large for applications. In order to keep the thickness around 50 nm and to fulfil all the requirements 3 dimensional structured MIM capacitors seem to be the opportunity to overcome this issue. For this purpose, keeping in mind that one of the advantages of AVD depositions is good step coverage for deposition in trenches, TiN as well as HfO<sub>2</sub> films were deposited in trenched Si wafers in 500 nm diameter vias with an aspect ratio of 2.0.

## 5.3.1. Optimization of AVD process

The example of TiN deposited in a trenched wafer is shown in Fig. 5.15. The standard process pressure of 3 mbar and the deposition temperature of 400°C allow achieving good step coverage of ~90% (bottom to top).



Fig. 5.15. Step coverage study. Cross-section view of TiN film grown on structured Si substrate.

 $HfO_2$  layers were also deposited on structured Si wafers with an aspect ratio of 2 at the temperatures of 400°C and 320°C. The effect of different temperatures is shown in Fig. 5.16.



Fig. 5.16. Step coverage study. Cross-section SEM views of an HfO<sub>2</sub> layers grown at a) 400°C and b) 320°C on structured Si substrates.

At 400°C (Fig. 5.16a), HfO<sub>2</sub> films grow 3 times faster on top of the substrate compared to the bottom, while the decrease of deposition temperature to 320°C (Fig. 5.16b) allows to improve the step coverage significantly (bottom coverage >90%). This effect could be explained by the fact that HfO<sub>2</sub> is grown under two different growth modes. As already shown in Chapter IV (Fig. 4.2), the growth of HfO<sub>2</sub> at 400°C is limited by the diffusion, and by the kinetics of the chemical reactions at 320°C.

As it is possible to obtain reasonable step coverage by AVD, such 3D structures could be applied for future MIM capacitors and thereby increase the capacitance density.

#### 5.3.2. Electrical properties of 3D MIMs

Electrical properties were extracted after forming the complete 3D MIM stack with TiN and  $HfO_2$  and contacting the MIMs in the same way as in the case of 2D. A SEM picture of one of the 3D structures with the trench height of 600 nm is shown in Fig. 5.17 where TiN electrodes and dielectric  $HfO_2$  are indicated.



Fig. 5.17. SEM picture of three dimensional MIM stack.

Fig. 5.18 compares the capacitance density of 2D and 3D MIMs. As can be seen, the capacitance density can be doubled for the same thickness of  $HfO_2$ .



Fig. 5.18. Capacitance density of HfO<sub>2</sub> based 2D (gray line) and 3D (black line) MIMs as a function of dielectric thickness.

Another important parameter that was changed in 3D MIMs was the quality factor. It increased from standard value of 50 for 50 nm  $HfO_2$  in the case of planar MIM structures to the value of 200 if 3D MIMs are constructed. This is related to the increased

bottom electrode area, which has some inhomogenity and influences the quality factor of the MIM stack.

In addition, leakage currents were almost comparable to the values obtained for 2D MIM structures, but the capacitance–voltage nonlinearity coefficients slightly increased due to the thickness deviations, because step coverage of TiN as well as of  $HfO_2$  are not 100 % and could impact the leakage currents. It should be mentioned that the optimization of depositions in trenches is in progress.

#### 5.3.3. Conclusions

Since capacitance density of MIMs should be higher than 5  $fF/\mu m^2$  for future applications, TiN and HfO<sub>2</sub> were successfully deposited by Atomic Vapour Deposition technique in trenched Si wafers. After the optimization, the optimization of depositions in trenches of TiN and HfO<sub>2</sub> were done and a step coverage higher that 90 % was achieved.

The C-V measurements showed that the capacitance density can be enhanced by a factor of 2 with keeping the same thickness of dielectric HfO<sub>2</sub> layer. Leakage currents remained as low as in the case of 2D MIMs. The increased capacitance voltage nonlinearity compared to the standard 2D capacitors is related to non-ideal step coverage, and this process is under optimization.

