VOLATILE GUANIDINATO-BASED METALORGANIC PRECURSORS FOR ALD PROCESS

A. Milanov, K. Xu, H. Parala, and A. Devi

Inorganic Materials Chemistry Group, Inorganic Chemistry II, Ruhr-University Bochum, Universitätsstr. 150, D-44801 Bochum, Germany
anjana.devi@rub.de

The scaling down of semiconductor device dimensions led to the exploration of new high-k dielectrics due to the high leakage currents observed with the conventionally used SiO$_2$. Hafnium dioxide (HfO$_2$) is one of the leading candidates to replace SiO$_2$ as the gate dielectric for future generation CMOS devices.$^{1,2}$ Atomic Layer Deposition (ALD) process has recently gained interest because of their suitability for fabrication of conformal films over non-planar device geometries with thicknesses in the nanometer range. Essential requirement for a successful ALD process is the availability of suitable precursors possessing appropriate physical and chemical properties.

We report the synthesis and characterisation of a new class of volatile guanidinato-based hafnium complexes namely [(R$_2$N)$_2$Hf{(PrN)$_2$CNR$_2$}]$_2$ (R = Et$_2$, EtMe and Me$_2$).$^3$ The beneficial thermal characteristics of these compounds, make them suitable precursors for ALD applications. Thin films of HfO$_2$ are grown by ALD in the temperature range of 250-425 °C, using both [(Et$_2$N)$_2$Hf{(PrN)$_2$CNEt$_2$}]$_2$ and [(EtMeN)$_2$Hf{(PrN)$_2$CNEtMe}]$_2$. Growth rate, surface morphology, crystal structure, crystal density of the as-deposited films are analysed as a function of deposition temperature and will be discussed in detail. XPS and SNMS analysis of the as deposited HfO$_2$ films reveal low carbon contamination (1.8-2.9 at.%) and the Hf:O ratio determined by RBS and SNMS is in the range of 1:2.07-2.1.

Optimized Ta(C)N Thin Films Prepared by PEALD for Copper Diffusion Barrier

Se-Hun Kwon*, Seong-Jun Jeonga, Kwang-Ho Kimb, Sang-Won Kanga

aDepartment Materials Science and Engineering, KAIST,
#373-1, Guseong-dong Yuseong-gu, Daejon, 305-701-Republic of Korea
bDivision of Materials Science and Engineering Pusan National University,
Busan 609-735, Republic of Korea
*email: yoluc@kaist.ac.kr

Copper (Cu) is widely adopted as an interconnection metal in advanced ultralarge-scale integration (ULSI) microelectronic devices due to its low electrical resistivity (1.67 μΩcm) and good electromigration (EM) resistance.[1,2] However, Cu easily diffuses into Si or SiO2 quickly, even at temperatures below 200°C.[2] Therefore, an adequate Cu diffusion barrier layer is required between Si and Cu to prevent the degradation of microelectronics devices caused by the diffusion of Cu. Of various barrier materials, tantalum nitride (TaN) has been widely used as barriers to Cu diffusion due to its immiscibility with Cu, superior thermal stability.[3,4] However, it requires an additional glue layer such as ruthenium (Ru) to enhance the adhesion properties between TaN and Cu. From a point of view on the metallization process, the insertion of additional layers, such as Ru, is not preferred because the integration of multi-layer stacked structure gets more difficult as the dimension of devices shrinks. Therefore, the development of one layered diffusion barrier material, which possesses a sufficient diffusion barrier property and an adequate adhesion property to Cu, has been focused for many researchers.[5,6]

In this study, we prepared Ta(C)N thin films using Tertiarymyimidao tris(dimethylamido)tantalum (TAIMATA) and H2 plasma at a deposition temperature of 230°C under a deposition pressure of 3 Torr. The saturated deposition rate was about 0.132nm/cycle. The compositions of deposited Ta(C)N thin films depending on the deposition parameters were evaluated by Auger Electron Spectroscopy (AES) and Rutherford Backscattering Spectroscopy (RBS). And, the binding state of Carbon in Ta(C)N thin film was investigated by X-ray Photoelectron Spectroscopy (XPS). Particularly, the evolution of microstructure in Ta(C)N thin films was carefully studied. Base on the results, we optimized PEALD- Ta(C)N thin films as a copper diffusion barrier. With the optimized Ta(C)N thin films, the adhesion properties to copper as well as copper diffusion barrier property was greatly improved. As a result, we showed the optimized Ta(C)N thin films prepared by PEALD as a one-layered copper diffusion barrier layer.

Properties of the lanthanum hafnium oxide (LHO) films deposited by electron cyclotron resonance-atomic layer deposition (ECR-ALD)

Woong-Sun Kim\textsuperscript{a}, Myoung-Gyun Ko, Dae-Yong Moon, Tae-Sub Kim, Byung-Woo Kang, Sang-Kyun Park and Jong-Wan Park

Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea
\textsuperscript{a}woongsun@hanyang.ac.kr

According to the scale-down rule, a gate oxide thickness of less than 1 nm is required for sub-0.1 µm devices. However, continuous scaling down of the SiO\textsubscript{2} gate oxide reaches a physical thickness limit. High-k materials such as Al\textsubscript{2}O\textsubscript{3}, Ta\textsubscript{2}O\textsubscript{5}, HfO\textsubscript{2}, and La\textsubscript{2}O\textsubscript{3} have attracted a great deal of interest as the gate oxide for future MOSFET devices. To overcome these drawbacks of high-k oxides, technologies for growing binary high-k oxides are required. Dimoulas et al. demonstrated that high quality lanthanum hafnium oxide (LHO) dielectrics layers deposited by MBE show promising thermodynamic and electrical properties. LHO is one of the promising gate dielectric because of its high dielectric constant, high crystalline temperature, and good metal oxide semiconductor capacitor characteristics.[1]

In this work, LHO thin films were grown using an electron cyclotron resonance atomic layer deposition technique. TEMAHf (tetrakis(ethylmethylamino)hafnium) and La(EtCp)\textsubscript{3} (tris(ethylcyclopentadienyl) lanthanum (III)) were utilized as the hafnium and lanthanum precursors, respectively. Rapid thermal annealing (RTA) of the LHO films induced dramatic changes in the electrical properties. In order to investigate the structural and electrical properties, we used transmission electron microscopy (TEM), and current-voltage (J-V) and capacitance-voltage (C-V) measurements. From I-V measurement of the LHO films, extremely low gate oxide leakage currents were observed. The C-V characteristics were analyzed at high frequency (1 MHz) with a sweep voltage. The C-V and leakage current measurements were obtained using an Agilent B1500A. The EOT was calculated using the CVC program. The film thicknesses with respect to the number of ALD cycles and structures were observed using cross-sectional transmission electron microscopy (FETEM, Tecnai F30 S-Twin) images and an ellipsometer (Rudolph AutoEL-II).