# Chapter VI

# 6. General conclusions and perspectives

### 6.1. Motivation

The rapid increase in wireless communications products has energized the need for process technologies that support both digital and analog (mixed-signal) devices at radio frequencies. Silicon-Germanium Bipolar Complimentary Metal Oxide Semiconductor technologies are ideal for many wireless applications. In these technologies, one of the key elements are so called passive devices, which are required for any highly integrated mixed-signal chip. Among these passive components, MIM capacitors are the most dominant ones since they are located in the level of interconnects in back-end-of-line and therefore significantly reduce the parasitic capacitance of the substrate. However, depending on the applications, MIM capacitors can require up to 50% of the chip area. This strongly affects the ability to reduce the form factor of the chip, but the reduction of the footprint of MIM capacitors is crucial in order to increase the functionality and performance of the devices. To achieve a higher capacitance per unit area for providing the analog scaling is the main objective, because currently used TiN/SiO<sub>2</sub>/TiN MIM stacks possess capacitance density of only 1 fF/um<sup>2</sup>, and this value, according to the ITRS should be increased to 5  $fF/\mu m^2$  in near future. Since capacitance is a direct function of the dielectric constant of the insulator, the replacement of currently used silicon oxide or silicon nitride films with the new alternative dielectrics which have higher permittivity values is a very promising approach.

A good alternative dielectric should have a k value higher than that of SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub>, a high band gap to limit the leakage currents, a high breakdown field to meet reliability specifications and has to be deposited at temperatures below 400°C to be compatible with back-end-of-line constrains. A variety of high–k materials are investigated as alternative dielectrics to replace the SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub>. Unfortunately, the miniaturization of the MIM capacitors and implementation of new materials also raises difficulties in fulfilling the challenges defined by the ITRS: capacitance–voltage linearity and leakage currents have to be decreased while quality factor and breakdown voltage should be

increased. Therefore, the choices of dielectric itself as well as engineering aspects are critical to meet the specifications. Among the alternative dielectrics,  $HfO_2$ ,  $Al_2O_3$  and  $Ta_2O_5$  are the most researched single high–*k* dielectrics. Recently systems of two metals such as, Sr-Ti-O, Sr-Ta-O or Ti-Ta-O have attracted attention due to their high bulk value of permittivity.

Due to the thermal budget of the back-end-of-line process, one of the main difficulties is to get good quality dielectric layer at the maximum allowed temperature of 400°C. All these mentioned dielectrics as well as metal TiN films can be deposited by PVD, but techniques such as MOCVD or ALD are preferred, because they offer the potential for large area growth, have advantages of good composition control, high films uniformity, and most importantly, they give excellent conformal step coverage on non-planar device geometries. An Atomic Vapor Deposition technique, which is an advanced modification of CVD, was used as the deposition tool for growing all the thin films used in this work.

The elaboration and characterization and integration of MIM capacitors were the main research topics in this thesis. The goal was to investigate, optimize and characterize the properties of alternative dielectrics such as  $HfO_2$ , SrTaO and TiTaO and electrode materials (TiN and TaN) for future Si based technologies since the properties of deposited thin films are strongly influenced by their growth conditions and post deposition treatments. As it is very difficult to find the optimal high–*k* material which fulfils all the requirements defined by ITRS for planar MIM capacitors, attempts to build three dimensional MIM stacks were also investigated in this work as possible solution to increase the capacitance density. Finally, the integration of  $HfO_2$  in the BEOL was demonstrated.

In the following, we present the conclusions of the materials that were investigated in this work

#### <u>6.2. TiN</u>

Thin films of TiN as electrode materials were successfully deposited by Atomic Vapor Deposition method for the first time. The influence of various deposition conditions (process temperature, concentration of TDEATi precursor and deposition pressure) was examined for the growth of TiN films on SiO<sub>2</sub>/Si substrates. 370–440  $\mu\Omega$ ·cm resistivity values of TiN films were obtained at 400°C from pure and diluted precursors, but it varies

with the temperature of deposition. The resistivity of the films could be reduced to 210  $\mu\Omega$ ·cm (when pure TDEATi is used) by increasing the process temperature to 500°C, but resistivity increases to the value of ~1300  $\mu\Omega$ ·cm if the temperature is increased to 600°C. XRD, XRR and XPS were used to investigate the origin of this increase of resistivity. The analysis revealed that the microscopic structure has the highest impact on the variation of resistivity. When the temperature of deposition is increased, the crystallinity of TiN is more pronounced, and therefore the diffusion of oxygen through grain boundaries is intensified and the absorption of oxygen in the polycrystalline films is enhanced. In order to prevent or to minimize the diffusion of oxygen, TiN should stay in amorphous state; therefore a deposition temperature of 400°C was used. This temperature fits very well the thermal budget of Back End of Line. The determined minimum thickness of 20 nm and a work function of 4.7 eV make AVD–grown TiN suitable as an electrode material for MIM applications.

#### 6.3. Alternative dielectrics

Atomic Vapor Deposition technique was also successfully applied for the preparation of HfO<sub>2</sub>, SrTaO and TiTaO dielectric layers.

HfO<sub>2</sub> films were deposited from an amide Hf(NEtMe)<sub>4</sub> precursor on TiN/Si substrates within a thermal budget of back-end of line (320–400°C). The best results were achieved at the deposition temperature of 320°C and process pressure of 4 mbar, whereas Sr-Ta-O films, deposited from a single-source Sr[Ta(OEt)<sub>5</sub>(me)]<sub>2</sub> and Sr[Ta(OEt)<sub>5</sub>(dmae)]<sub>2</sub> precursors on TiN substrates showed the best results at the deposition temperature of 400°C. The Sr/Ta ratio was altered by varying the process pressure. Two stoichiometries, obtained at 10 and 5 mbar, namely Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7- $\delta$ </sub> and Sr<sub>5</sub>Ta<sub>4</sub>O<sub>15- $\delta$ </sub>, were intensively characterized, whereby Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7- $\delta$ </sub> based MIM capacitors offer better electrical performance.

Additionally, TiTaO were successfully deposited for the first time by Atomic Vapor Deposition on TiN electrodes as well as on Si substrates. Amorphous TTO films, with Ta/Ti ratio of 1.5/1, were obtained at 400°C using TBTDET and Ti(OPr<sup>i</sup>)<sub>2</sub>(mmp)<sub>2</sub> precursors. The dielectric layers remain amorphous until the annealing temperature of 700°C and crystallize in the orthorhombic Ta<sub>2</sub>O<sub>5</sub> phase at 800°C.

By choosing the decent deposition conditions, it is possible to develop the MIM capacitors with thin films of alternative high–k materials which meet the specifications for

ITRS. The main electrical results are summarized and compared with respect to the main requirements for MIM capacitors listed in Chapter I in the following Table VII.

	Capacitance Density, [fF/µm <sup>2</sup> ] (at 100 ppm/V <sup>2</sup> )	k value	Leakage current at 2V [A/cm <sup>2</sup> ]	Breakdown Strength, [MV/cm]	Quality factor at 10 [kHz]
SiO <sub>2</sub>	1	3.9	5.10-11	15	>100
HfO <sub>2</sub>	3	18-22	3.10-9	6	50
Sr <sub>5</sub> Ta <sub>4</sub> O <sub>15-x</sub>	4.5	18-25	5.10-9	3.3	37
Sr <sub>2</sub> Ta <sub>2</sub> O <sub>7-x</sub>	5.5	18-25	3.10-9	2.9	51
TiTaO	10	50	$2 \cdot 10^{-7}$	Soft breakdown	20

Table VII. Comparison of the properties of 50 nm thick oxides for MIM applications.

In general it could be concluded that Sr-Ta-O as well as TiTaO MIMs fulfil most of the requirements for ITRS and are perfect insulators and probably are on the most promising alternative high–k dielectrics, but some special issues such as device reliability, contamination tests and other specific requirements for different applications have to be satisfied before integration of the films into technology.

Since the performance of MIM capacitors are also influenced by the bottom electrode, the effect of different bottom electrode material on electrical properties was evaluated in Au/HfO<sub>2</sub>/TaN and Au/HfO<sub>2</sub>/TiN MIM capacitors. Due to the growth of interfacial TaN<sub>x</sub>O<sub>y</sub> layer during the HfO<sub>2</sub> deposition, TaN based capacitors possess lower quadratic voltage capacitance coefficient  $\alpha$  as well as lower capacitance density. The leakage current densities can also be reduced by using TaN as bottom electrode. The breakdown strength is also affected by the type of electrode material. The extracted value of 6.4 MV/cm for the HfO<sub>2</sub>/TaN stack is higher than that for HfO<sub>2</sub>/TiN (4.4MV/cm).