ALD GROWTH AND CHARACTERIZATION OF LOW-RESISTIVE Ga-DOPED ZnO THIN FILMS

K. Saito\textsuperscript{a}, Y. Hiratsuka\textsuperscript{a}, A. Omata\textsuperscript{a}, H. Makino\textsuperscript{b}, S. Kishimoto\textsuperscript{b}, T. Yamamoto\textsuperscript{b}

\textsuperscript{a}Department of Media and Information Systems, Teikyo University of Science and Technology, 2525 Yatsusawa, Ueno, Yamanashi 409-0193, Japan
\textsuperscript{b}Material Design Centre, Research Institute, Kochi University of Technology, 185 Miyanokuchi, Tosayamada-cho, Kochi 782-8502, Japan

e-mail: saito@ntu.ac.jp, Phone: +81-554-63-6823, Fax: +81-554-63-4431

Zinc Oxide (ZnO) thin film is the promising material for a variety of practical uses such as transparent conductive oxide (TCO) in flat panel displays or solar cells, touch panels and coating films in UV-cut filters. The growth technique of ALD is effective to realize precise control of impurity incorporation and large area uniformity at low growth temperature. In this work, low-resistive Ga-doped n-type ZnO thin films were grown by ALD and characterized by XRD, Hall and photoluminescence (PL) measurements.

Diethylzinc (DEZ), H\textsubscript{2}O and triethylgallium (TEG) were used as Zn, O and Ga precursors, respectively, and these precursors were alternately introduced into the growth chamber with argon as a carrier gas. The typical pulse lengths were 2 s for the reactants and 10 s for the evacuation between the reactants. The opening and closing sequences of the air valves were controlled by using a personal computer. The substrate temperature was varied from 150 to 300 \textdegree C.

By XRD measurements, both (0 0 0 2) and (1 0 -1 1) reflection peaks were observed predominantly. For undoped ZnO thin films, it was found that the intensity of ZnO (1 0 -1 1) reflection peak was increased and the electron concentration was increased from 6.8\times10\textsuperscript{18} to 1.1\times10\textsuperscript{20} cm\textsuperscript{-3} with the increase of DEZ flow rate, which indicates the increase of O vacancies (V\textsubscript{O}) and/or Zn interstitials (Zn\textsubscript{i}). Ga-doping was performed under Zn-rich growth conditions. ZnO (1 0 -1 1) reflection peak was predominantly observed for Ga-doped ZnO thin films. By increasing the TEG flow rate, the electron concentration was increased and the resistivity was decreased, and the resistivity of 8.0\times10\textsuperscript{-4} \textOmega cm was achieved at the TEG flow rate of 0.24 \textmu mol/min.

The optical properties of ZnO thin films were characterized by low temperature (4.2K) PL measurements. For undoped ZnO thin film, only the near bandedge emission was observed, and the emission at 3.33 eV was dominant, which was assigned to exciton bound to oxygen vacancy. By increasing Ga concentration, the emission at 3.36 eV was increased, which was assigned to exciton bound to neutral Ga-donor. However, by further increase of Ga concentration, it was found that the deep level emission at around 2.9 eV was increased.
DESIGNING VOLATILE METAL COMPLEXES AS ALD PRECURSORS FOR SEMICONDUCTOR APPLICATIONS

Xinjian Lei and Daniel P. Spence

Air Products and Chemicals
1969 Palomar Oaks Way
Carlsbad, CA 92011
leix@airproducts.com

As the feature size for semiconductor devices shrinks for the future generation, there is a constant demand for new metal complexes as precursors for atomic layer deposition (ALD) to make conformal thin metal containing films such as metal oxides as high k materials, metal nitrides as diffusion barrier for copper interconnect, and metal thin films as electrodes. The basic requirements for ALD precursors are volatile, thermal stable during delivery and high reactivity at the ALD process window. Recently we have molecularly designed a series of tridentate β-ketoimine ligands, novel β-ketoimimates including alkaline and transition metals have been synthesized in good yield and fully characterized. All the compounds are monomeric and their physical properties suggest they are suitable as precursors for ALD of metal thin films or metal oxides in the semiconductor applications. Figure 1 is a TGA diagram of one strontium β-ketoiminate, indicating it is volatile. Figure 2 is the vapor pressure of the strontium β-ketoiminate (solid line) vs that of traditional strontium precursor Sr(TMHD)_2 (dashed line), showing the new strontium β-ketoiminate is much more volatile than Sr(TMHD)_2.

Figure 1

Figure 2
Thin film dielectrics based on hafnium or zirconium oxides are being introduced to increase the permittivity of insulating layers in nanoelectronic transistor and memory devices. Atomic layer deposition (ALD) is the process of choice for fabricating these films, and the success of this method depends crucially on the chemical properties of the precursor molecules. Much promise is shown by Hf and Zr precursors that contain cyclopentadienyl (Cp=C₅H₅ₓRₓ⁻) ligands.

We have carried out ab initio calculations of a range of heteroleptic metallocenes [M(Cp)₄-n(L)ₙ], M=Hf/Zr, L=Me and OMe. Based on optimized monomer structures, we analyze reactivity with respect to ligand elimination, independent of surface effects. The order in which different ligands are eliminated during ALD is predicted to follow their energetics of hydrolysis and this is confirmed by in situ mass spectrometry [1]. We identify the properties of the ligands that lead to this mechanism.

Thermogravimetric analysis of these precursors shows significant differences in thermal stability. In particular, (MeCp)₂ZrMe₂ was found to be unstable when held at elevated temperatures. We therefore compute pathways for thermal decomposition and find a mechanism via intramolecular α-H-transfer that is possible for (MeCp)₂ZrMe₂ but not for (MeCp)₂Zr(Me)(OMe).

Investigation on Structural and Electrical Properties of High-k Dielectrics Prepared by ALD with Non-Uniform Gas Flow and Wafer Temperature

Chun-I Hsieha, Shih-shu Tsaia, Tsai-Yu Huanga, Wei-hui Hsua, Hung-Fu Tsaib, Chia-Chieh Yangb, Chang-Rong Wua, and Steven Shihb

aAdvanced Technology Development Division, & bIntegration Division, Nanya Technology Corp. No. 98, Nanlin Rd., Taishan Shiang, Taipei County 243-08, Taiwan
E-mail: chunihsieh@ntc.com.tw

Batch-type atomic layer deposition (ALD) process is developed for better cost of ownership (CoO) and throughput than single wafer chamber. However the step coverage and the uniformity are still critical issues for batch-type ALD tool makers due to the non-uniform gas flow and wafer temperature. Recently, additional precursor injectors are introduced to furnace ALD to improve the within wafer uniformity of thickness by the independent gas flow across each wafer. Although these efforts are reported exhibiting an excellent within wafer uniformity of about 3%, the structural and the electrical properties still lack for study.

In this work, we disclose the effect of gas flow and wafer temperature distribution on the dielectric properties. The ZrO₂/Al₂O₃/ZrO₂ (ZAZ) stacks of varied thickness were deposited by furnace ALD process on 300mm silicon wafers and nozzle injectors are placed in front of each wafer in the reactor. The ZAZ film with thickness uniformity lower than 3% exhibits three different C-V curves within a wafer that the center area has the sharpest slope and top area which is closest to nozzle injector has the most significant hump. In spite of lowest capacitance, the highest dielectric constant appears in the center area where the thickest interfacial layer is found thereby. The tendency of leakage versus EOT and the leakage level can be attributed to the interfacial layer and k-value where high-quality interfacial layers help suppress leakage, but poor interface and crystalline in bulk film degrade leakage performance instead. Furthermore, the structural properties were investigated by transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), and X-ray photoelectron spectroscopy (XPS)
OPTICAL EMISSION SPECTROSCOPY AS A TOOL FOR STUDYING, OPTIMIZING, AND MONITORING PLASMA-ASSISTED ATOMIC LAYER DEPOSITION PROCESSES

A.J.M. Mackus, S.B.S. Heil, E. Langereis, H.C.M. Knoops, M.C.M. van de Sanden and W.M.M. Kessels