The correlation between quadratic capacitance–voltage variation and interfacial layer thickness was demonstrated by using  $HfO_2$  as high-k dielectric and TiN as bottom electrode. For this purpose, TiN electrodes were partially oxidized at 450°C and 500°C before depositing the  $HfO_2$  films. With increasing interfacial  $TiO_xN_y$  layer thickness the quadratic voltage coefficient of the dielectric stack can be reduced by a factor of 3, but due

to the low k-value of  $TiO_xN_y$  the total capacitance density of the stacked MIM capacitor is also strongly reduced.

Since capacitance density has to be higher than 5  $fF/\mu m^2$  for future applications, TiN and HfO<sub>2</sub> were successfully deposited by AVD in trenched Si wafers to form three dimensional MIM capacitors. Firstly, the optimization of depositions in trenches with aspect ratio of 2 was performed and step coverage higher than 90 % for both, TiN and HfO<sub>2</sub>, was achieved. The *C*–*V* measurements of 3D MIMs showed that capacitance density can be enhanced by a factor of 2 with keeping the same thickness of dielectric layer while leakage currents remained as low as in the case of 2D MIMs. The increased capacitance voltage nonlinearity compared to the standard 2D capacitors is related to non-ideal step coverage, which is still under optimization.

Finally, we demonstrated the integration of a complete MIM stack (75nm TiN/50nm HfO<sub>2</sub>/150nm TiN) into the back–end–of–line process. Extracted capacitance density possess 3 times higher capacitance density compared to SiO<sub>2</sub> based MIM capacitors. The capacitance voltage nonlinearity of integrated HfO<sub>2</sub> MIMs also satisfy the requirement of < 100 ppm/V<sup>2</sup>, but leakages currents (especially at 125°C) and reliability should be improved.

#### 6.4. Perspectives

Since the Atomic Vapor Deposition process is strongly precursor sensitive (due to the thermal stability, volatility and others) further tests and investigations of alternative precursors are planed in order to obtain the dielectrics with the improved properties. In addition, TaN, as alternative electrode material, is planned to be deposited by AVD. Naturally, other possible high–k candidates such as SrTiO<sub>3</sub> or CeAlO<sub>3</sub> and the stacks of several dielectrics are in the scope of further activities.

It is also important to improve the step coverage of electrodes (TiN and TaN) as well as of the oxides for three dimensional MIM capacitors. The achieved step coverage of 90% is quite promising; therefore depositions in the trenched wafers with aspect ratio of 1:10 will be investigated.

Finally, it would be also interesting to investigate in more details the effects of both interfaces between electrodes and dielectric layers, since electrical properties strongly depend on them. Techniques such as synchrotron XPS could be applied to investigate these interfaces.

# Zusammenfassung

Die drahtlose Kommunikation hat in den letzten Jahren enorm an Bedeutung gewonnen und Prozess-Technologien notwendig gemacht, die sowohl analoge als auch digitale und gemischt analog/digitale Schaltkreise (Mixed-Signal) und Systeme für RF Applikationen bereitstellen. Silizium-Germanium BiCMOS Technologien sind für viele drahtlose Anwendungen ideal geeignet. In diesen Technologien sind eines der wichtigsten Bauelemente sogenannte passive Bauelemente, die für viele hoch-integrierte Mixed-Signal Schaltungen benötigt werden. Unter diesen passiven Komponenten dominieren MIM-Kondensatoren, da sie sich in der Ebene zwischen den Interconnects befinden, Back-Endof-line kompatibel sind und insgesamt parasitäre Kapazitäten des Substrats deutlich reduzieren. Allerdings können MIM-Kondensatoren je nach Anwendung bis zu 50% der Chipfläche einnehmen. Dies wirkt sich stark negativ auf den Formfaktor der Schaltungen aus. Eine Reduzierung der Grundfläche von MIM-Kondensatoren ist jedoch entscheidend, um die Funktionalität und Leistungsfähigkeit der Bauelemente zu erhöhen. Das Hauptziel ist es, die Kapazität pro Fläche zu erhöhen, da derzeitige TiN/SiO<sub>2</sub>/TiN MIM Strukturen eine Kapazitätsdichte von nur 1 fF/um<sup>2</sup> aufweisen, und dieser Wert entsprechend der ITRS in naher Zukunft auf 5  $fF/\mu m^2$  erhöht werden soll. Da die Kapazität von der Dielektrizitätskonstante des Isolators direkt abhängt, ist die Ersetzung der derzeit verwendeten Siliziumoxid oder Siliziumnitrid Filme mit neuen, alternativen Dielektrika mit höheren Dielektrizitätskonstanten ein aussichtsreicher Ansatz.