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
a.j.m.mackus@student.tue.nl

In this contribution it is demonstrated that optical emission spectroscopy (OES) is an easy-to-implement and valuable tool to study, optimize, and monitor thin film growth by plasma-assisted atomic layer deposition (ALD). The species in the plasma can be identified through the analysis of the light emitted by the plasma. OES provides therefore information on the reactant species delivered to the surface by the plasma but it also yields unique insight into the surface reaction products and therefore on the reaction mechanisms of the deposition process (see, e.g., Fig. 1). Time-resolved measurements reveal information about the amount of precursor dosing and length of plasma exposure needed to saturate the self-limiting half reactions, which is useful for the optimization of the ALD process (see, e.g., Fig. 2). Furthermore, time-resolved OES can also be used as an easy-to-implement process monitoring tool in plasma-assisted ALD processes on production equipment; for example to monitor reactor wall conditions or as a real-time fault detection tool. These aspects will be illustrated by data obtained during plasma-assisted ALD of Al₂O₃ (Al(CH₃)₃, O₂ plasma), Ta₂O₅ (Ta[N(CH₃)₂]₅, O₂ plasma), TaN (Ta[N(CH₃)₂]₅, H₂ plasma) and TiN (TiCl₄, H₂-N₂ plasma).

**Figure 1:** Emission spectrum from a steady-state O₂ plasma and a spectrum of an O₂ plasma exposure during a plasma-assisted ALD cycle of Ta₂O₅. The latter spectrum was recorded after a Ta[N(CH₃)₂]₅ dosing step during the first 200 ms of plasma exposure. Combustion-like reactions rule the plasma half-reaction indicated by the intense CO emission. The presence of CN emission suggests that Ta-N bonds are broken during the oxidation of the film and the combustion of the surface groups.

**Figure 2:** Time-resolved intensities of emission lines of plasma species and reaction products after a Ta[N(CH₃)₂]₅ dose had preceded. The plasma was ignited at time \( t \approx 0.5 \) s. Surface ligand exchange is finished after approximately 3 s, when the signals reach their steady-state value.
ATOMIC LAYER DEPOSITION OF STRONTIUM-DOPED ZrO\(_2\) AND STRONTIUM ZIRCONIUM OXIDE

Kaupo Kukli,\(^1\) Jaakko Niinistö,\(^1\) Mikko Ritala,\(^1\) Markku Leskelä,\(^1\) Lars Oberbeck,\(^3\) Jonas Sundqvist,\(^3\) Uwe Schröder\(^3\)

\(^1\) University of Helsinki, Department of Chemistry, P.O. Box 55, FIN-00014 Univ. Helsinki, Finland
\(^2\) also at: University of Tartu, Institute of Physics, Tähe 4, 51010 Tartu, Estonia
\(^3\) Qimonda Dresden GmbH & Co. OHG, Königsbrücker Straße 180, 01099 Dresden, Germany

E-mails: kaupo.kukli@helsinki.fi, kaupo.kukli@ut.ee

Studies on atomic layer deposition (ALD) of high-permittivity metal oxides have been conducted in order to seek routes to the growth of materials of enhanced permittivity (30-50). These materials are investigated for the accommodation of dielectric oxides to the next-generation complementary metal-oxide-semiconductor or metal-insulator-metal devices. This study reports the deposition and some properties of ZrO\(_2\) films doped with strontium in order to stabilize high-permittivity cubic or tetragonal polymorphs of ZrO\(_2\). Furthermore, the goal of the study has been the deposition of zirconate phases, in particular, aiming at SrZrO\(_3\) stoichiometry.

The zirconium precursors used were either (CpMe)\(_2\)Zr(OMe)Me (ZrD-04) or Zr[N(CH\(_3\)](C\(_2\)H\(_5\)]\(_4\) (TEMAZr). Sr(P\(_3\)Pr\(_3\)Cp)\(_2\) was applied as Sr precursor. Ozone was used as oxygen source. The growth experiments on films with thickness in the range of 6-50 nm were conducted using a research-scale flow-type hot-wall F120 ALD reactor. The films were deposited on SiO\(_2\)/Si and TiN substrates at 250-275 °C in the case of Zr[N(CH\(_3\)](C\(_2\)H\(_5\)]\(_4\)-process, and at 300-350 °C in the case of (CpMe)\(_2\)Zr(OMe)Me–process. The doping of ZrO\(_2\) by Sr, as well as the growth of mixed Sr-Zr-O phases, was realized via alternate deposition of ZrO\(_2\) and SrO layers, i.e. changing the ZrO\(_2\):SrO ratio of deposition cycles, ranging between 20:1 and 5:3.

The structure and composition of the films deposited were studied by using XRD (Fig. 1), PIXE (Fig. 1) and FTIR. Electrical properties were evaluated carrying out capacitance-voltage and current-voltage measurements. Onset of crystallization of ZrO\(_2\):Sr films against different cycle ratios were studied, partially revealing the decrement of the critical crystallization temperature with increasing Sr content. Development of the phase composition upon annealing time and temperature was registered. Leakage current densities in the order of 10\(^{-6}\)-10\(^{-7}\) A/cm\(^2\) were achieved at capacitance equivalent oxide thickness values below 1 nm.

---

Figure 1. Results of the composition analysis of the Sr-Zr-O films (left panel) grown from two different metal precursors, and representative X-ray diffraction patterns of 17-20 nm thick films grown with ZrO\(_2\):SrO cycle ratio 1:1, using Zr[N(CH\(_3\)](C\(_2\)H\(_5\)]\(_4\), at 275 °C.
**ALD-AlN and TiAlN film for improvement of effective work function in Metal/High-k p-MOSFET**

Kazuhiro Harada\(^1\), Masaru Kadoshima\(^1\), Hideharu Itatani\(^2\), Sadayoshi Horii\(^2\), Takayuki Aoyama\(^1\), and Yasuo Nara\(^1\)

\(^1\)Research Dept. 1, Semiconductor Leading Edge Technologies (Selete), Inc. 16-1 Onogawa, Tsukuba-city, Ibaraki, 305-8569, Japan
\(^2\)Research Dept. 2, Semiconductor Equipment System Lab., Hitachi Kokusai Electric Inc. 2-1 Yasuuchi, Toyama-city, Toyama, 939-2393, Japan

E-mail : harada.kazuhiro@selete.co.jp  Tel:+81-29-849-1573

Metal/High-k gate stack has been required for the downsizing of CMOS devices. Serious problem of Metal/High-k gate stack is that the effective work function of gate electrode shifts to midgap by “Fermi-level-pinning” phenomenon after high temperature annealing process. Especially, this phenomenon appears prominently in p-MOSFET. In order to prevent the phenomenon, authors proposed a new integration technology using sputtered TiAIN gate HfAlSiON p-FET. As the results, high effective work function of 4.8 eV was obtained due to spontaneous AlN-cap formation of TiAlN and subsequent intermixing between AlN-cap and HfSiON by high temperature annealing.[1] However, in the viewpoint of the thickness uniformity and the plasma damage, the atomic layer deposition (ALD) method is preferable to the sputtering. Then, we investigated the ALD formation of capping ultra thin (~1nm) AlN film and the TiAlN film.

The AlN film was formed by ALD method using trimethyl aluminum (TMA) and NH\(_3\). Fig. 1 shows the ALD film thickness as a function of number of ALD cycles. The details of the deposition condition are shown in the Fig. 1. It can be confirmed that the thickness is controllable by the cycle number even though an ultra thin film area. In addition, it was found that carbon concentration of ALD-AlN film is lower than the detection limit of high-resolution Rutherford backscattering spectroscopy (HR-RBS) analysis.

TiAlN film was formed by the laminate structure with an AlN layer by ALD and a TiN layer by CVD. The precursor for TiN CVD was Tetrakisdimethylamidotitanium (TDMAT). Fig. 2 shows the concentration of Al and Ti in the TiAlN film as a function of the ALD cycle number of the AlN layer. In this case, the thickness of TiN layer was 2nm. It is confirmed that the Al concentration in the TiAlN films can be controlled up to about 35% by changing the ALD cycle number. Fig. 3 shows the x-ray photoelectron spectroscopy (XPS) depth profile of TiAlN film. The carbon concentration in the TiAIN film is lower than 5 at.%. Moreover, the grain condensation and the film exfoliation was not found in the AlN film and TiAIN film, and these films had a relatively smooth surface (RMS=1.0nm) after 900°C anneal.

From these results, it is concluded that the ALD process is adaptable to the capping layer and the TiAIN film can apply to gate first process. In the presentation, the electrical properties of the TiAIN gate HfAlSiON p-FET will be reported.

**Reference**

THERMAL AND PLASMA ENHANCED ATOMIC LAYER DEPOSITION OF TITANIUM OXIDE PASSIVATION LAYERS

Tae-Sub Kim, Myoung-Gyun Ko, Woong-Sun Kim, Dae-Yong Moon, Byung-Woo Kang and Jong-Wan Park*

Department of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea
E-mail: taesub@hanyang.ac.kr

The passivation layers of devices or substrates for organic light-emitting diodes (OLED) or flexible display panels have been intensively studied because they are easily degraded by water vapor, gaseous oxygen and high deposition temperature. Titanium oxide film deposited by CVD or sputtering has been reported as a good passivation layer of plastic substrate and optical devices [1].

In this study, ultra-thin titanium oxide was deposited on a polyethersulfon (PES), poly N-vinylcarbazole (PVK) and Si (001) substrates by plasma-enhanced atomic layer deposition (PEALD) using direct RF plasma and thermal ALD using O₂ gas as a reactant at a deposition temperature of 90 °C. In order to investigate structural behaviors, morphology, chemical composition and hygroscopic property of deposited films, we used Rutherford Backscattering Spectrometry (RBS), Atomic Force Microscopy (AFM), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Fourier Transform Infrared Spectroscopy (FT-IR).

Titanium oxide film thickness with 1000 ALD cycle is about 80 nm on Si, 30 nm on PES, 20 nm on PVK substrate, respectively. And it was expected that O₂ plasma could damage to the deposited thin film and plastic substrate. Root Mean Square (RMS) values of TiO₂ thin films are 1.5 nm when using PEALD, and 0.7 nm when using thermal ALD. TEM photographs show that plastic substrates are etched by O₂ plasma when using PEALD. –OH peak detected in TiO₂ thin film deposited by thermal ALD was less than –OH peak in TiO₂ thin film deposited by PEALD.

Reference
Polyatomic Layer Chemical Vapor Deposition (PLCVD) process is attractive for production of high-k gate dielectric because of its capability of fabricating high quality film with high throughput. In this paper, we have optimized PLCVD process to fabricate sub-nm EOT Hf-based gate dielectric applicable to the gate-first process. Thin Hf-silicate and Hf-oxide films were formed by repeating polyatomic film deposition and post-deposition O\textsubscript{3} treatment using Hf(MMP)\textsubscript{4} and Si(MMP)\textsubscript{4} as precursors. By inserting O\textsubscript{3} treatment of 10 s/cycle, carbon concentration in as-deposited film is effectively reduced to as low as 2x10\textsuperscript{20} atoms/cm\textsuperscript{3}. HfSiON and HfON gate dielectrics were fabricated by forming Hf-silicate or Hf-oxide film on a 0.6-nm-thick SiON interface layer followed by plasma nitridation and post-nitridation annealing at 1050\textdegree C. MISFETs were fabricated by a gate-first process using TaSiN as a gate electrode.

One of the most critical concerns to realize sub-nm EOT high-k gate dielectric by the PLCVD process is to suppress growth of interfacial layer during O\textsubscript{3} treatment. Fig.1 shows EOT vs gate leakage current (J\textsubscript{G}) trend lines obtained by changing thickness of HfSiON from 2 to 2.5 nm at different deposition rate. Among them, the trend line of those formed by 0.7 nm/cyc shows the lowest J\textsubscript{G}, which indicates that growth of IL is suppressed by increasing the deposition rate. With optimized conditions, EOT scalability to 0.82 nm is achieved with keeping high carrier mobility and sufficient reliability. To achieve higher k-value, we also investigated applicability of Hf-oxide. It is concerned that high-temperature annealing applied in the gate-first process is detrimental for the Hf-oxide, because of crystallization into monoclinic phase which degrades k-value [1]. Thus, we examined its crystalline structures after 1050\textdegree C annealing as shown in Fig.2. It is clearly observed that nitridation converts the crystalline structure into tetragonal phase whose k-value is higher than that of the monoclinic phase [2]. As a result, lower J\textsubscript{G} compared to the HfSiON is obtained with the HfON as shown in Fig.1, indicating higher k-value of HfON. EOT can be further scaled to 0.66 nm by skipping O\textsubscript{3} treatment, while accompanying degraded reliability due to carbon impurities. These results suggest capability of further scaling with HfON and confirm its compatibility with the gate-first process.

---

**Figure 1.** EOT vs J\textsubscript{G} of HfSiON formed at different deposition rate and HfON.

**Figure 2.** In-plane XRD spectrum of annealed Hf-oxide with and without nitridation.

NEW INJECTION/VAPORIZATION TECHNOLOGY FOR ALL ALD PROCESSES REQUIRING VAPORIZATION OF SOLID AND LIQUID ORGANIC, ORGANOMETALLIC OR INORGANIC COMPOUNDS

H. Guillon and S. Bonnafous

A new injection/vaporization technology is presented [1]. It is adapted to liquid and solid precursors delivery and vaporization for ALD, CVD, MOCVD, PECVD and all processes requiring a gas phase containing the vapors of organic, organometallic or inorganic compounds. The new technology can inject and vaporize pure liquid compounds and solid ones dissolved in a carrier liquid (organic solvent). It is able to handle and vaporize most of solid and liquid organic, organometallic or inorganic compounds including low vapor pressure, thermally labile and viscous ones provided they have a sufficient vapor pressure below their decomposition temperature. The new technology presented provides unmatched performances based on a very fine atomization of a pulsed liquid mixed with a carrier gas prior to injection inside the vaporizer.

The very fine atomization is achieved by what is called an injection head. The injection head uses a unique proprietary way to deliver and atomize the liquid inside the vaporizer. This technology will be presented in details. A focus will be done on the way the liquid and carrier gas flows injected in the vaporizer are controlled. The flows control unit developed has been adapted to the architecture of the injection head. The new technology will also be compared to the other existing injection/vaporization technologies.