Alternative Dielektrika sollten einen höheren k-Wert als SiO<sub>2</sub> oder Si<sub>3</sub>N<sub>4</sub> haben und eine hohe Bandlücke aufweisen, um auftretende Leckströme zu reduzieren. Zudem ist eine hohe Durchbruchfeldstärke entsprechend den Spezifikationen der Zuverlässigkeit erforderlich. Weiterhin sollte das Dielektrikum bei einer Temperatur unter 400°C deponiert werden, um Back-End-of-Line kompatibel zu bleiben. Eine Vielzahl von hoch-*k* Materialien wurden bereits als alternative Dielektrika untersucht, um SiO<sub>2</sub> oder Si<sub>3</sub>N<sub>4</sub> zu ersetzen. Die Miniaturisierung der MIM- Kondensatoren und der Einsatz neuer Materialien ist aber auch mit Schwierigkeiten in Zusammenhang mit den Vorgaben der ITRS verbunden: die Kapazitäts-Spannungs-Linearität und die Leckströme müssen reduziert werden, während der Qualitätsfaktor und die Durchbruchspannung erhöht werden sollten. Daher ist die Wahl des Dielektrikums von besonderer Bedeutung, um die genannten Vorgaben zu erfüllen. Unter den alternativen Dielektrika stellen HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> und Ta<sub>2</sub>O<sub>5</sub> die am meisten untersuchten hoch-*k* Dielektrika dar. In den letzten Jahren haben Dielektrika bestehend aus dem System Sr-Ti-O, Sr-Ta-O oder Ti-Ta-O aufgrund ihrer hohen Permittivität Aufmerksamkeit erregt.

Die genannten Dielektrika sowie TiN Filme als Metallelektrode können mittels PVD abgeschieden werden, allerdings ist die MOCVD bzw. ALD-Abscheidung gegenüber der PVD bevorzugt, weil es das Potenzial für eine großflächige Abscheidung bietet, eine gute Kontrolle der Komposition und Uniformität der Filme ermöglicht, vor allem aber eine hervorragende konforme Abscheidung bietet. Die AVD Abscheidung, die eine Erweiterung der CVD darstellt, wurde für die Deposition der in dieser Arbeit verwendeten Filme benutzt. Die Integration und Charakterisierung von MIM-Kondensatoren stellt den Schwerpunkt dieser Arbeit dar. Im Rahmen dieser Arbeit werden die Eigenschaften von HfO<sub>2</sub>, SrTaO und TiTaO sowie der Elektrodenmaterialien TiN und TaN für zukünftige Sibasierte Technologien untersucht, optimiert und charakterisiert. Da es schwierig ist, ein hoch-*k* Material für planare MIM-Kondensatoren zu finden, wurden auch dreidimensionale MIM-Stacks als mögliche Lösung untersucht. Schließlich wurde die Integration von HfO<sub>2</sub> im BEOL-Prozeß demonstriert. Im Folgenden werden die Schlussfolgerungen der Materialuntersuchungen dargestellt.

#### <u>TiN</u>

Dünne TiN Filme als Elektrodenmaterial wurden zum ersten Mal mit dem AVD-Verfahren erfolgreich abgeschieden. Der Einfluss verschiedener Depositionskonditionen (Prozesstemperatur, Konzentration des TDEATi Prekursors, Depositionsdruck) wurde für das Wachstum von TiN Schichten auf SiO<sub>2</sub>/Si Substraten untersucht. Flächenwiderstände von 370-440  $\mu\Omega$ ·cm wurden für TiN Filme, die bei 400°C aus reinen und verdünnten Prekursoren abgeschieden wurden, gemessen.

Der Flächenwiderstand der Filme, der zusätzlich von der Depositionstemperatur abhängt, konnte bei einer Prozesstemperatur von 500°C auf 210  $\mu\Omega$ ·cm reduziert werden (bei Benutzung von reinem TDEATi), erreichte aber Werte von ~1300  $\mu\Omega$ ·cm, wenn die Temperatur auf 600°C erhöht wurde. XRD, XRR und XPS wurden verwendet, um die physikalische Ursache dieser Erhöhung des Widerstands zu verstehen. Die Analyse ergab, dass die mikroskopische Struktur den größten Einfluss auf die Veränderung des Flächenwiderstands hat. Bei Erhöhung der Depositionstemperatur ist die Kristallinität von TiN stärker ausgeprägt, wobei eine Diffusion von Sauerstoff entlang von Korngrenzen verstärkt und die Absorption von Sauerstoff in den polykristallinen Filmen erhöht wird.