Hafnium oxide based dielectric thin films were deposited onto Silicon substrates by atomic layer deposition (ALD). Their structural properties were investigated by X-ray diffraction, X-ray reflection and transmission electron microscopy. The high-κ dielectric film with a thickness of 10 to 30 nm was deposited onto plain silicon wafer substrate and onto deep trench structured substrates (approximately 100 nm wide, aspect ratio $\leq 1:50$) as used for DRAM capacitors. ALD was used because of the exceptional step coverage that is not reached by any other method. Hafnium chloride and water were used as metal precursor and oxygen source, respectively. With help of a sophisticated sample preparation techniques it could be shown that the coverage inside the deep trench does strongly depend on the deposition parameters. X-ray diffraction analysis under grazing incidence showed that the crystallinity of the layers depends on thickness and a possible heat treatment. Further a phase stabilization of high temperature phases was achieved by doping the hafnium oxide layer with yttrium.
Low-temperature atomic-layer-deposition of SiO$_2$ with tris(dimethylamino)silane (TDMAS), ozone and H$_2$O vapor investigated by infrared absorption spectroscopy

Fumihiko Hirose$^1$, Yuta Kinoshita$^1$, Suguru Shibuya$^1$, Hironobu Miya$^2$, Kazuhiro Hirahara$^3$, Yasuo Kimura$^4$, Michio Niwano$^4$

$^1$Graduate School of Science and Engineering, Yamagata University
$^2$ Semiconductor Equipment Division, Hitachi Kokusai Electric Inc.
$^3$ Shin-Etsu Chemical Co., Ltd.
$^4$RIEC, Tohoku University

Corresponding author: fhirose@yz.yamagata-u.ac.jp

Methylaminosilane has attracted much attention as a precursor for SiO$_2$ atomic layer deposition (ALD) since it easily vaporizes at room temperature and reacts with oxidant like ozone or H$_2$O at lower temperatures. To realize SiO$_2$ ALD, it is important to elucidate adsorption and decomposition of the precursor on Si surfaces. So far, we have reported a study on the direct observation of the TDMAS adsorption and the ozone oxidation by infrared absorption spectroscopy (IRAS) with a multiple internal reflection (MIR) elsewhere $^1$. We have found that TDMAS dissociatively adsorbs on the Si(100) surface even at room temperature. IRAS suggested that TDMAS adsorbs preferentially on OH sites on hydroxylated Si surfaces. Ozone oxidizes chemically adsorbed TDMAS on the Si surface at room temperature. However, we have also found that continuous generation of OH sites on the surface is necessary to sustain the cyclic growth of SiO$_2$ at room temperature.

In the present paper, we have achieved the OH compensation after the ozone exposure by an H$_2$O vapor treatment with a temperature controlled technique. IRAS clearly indicated that the sample annealing during the H$_2$O vapor treatment around 160$^\circ$C was effective to the hydroxylation. We have confirmed the cyclic growth of SiO$_2$ by repeating TDMAS-ozone saturation at room temperature and the H$_2$O vapor treatment with a temperature of 160$^\circ$C by the IRAS measurements. We believe the present results give a deep insight to achieve near room temperature process of SiO$_2$ ALD on Si surfaces.

Reference

Precise Control of ALD TaN-based Metal Resistivity

Akiko Kobayashi*, Akira Shimizu, Akira Watanabe and Nobuyoshi Kobayashi

*ASM Japan, 6-23-1 Nagayama Tama-shi Tokyo, Japan
a.kobayashi@asm.com

Abstract: Film properties of TaN-based metal (TaCN and TaSiN) have been precisely controlled for plasma enhanced ALD (PEALD) and thermal ALD with additives of N₂ or NH₃. Film resistivity (ρ) strongly depended on the nitrogen concentration of TaN-based metal. These films showed conformal step-coverage for high-aspect (>6) 50nm-wide trenches. Consequently, ALD TaN-based metal is promising for microelectronic applications such as resistor of RF devices, electrode of high-k MIM capacitors, and Cu barrier metal.

Experiment: TaN-based films were deposited on thermally oxidized Si wafer with Eagle12™ reactor. The precursor for PEALD TaCN was metal organic precursor, Taimata™ (Ta(N-t-C₅H₁₁)₃[N(CH₃)₃]₃) and RF plasma was generated between shower head and substrate stage using H₂ gas. RF power was fixed at 300W or 400W. The precursors for thermal ALD TaSiN were TaF₅ and TSA (Trisilylammine). The substrate temperature was fixed at 300C. Nitrogen was added during PEALD process and NH₃ gas cycle in thermal ALD process.

Result and Discussion: The film properties without using additive gases were shown in Table 1. For PEALD TaCN films, ρ became lower with the higher RF power and the longer RF time. The ρ value saturated at around 200 μΩcm with RF 400W for 2sec. The N concentration in film was relatively low so that ρ was almost same as that of beta-phase Ta. Thermal ALD TaSiN process showed self-limiting growth and ρ saturated at around 500 μΩcm. For PEALD TaCN film, ρ increased with N₂ flow rate (Fig. 1). The resistivity increased with higher RF power and longer RF time. The film step-coverage factor became relatively the smaller as ρ became the higher. In the case of thermal ALD TaSiN, dielectric-like Ta₂N₃ film was formed when only TaF₅ and NH₃ precursors were used. We added NH₃ once every several TaF₅/TSA cycles. The ρ value increased with increasing additive NH₃ cycle time (Fig.2), while the film step-coverage factor was still high (Fig.3).

Conclusion: TaN-based film resistivity could be precisely controlled from 200 to 15000 μΩcm by ALD with nitrogen or NH₃ additives.


<table>
<thead>
<tr>
<th>PEALD</th>
<th>Precursor</th>
<th>Composition</th>
<th>Low Resistivity</th>
<th>Density</th>
<th>Depo Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taimata</td>
<td>H₂ plasma</td>
<td>TaCN=56:25:4</td>
<td>200 μΩcm</td>
<td>13 g/cm³</td>
<td>0.5 Å/cycle</td>
</tr>
<tr>
<td>ALD</td>
<td>TaF₅</td>
<td>TSA</td>
<td>TaSiN=50:18:30</td>
<td>500 μΩcm</td>
<td>10 g/cm³</td>
</tr>
</tbody>
</table>

Table 1. Film property

![Fig.1 N₂ flow rate dependence of resistivity of PEALD film.](image1)

![Fig.2 NH₃ cycle ratio dependence of resistivity of thermal ALD film.](image2)

![Fig.3 Cross section of AR 6 Trench TaN deposited thermal ALD with NH₃ cycle.](image3)
Ongoing research on unsaturated carboxylic acids combined with both TMA (TMA = trimethylaluminium) and TiCl$_4$ (titaniumtetrachloride) shows promising results. The systems investigated so far show ALD-type growth. The maleic acid (HOOCCH=CHCOOH) – TMA-system is such an example. Growth rate as function of deposition temperature of the system, and an atomic force microscopy (AFM) image of the surface deposited at 186 °C is shown in Fig. 1. A surface roughness (RMS) of 0.23 nm is measured for a film with a thickness of 81.4 nm when deposited at 186 °C using 150 cycles. The low surface roughness corresponds well with the results obtained by X-ray diffraction, which reveals that the as-deposited films are x-ray amorphous.

In-situ analysis by quartz crystal microbalance have been used to establish growth parameters for the systems. Growth rates as function of deposition temperature are established using X-ray reflectometry. As-deposited films have been investigated by infrared spectroscopy, atomic force microscopy, and X-ray diffraction.

Fig.1: Growth rates as function of deposition temperature of the maleic acid – TMA-system, and an AFM image of the surface of a 81.4 nm thick film deposited at 186 °C.
Improvement of \( V_{th} \) and Device Performance of HfSiON/Metal Gate-First n-MOSFETs by using an ALD-La\(_2\)O\(_3\) Capping Layer

Satoshi Kamiyama, Dai Ishikawa, Etsuo Kurosawa, Hiroyuki Nakata, Masashi Kitajima, Minoru Ootuka, Takayuki Aoyama, and Yasuo Nara
Research Dept. 1, Semiconductor Leading Edge Technologies (Selete), Inc.
16-1, Onogawa, Tsukuba, Ibaraki 305-8569, Japan (e-mail: kamiyama.satoshi@selete.co.jp)

HfSiON films are the most promising of the high-k gate dielectrics for scaled devices. Recently, HfSiON/metal gate with La\(_2\)O\(_3\) capping layers have been reported to improve \( V_{th} \) control [1-3]. However, these are still challenging technologies to apply to layers on V-th control and device performance of HfSiON/metal gate-first stacks with TaSiN gate electrode materials. Furthermore, \( V_{th} \) can be effectively controlled by post-deposition-annealing (PDA) temperature with excellent uniformity over 300 mm wafers. The EOT ranges are applicable to hp 32 nm metal gated bulk devices and these devices are demonstrated to exhibit high performance and reliability.

A La(i-PrCp)\(_3\) precursor was used for ALD-La\(_2\)O\(_3\) film formation because the melting point (\(-38^\circ\)C) is the lowest of the typical La precursors [3]. La\(_2\)O\(_3\) films were deposited for \( V_{th} \)-control capping layers on HfSiON based films with La(i-PrCp)\(_3\) and O\(_3\) at 250 \(^\circ\)C. Following La\(_2\)O\(_3\) capping layer deposition, these samples were annealed in N\(_2\) as PDA. TaSiN(30 nm)/W(50 nm) gate electrodes were deposited by PVD. After SiN hard mask formation, metal gate stacks were formed using dry etching. Dopants were activated using spike-RTA at 950 \(^\circ\)C.

Fig. 1 shows the dependence of \( V_{th} \) on the number of ALD-La\(_2\)O\(_3\) cycles for HfSiON/TaSiN gate stacks. Thickness of HfSiON based films were formed from 1.4 nm to 2.5 nm. The value of \( V_{th} \) becomes more negative with the increasing number of ALD cycles and \( AV_{th} \) are dependent on the HfSiON thickness. PDA at 1050 \(^\circ\)C caused La diffusion into the HfSiON/SiON gate stack by SIMS analyses, forming La-O bonds at the Hf[La]SiON/Si[La]ON interface and increasing the dielectric constant. It is thought that the number of La-O bonds is greater than the number of Hf-O bonds for thick capping layers, so that the shift in \( V_{th} \) is changed by La\(_2\)O\(_3\) and HfSiON film thickness. As shown in Fig. 2, the \( I_d-V_{g} \) curves clearly show more negative values as the number of ALD cycles increases, \( V_{th} \) can be effectively controlled by the number of cycles. The sub-threshold swing, \( S \), for all samples is good, being less than 75 mV/decade. The drain current (\( I_d \)) at \( V_{th} = +1.1\) V improve dramatically with the increasing number of ALD cycles that of capped gate stacks being more than 1.5 times that of uncapped gate stacks. In Fig. 3, \( V_{th} \) can be effectively controlled by PDA temperature and the \( V_{th} \) distributions of HfSiON/TaSiN gate stacks are seen to be very tight over 300 mm wafers, both with and without ALD-La\(_2\)O\(_3\) cap layers. The leakage current densities are reduced further with the increasing number of ALD cycles. EOTs and gate leakage current densities clearly meet the criteria for hp 32 nm metal gate bulk devices in ITRS 2006 [4]. Furthermore, the positive-bias temperature instability (PBTTI) over a 10-year lifetime can be held to an acceptably low level at \( V_{th} = +1.0\) V.

Strontium oxide (SrO) thin films were deposited on Si wafers by a plasma-enhanced atomic layer deposition (PEALD) technique using novel strontium ketominate and O2 plasma as a precursor and an oxidant, respectively, using a shower head type ALD chamber. SrO is a component oxide of SrTiO3 high dielectric film for the capacitors of next generation dynamic random access memories. The Sr precursor was dissolved in a solvent, and a vaporizer with an injector was used to feed Sr precursor into the chamber. ALD window for a self-limiting film growth was found at wafer temperatures up to 325 °C where a saturated film deposition rate of 0.02 nm/cycle was obtained. Saturated growth behaviors of the SrO film with respect to the precursor and oxidant input were also confirmed. Film composition was measured with XPS, and carbon content was around 10 at%. The quick formation of Sr-carbonate during the exposure of the sample to the air atmosphere may be responsible for the high carbon content.

Atomic layer deposition (ALD) is an excellent technique for atomic level materials engineering. The technique allows the film composition to be controlled by atomic layer accuracy in the growth direction. The film growth can be controlled on the surface with selective-area ALD in which case the film can be grown to wanted parts of the surface.

In this study films that were grown selectively were prepared by using a poly(methyl methacrylate) (PMMA) films as mask layers. PMMA films were prepared from PMMA-toluene solution by spin coating and films were patterned by UV lithography through a mechanical mask.

Patterned PMMA films were tested in several ALD processes, both noble metals and oxides. Tested noble metal processes were iridium, platinum and ruthenium and oxide processes were Al₂O₃ and TiO₂. Al₂O₃ was deposited using AlCl₃ and H₂O and trimethylaluminum (TMA) and H₂O. TiO₂ was deposited using Ti(OMe)₄ and H₂O and TiCl₄ and H₂O. Growth temperatures were 250 - 350 °C.

Tested precursors act differently with PMMA mask. PMMA mask passivated the surface against the tested noble metals and TiO₂ when deposited from Ti(OMe)₄. With other tested processes film grew on the PMMA film. Films did not grow through PMMA, however, and therefore these processes can still be exploited in lift-off mode.

Figure 1. Patterned iridium film (left) and patterned TiO₂ film from TiCl₄ and H₂O (right).
Enhancement of thermal stability of atomic layer deposited Ru films by *in-situ* H\textsubscript{2} plasma treatment

Sang Young Lee,\textsuperscript{a} Seong Keun Kim, Jeong Hwan Han, and Cheol Seong Hwang

\textsuperscript{a}Department of Materials Science and Engineering, and Inter-university Semiconductor Research Center, Seoul National University,
San #56-1 Shillim-dong, Kwanak-ku, Seoul, 151-742, Korea
jjmama@snu.ac.kr

Ruthenium is promising material as capacitor electrode for sub 40 nm DRAM devices. ALD Ru thin films were deposited by using 2,4-(Dimethylpentadienyl)(Ethylcyclopentadienyl) Ruthenium precursor and O\textsubscript{2} as reactant gas through liquid injection system. In some cases, H\textsubscript{2} plasma treatment was performed after the O\textsubscript{2} pulse/purge cycle. In case of using H\textsubscript{2} plasma, the Ru thin films have characterized better step coverage on 3D hole structure. The crystallinity and preferred orientation of Ru thin films were different according to the use of the H\textsubscript{2} plasma. The thermally grown Ru thin films were randomly orientated (101, 002, 100 XRD peaks were observed), whereas the Ru thin films using H\textsubscript{2} plasma was 002 preferentially orientated. Furthermore, the grain growth of Ru thin films after 650°C post deposition anneal in N\textsubscript{2} ambient for 1 min. was suppressed by using H\textsubscript{2} plasma. (See Fig. 1) This means the thermal stability of Ru thin films was highly improved by adopting H\textsubscript{2} plasma. Systematic investigation results on the influence of the H\textsubscript{2} plasma on the growth, structure and thermal stability of the ALD Ru films will be reported.