Um die Diffusion von Sauerstoff zu verhindern oder zu minimieren, sollten TiN Filme amorph abgeschieden werden. Es wurde deshalb eine Depositionstemperatur von 400°C gewählt. Die ermittelte minimalen Dicke von 20 nm sowie eine Austrittsarbeit von 4.7 eV stellen die in AVD abgeschiedenen TiN Schichten als geeignetes Elektrodenmaterial für MIM Anwendungen dar.

#### Alternative Dielektrika

Das AVD-Verfahren wurde ebenfalls für die Abscheidung von HfO<sub>2</sub>, SrTaO und TiTaO angewandt. HfO<sub>2</sub> Filme wurden mit Hilfe des Amid Prekursors Hf(NEtMe)<sub>4</sub> auf TiN/Si Substraten innerhalb eines thermischen Budgets von 320-400°C im BEOL Prozeß abgeschieden. Die besten Ergebnisse wurden bei einer Depositionstemperatur von 320°C und einem Prozessdruck von 4 mbar erzielt.

SrTaO Filme, die mit Sr[Ta(OEt)<sub>5</sub>(me)]<sub>2</sub> und Sr[Ta(OEt)<sub>5</sub>(dmae)]<sub>2</sub> als Prekursor abgeschieden wurden, zeigten die besten Ergebnisse auf TiN Substraten bei einer Depositionstemperatur von 400°C. Die Änderung des Sr/Ta-Verhältnisses wurde durch Variation des Prozessdrucks erreicht. Bei stöchiometrischen Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7- $\delta$ </sub> und Sr<sub>5</sub>Ta<sub>4</sub>O<sub>15- $\delta$ </sub> Filmen, die unter 10 bzw. 5 mbar abgeschieden wurden, zeigte Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7- $\delta$ </sub> in MIM-Kondensatoren hinsichtlich der elektrischen Daten eine bessere Performance.

Desweiteren wurden erstmals TiTaO Filme mit dem AVD-Verfahren auf TiN Elektroden als auch auf Si Substraten erfolgreich abgeschieden. Amorphe TiTaO Filme mit einem Ta/Ti-Verhältnis von 1.5/1 wurden mit TBTDET und Ti(OPri)<sub>2</sub>(mmp)<sub>2</sub> als Prekursoren bei 400°C erzielt. Die TiTaO Schichten bleiben bis zu einer Annealingtemperatur von 700°C amorph und kristallisieren in der orthorhombischen Ta<sub>2</sub>O<sub>5</sub> Phase erst bei einer Temperatur von 800°C. Die Ergebnisse der elektrischen Messungen im Hinblick auf die wesentlichen Anforderungen für MIM-Kondensatoren sind in Tabelle VII. zusammengefaßt.

Im Allgemeinen erfüllen SrTaO sowie TiTaO alle Anforderungen der ITRS und stellen vielversprechende alternative hoch-*k* Dielektrika dar, obgleich einige spezielle Punkte wie die Zuverlässigkeit, der Einfluß der Kontamination und andere spezifische Anforderungen weiter untersucht werden müssen.

			Leckstrom-		
	Kapazitätsdichte,	Dielektri-	dichte	Durchbruch	Qualitäts-
	[fF/µm <sup>2</sup> ] (bei	sche Konstante	bei 2V	feldstärke,	faktor
	100 ppm/V <sup>2</sup> )		[A/cm <sup>2</sup> ]	[MV/cm]	bei 10 [kHz]
SiO <sub>2</sub>	1	3.9	5.10-11	15	>100
HfO <sub>2</sub>	3	18-22	3·10 <sup>-9</sup>	6	50
Sr <sub>5</sub> Ta <sub>4</sub> O <sub>15-x</sub>	4.5	18-25	5·10 <sup>-9</sup>	3.3	37
Sr <sub>2</sub> Ta <sub>2</sub> O <sub>7-x</sub>	5.5	18-25	3.10-9	2.9	51
TiTaO	10	50	$2 \cdot 10^{-7}$	Soft	20
				breakdown	

TabelleVII.Vergleich der Eigenschaften von 50nm dicken Oxiden für MIM Applikationen.