![Figure 1](image-url)  
Figure 1. The different thermal stability of Ru thin films in the bottom region of capacitor hole after PDA by (a) thermal deposition (b) using H\textsubscript{2} plasma
Atomic layer deposition (ALD) of the PbO, TiO₂, ZrO₂ and the ferroelectric PbTiO₃ (PTO) thin films were attempted using the Pb(DMAMP)₂, Ti(Oi-Pr)₄, and Zr(Ot-Bu)₂(DMAMP)₂ as the Pb-, Ti- and Zr-precursors, respectively, and H₂O or O₃ as an oxidant at wafer temperatures ranging from 200 to 250°C on Ir/IrO₂/SiO₂/Si and Si substrates. The ALD characteristics of the PbO, TiO₂, and ZrO₂ films were investigated in detail for determining the ALD conditions of PTO thin films. The PbO and ZrO₂ films showed higher growth rate in the early stage than that in the later stage of the film growth due to the catalytic activity of the Ir substrate on the chemical adsorption of the precursors and H₂O. Chemical structures of the PbO and ZrO₂ films were different depending on the two growth regimes. However, the TiO₂ films showed an inverse trend; lower and higher growth at the initial and later stages, respectively, which is believe to be related to the in-situ crystallization of the films when the films become thicker. The stoichiometric PTO thin films were grown by a proper control of the cycle ratio of the PbO and TiO₂ cycles. The increase of the PTO film growth rate in the initial stage of the ALD due to the catalytic effect of the Ir was also observed. PTO films grown using H₂O at 200°C showed sparse structure with the high density of micro-pores inside as well as surface of film after fast-furnace annealing at 600°C, which resulted in a large leakage current. Although slow-furnace annealing method could reduce the density of micro-pores and improve the surface morphology, the leakage current was still quite high. The less dense structure of PTO films was resulted from the high growth rate of PTO films due to the high growth rate of TiO₂ thin film. Therefore, the property of PTO films could be improved by controlling the incorporation behavior of the TiO₂ into the PTO film. When TiO₂ thin films were grown at 250°C using H₂O or O₃ as an oxidant, the growth rate of films were 0.47 Å/cycle and 0.59 Å/cycle, respectively. Despite the higher growth rate, TiO₂ thin films grown using O₃ showed a denser structure compared to the case using H₂O. This was confirmed from the larger refractive index of TiO₂ film grown using O₃ (2.8) compared with that using H₂O (2.4), which were measured by ellipsometry. In addition, the deposition time for the case using O₃ is much shorter than that using H₂O. A quite long time was needed for purging the excesive H₂O because physi-sorbed H₂O cannot be removed effectively at the low growth temperature, i.e. 200~250°C. The short processing time can reduce a thermal damage, such as inter-diffusion at the interface, from which thin film can suffer during the growth process for long time. Consequently, it can be expected that the film structure and the electrical properties of PTO film can be improved by the use of O₃. The growth characteristics and electrical properties of PTO films grown using O₃ will be reported.

RuO₂ is also an electrically conductive material with a low enough resistivity. In this study, ruthenium electrical conductivity, low reactivity with dielectric films and easier fabrication process compared to Pt. Ruthenium is an attractive material as the capacitor electrode of next generation DRAMs due to its good resistivity of Ru and RuO₂ film was 20 µΩ cm.

RuO₂ was also deposited by controlling the flow rate of N₂/H₂ deoxidizing agent from 200 sccm to 500 sccm. Figure 2 shows an X-ray photoelectron spectra of Ru 3d peak. As N₂/H₂ flow rate is decreased from 1000 sccm to 200–500 sccm, Ru 3d peak is shifted to the higher binding energy suggesting that RuO₂ phase is formed. It was also confirmed that controlled formation Ru or RuO₂ films was possible by by changing the N₂/H₂ flow rate by X-ray diffraction and resistivity measurement. The resistivity of Ru and RuO₂ film was 20 µΩ cm and 105 µΩ cm.

Platinum is an important material for many nanoscale applications. As one of the noble metals it is well known from its chemical stability against oxidation even at high temperatures. Therefore platinum oxide, although existing in several bulk stoichiometric compositions, has not been as extensively studied as platinum. Physical methods, such as sputtering, have usually been employed for platinum oxide thin film depositions.

Reduction of platinum oxide films by heat or energetic ions makes platinum oxide an interesting material for several applications. The super-resolution near-field structure (super-RENS), in which the diffraction limitations of a laser can be circumvented, is considered a promising technology to increase the data storage capacity of optical media. Thin platinum oxide layer can be used in super-RENS as a mask layer. On the other hand, focused ion beam or laser irradiation can be applied to high resistivity platinum oxide for metallization, patterning or writing electrical connections to the films. Additionally, thermal decomposition behavior of platinum oxide has been proposed to be exploited even as a thermal lithography technique for fabricating nanoscale structures with a high aspect ratio over large areas.

We shall demonstrate the preparation of platinum oxide thin films by atomic layer deposition (ALD). Uniform films were obtained by employing more reactive oxidizing agent than molecular oxygen that is commonly used in ALD of metallic Pt, and by lowering the deposition temperature so that adsorbed oxygen atoms do not become consumed in the reaction between oxygen and noble metal precursor. Amorphous platinum oxide thin films were grown using Pt(acac)₂ and ozone as precursors at 120 and 130 °C. The applicable deposition temperature was found narrow as the sublimation temperature of Pt(acac)₂ is 110 °C while metallic film was obtained already at 140 °C. The platinum oxide films were successfully deposited on TiO₂ and Al₂O₃ adhesion layers, on soda lime glass, and on native silicon oxide on top of silicon substrates. Films adhered well to all tested substrate surfaces. Resistivities of about 50 to 60 nm thick platinum oxide films were between 1.5 and 5 Ω cm, and could be varied as a function of both precursor pulse lengths. Additionally, deposited platinum oxide films were reduced at room temperature in 5 % H₂ gas under reduced pressure to obtain porous metallic structures. The possibility to reduce platinum oxide easily might be beneficial in making platinum catalyst surfaces or conductive electrodes.

The conformality of ALD is usually studied by means of special substrates, where high aspect ratio features were realized e.g. by means of reactive ion etching. After ALD deposition, cross-sectional SEM and/or TEM are then used to determine whether conformal coating could be achieved on the entire inner surface of the trenches / holes.

In this work, we propose the use of simple and inexpensive macroscopic structures to quantify the conformality of the deposition process. A rectangle is cut from an aluminum foil (figure). The foil is then clamped between 2 pieces of SiO₂ wafer, thus creating a rectangular hole lined with SiO₂ surfaces. The aspect ratio can be varied by changing the dimensions of the rectangular opening and the thickness of the Al-foil. Because of the low pressure in the ALD reactor, the precursor flow inside these macroscopic structures will be in the Knudsen regime, as it is for microscopic trenches and vias. After ALD, both the upper and lower SiO₂ substrate can be retrieved and standard techniques such as ellipsometry can be used to measure the film thickness as a function of depth within the trench.