Da die Eigenschaften der MIM-Kondensatoren auch von der Bottomelektrode beeinflußt werden, wurde der Einfluß am Beispiel von Au/HfO<sub>2</sub>/TaN und Au/HfO<sub>2</sub>/TiN MIM-Kondensatoren studiert. Kondensatoren mit einer TaN Bottomelektrode weisen aufgrund der Formation einer TaN<sub>x</sub>O<sub>y</sub> Grenzschicht während der HfO<sub>2</sub> Abscheidung einen geringeren quadratischen Koeffizienten  $\alpha$  und eine niedrigere Kapazitätsdichte auf.

Zusätzlich können die Leckstromdichten bei TaN als untere Elektrode reduziert werden. Die Durchschlagsfestigkeit ist abhängig von der Wahl des Elektrodenmaterials. Die extrahierten Werte von 6.4 MV/cm sind für HfO<sub>2</sub>/TaN Stacks höher als für HfO<sub>2</sub>/TiN Stacks mit 4.4 MV/cm.

Eine Korrelation zwischen quadratischen Kapazitäts-Spannungs-Variationen und der Grenzflächenschichtdicke wurde unter Verwendung von HfO2 als hoch-k Dielektrikum und TiN als Bottomelektrode gezeigt. Zu diesem Zweck wurden TiN Bottomelektroden bei 450°C und 500°C vor der HfO<sub>2</sub> Abscheidung partiell oxidiert. Mit zunehmender TiO<sub>x</sub>N<sub>y</sub> Grenzflächenschichtdicke kann der quadratische Spannungskoeffizient  $\alpha$  der dielektrischen Schicht um den Faktor 3 reduziert werden. Aufgrund des geringen *k*-Wertes der TiOxNy Grenzfläche ist allerdings auch die Gesamtkapazitätsdichte des MIM-Kondensators stark reduziert.

Da die Kapazitätsdichte für zukünftige Applikationen größer als 5  $fF/\mu m^2$ betragen muß, wurden TiN und HfO<sub>2</sub> Filme mit AVD auch in Gräben auf dem Si-Wafer aufgebracht, um dreidimensionale MIM-Kondensatoren zu bilden. Zunächst wurde die Optimierung der Deposition in Gräben mit einem Aspektverhältnis von 2 durchgeführt und es wurde eine Kantenbedeckung von mehr als 90 % für TiN und HfO<sub>2</sub> erzielt. Die *C-V* Messungen der 3D MIMs zeigten, dass die Kapazitätsdichte bei gleichbleibender Dicke der dielektrischen Schicht um den Faktor 2 erhöht werden konnte. Gleichzeitig blieben die Leckstromdichten so niedrig wie im Falle der 2D MIMs. Die erhöhte Kapazitäts-Spannungs-Nichtlinearität im Vergleich zum herkömmlichen 2D-Kondensator ist im Zusammenhang mit der nicht-idealen Kantenbedeckung zu verstehen, die weiter optimiert wird.

Abschließend wurde die Integration eines kompletten MIM-Stacks (75 nm TiN/ 50 nm HfO<sub>2</sub>/ 150 nm TiN) im Back-End-of-line Prozeß gezeigt. Die extrahierte Kapazitätsdichte liegt um den Faktor 3 höher als die Kapazitätsdichte von SiO<sub>2</sub>-basierten MIM-Kondensatoren. Die Kapazitäts-Spannungs-Nichtlinearität liegt zudem  $<100 \text{ ppm/V}^2$  für integrierte HfO<sub>2</sub> MIMs. Die Lecktromdichten (insbesondere bei 125°C) und die Zuverlässigkeit müssen aber weiter verbessert werden.

#### <u>Ausblick</u>

Da die AVD stark vom verwendeten Prekursor abhängt (thermische Stabilität, Volatilität, usw.), sind weitere Untersuchungen alternativer Prekursoren geplant. Darüberhinaus wurden insbesondere Fortschritte in der AVD von TaN als Elektrodenmaterial gemacht. Andere mögliche hoch-*k* Dielektrika wie SrTiO<sub>3</sub> oder CeAlO<sub>3</sub> und Stapel von mehreren Dielektrika sind im Rahmen weiterer Aktivitäten geplant.

Insbesondere ist die Kantenbedeckung der Elektroden (TiN und TaN) sowie der Oxide für 3D MIM-Kondensatoren zu optimieren. Die bereits erzielte Kantenbedeckung von 90 % ist recht vielversprechend. Deshalb wird weiterhin die Deposition von Gräben mit einem Aspektverhältnis von 1:10 untersucht werden. Es wäre schließlich interessant, die Auswirkungen der AVD Abscheidung auf die Formation von Grenzflächen an beiden Elektroden detaillierter zu untersuchen, da die elektrischen Eigenschaften stark von den Grenzflächen abhängen können. Nichtdestruktive HA-XPS Messungen könnten hier angewandt werden, um die Formation dieser Grenzflächen besser zu verstehen.

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	<b>2004-2006</b> , Vilnius University, Faculty of Chemistry, Naugarduko g. 24, Vilnius, Lithuania. Diploma of Master.			
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LANGUAGES	Native Lithuanian, Fluent English, German, Russian.			

# Scientific visibility during PhD

## **Publications in peer-reviewed journals**

#### 2010

<u>M. Lukosius</u>, Ch. Walczyk, M. Fraschke, D. Wolansky, H. Richter, Ch. Wenger, "High performance Metal – Insulator – Metal capacitors with Atomic Vapor Deposited HfO<sub>2</sub> dielectrics" Thin Solid Films February 2010.

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### Presentations at conferences and courses

March 24, 2010, DPG 2010 Regensburg, Germany.

Oral presentation "Atomic Vapour Deposition of TiTaO for MIM applications".

**February 21-27, 2010**, International Workshop and Winter School: Photoemission, Dijon, France.

Poster presentation "High performance MIM capacitors with Atomic Vapor Deposited HfO<sub>2</sub> dielectrics".

August 3-8, 2009, Physic School "Nanoscaled Oxides – Big Opportunities in Small Structures" Bad Honnef, Germany.

Poster presentation: "Role of the HfO<sub>2</sub>-TiN interface in C-V nonlinearity of MIM capacitors".

June 8-12, 2009, EMRS 2009, Strasbourg, France.

Oral presentation "AVD Growth and Properties of Titanium Nitride Metal Electrodes for MIM Capacitors".

March 23-24, 2009, DPG 2009 Dresden, Germany.

Oral presentation "High performance MIM capacitors with Atomic Vapor Deposited HfO<sub>2</sub> dielectrics".

**June 23-25, 2008,** WoDiM 2008, Bad Saarow, Germany. Poster presentation": "The influence of the electrode material on HfO<sub>2</sub> MIM capacitors".

**June 14-16**, **2008**, PhD Seminar of Oldenburg University, Sonderborg, Denmark. Oral presentation "Atomic vapour deposition of Sr-Ta-O films for MIM applications"

May 26-30, 2008, EMRS 2008, Strasbourg, France.

Poster presentation: "The role of the HfO<sub>2</sub>-TiN interface in the capacitance-voltage nonlinearity of metal insulator metal capacitors".

April 23-23, 2008, PhD Symposium in Szklarska Poreba (Poland) Oral presentation "Atomic Vapor Depositions Metal-Insulator-Metal stacks".

February 25-29, 2008, DPG 2008, Berlin, Germany.

Oral presentation "Atomic Vapor Deposition of Sr-Ta-O films for MIM applications".

June 20-23, 2007, INFOS 2007, Athens, Greece.

Oral presentation "Atomic-vapour-deposited HfO<sub>2</sub> and Sr<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub> layers for metal-insulatormetal applications".

September 4-9, 2005, EUROCVD -15, Bochum, Germany.

"MOCVD growth and properties of high-k dielectric praseodymium oxides layers on silicon".

**November 11-14, 2004,** ECO-NET meeting, Bratislava, Slovakia. Oral presentation "MOCVD growth and properties of high-k dielectric oxide films".

## Selbstständigkeitserklärung:

Hiermit erkläre ich, dass ich die vorliegende Doktorarbeit selbstständig angefertigt habe und nur die angegebenen Quellen und Hilfsmittel verwendet habe.

(Datum, Ort)

Mindaugas Lukosius