We deposited Al₂O₃ with a thermal process at 200°C with trimethyl aluminum (TMA) and H₂O precursors. AlN was deposited by a plasma ALD process at 200°C from TMA and N₂ plasma. The normalized film thicknesses (with respect to the film thickness outside the hole) are shown as a function of depth in the figure below. Further work is ongoing to characterize and model the conformality as a function of aspect ratio, pressure, precursor pulse time etc.

Figure: Macroscopic structure used to quantify the conformality of ALD processes (left), and initial results (thickness of the Al-foil was 0.4mm) for thermal ALD of Al₂O₃ and plasma ALD of AlN (right)

Thin film growth of TiO$_2$ and La$_2$O$_3$ are well investigated for Atomic Layer Deposition, ALD\cite{1,2}. This work has investigated deposition of films in the La$_2$O$_3$ – TiO$_2$ system as prepared by ALD using the precursor combinations TiCl$_4$ + H$_2$O and La(thd)$_3$ and O$_3$ (Hthd = 2,2,6,6-tetramethyl-3,5-dionato). The main focus is on making the La$_{2/3}$TiO$_3$ perovskite which seems to be a good starting material for making piezo-, ferro-, pyroelectric and electro-optic materials. Earlier reports highlight the problem of making this phase, due to the stable phase of La$_2$Ti$_2$O$_7$ \cite{3}.

The advantage of ALD is the ability to make amorphous films with any ratio of Ti/La. This provides a possibility to investigate how the growth rate of the different compounds is affected by the other. From such an analysis the different compositions can be prepared. The phase-diagram of this system \cite{4} consists of a limited number of crystalline phases with neglectable solid solution. The films have been crystallized by annealing in O$_2$ atmosphere and analyzed by X-ray diffraction. Thin film thicknesses have been measured by X-ray reflectometry and their composition by X-ray fluorescence. We have observed a suppression of deposition of La when the precursor pairs are grown in combination. Fig. 1 show the observed dependency between the deposited and pulsed compositions for the selected precursor pair, together with the expected dependency based on their individual growth rates, and a fit to the concept of surface utilization \cite{5}.

![Figure 1: Observed dependency between pulsed and deposited composition compared to different theoretical models.](image)

The authors recently reported the growth of Ge$_2$Sb$_2$Te$_5$ (GST) thin films by a combined plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PEALD) with a quality equivalent or superior to the sputtered material. The PECVD/PEALD process should be preferred deposition method for the GST material for its use in highly integrated devices (> 1 Gb). However, in contrast to the sputtering method, this chemical process showed a very substrate surface dependent growth behavior, which might be positively used in the formation of integrated structure formation. On the other hand, the substrate dependent growth behavior is a crucial demerit for fabricating the conventional T-shaped PCRAM cells because the GST thin films should be homogeneously and evenly deposited on the metallic contact plug surface as well as the inter-layer dielectric (ILD), which is usually CVD SiO$_2$, wherein the metal plugs are embedded. In this study, substrate dependent growth behavior of GST films on TiN, SiO$_2$ and TiO$_2$ films was investigated.

Stoichiometric GST films were deposited using a shower-head type 8-inch-scale PEALD reactor at a wafer temperature of 150°C. Ge(i-C$_4$H$_9$)$_4$, Sb(i-C$_3$H$_7$)$_3$, and Te(i-C$_3$H$_7$)$_2$ were used as the Ge, Sb and Te precursors, respectively. For investigating the nucleation and growth behaviors on each substrate, chemical composition and area layer density of the film were investigated by an X-ray fluorescence analyzer. The nucleation of GST film on the SiO$_2$ film was seriously retarded (long incubation cycles) whereas those on the TiN and TiO$_2$ were fluent with negligible incubation cycles. The structure, cross-section and surface morphology of GST film were investigated by X-ray diffraction, field-emission scanning electron microscopy and atomic force microscopy. The X-ray diffraction showed that the as-deposited GST films on the TiN and TiO$_2$ substrates have an fcc structure with (200) preferred growth directions. They also have fcc structure but with (111) preferred directions on SiO$_2$ substrates when a sufficient deposition cycles were performed. The reason for the enhanced nucleation and growth properties of the GST on TiO$_2$ substrate was investigated by X-ray photoemission spectroscopy, atomic force microscopy and high resolution transmission electron microscopy. XP spectra of Ge 2p of GST films showed the formation of GeO$_x$ phase on TiO$_2$ as well as TiN substrate at the initial deposition stage. On the other hand, not only GeO$_x$ but also SbO$_x$ phase was formed on SiO$_2$ substrate. It seemed that both Ge and Sb worked as a nucleation site on the various substrates. Te incorporation on the pre-deposited Ge and Sb layer was more efficient so that uniform and stoichiometric GST films were obtained on TiN and TiO$_2$. Details of chemical interaction between each element and substrate, and initial growth mechanisms will be presented.

Atomic Layer Deposition of Ta-N Based Thin Films Using a Novel Liquid Tantalum Chloride Precursor.

D. Schmidt, J. Sundqvist, B. Hintze, M. Albert, and J. W. Bartha;
 Institute of Semiconductor and Microsystems Technology, Technische Universität Dresden, 01062 Dresden
 Qimonda Dresden GmbH & Co. OHG
 Daniela.Schmidt@tu-dresden.de

The growing complexity of microelectronic circuits necessitate a steady miniaturization of semiconductor devices. The required structures increase essentially the standards in conformity, growth control as well as important physical and electrical film properties. Based on cyclic, self-limited surface reactions the atomic layer deposition (ALD) technique features good conditions for depositing thin, homogenous films.

Due to their good electrical and physical properties, metal nitrides are promising materials as diffusion barriers, electrodes of integrated capacitors or as gates in future CMOS circuits. The main problem with the existing metal nitride thermal ALD processes based on metalorganic precursors like tert-Butylimidotris(diethylamido)tantalum (TBTDET) are poor electrical film properties. It is well known that the utilization of halide precursors for example TaCl₃ give an significant improvement [1], however these precursors are solid and suffer from difficulties in handling.

In this work, we utilized a novel liquid TaCl₃-precursor for ALD of TaN. TAPEDIS was synthesized by Air Liquide and can be allocated to the chemical family of ‘Lewis Acid Base Complex’ as an adduct of Tantalum Chloride and Diethyl Sulfide (TaCl₃ : SEt₂). We used this pre cursor in combination with ammonia (NH₃) as nitrogen source and determined a process window for the Ta-N based film deposition. It turned out that the TAPEDIS process matches closely with the known TaCl₃ (solid precursor) process [1]. For instance in both cases the growth rate saturates between 0.2–0.25 Å/cycles within the same temperature window.

With XPS we did not observe sulphur in the TAPEDIS Ta-N based films, which would be expected to originate from the SEt₂-complex. Furthermore changes of the electrical and physical properties of the films were studied depending on the addition of Trimethylaluminium (TMA) as reducing agent besides NH₃. The deposition behaviour of the process also was investigated on plane surfaces as well as deep trench structures.

The work for this paper was supported within the scope of technology development by the EFRE fund of the European Community and by funding of the State Saxony of the Federal Republic of Germany.

GaAs passivation by atomic layer deposition technique

M. Bosund, A. Aierken, T. Hakkarainen, J. Tiilikainen and H. Lipsanen

Department of Micro and Nanosciences, Helsinki University of Technology, Tietotie 3 Espoo, Finland
Markus.Bosund@tkk.fi

GaAs based technology is not fully exploited because of the high density of the surface states which cause the Fermi-level pinning near the GaAs surface. It has been earlier shown that a functional part of a component should be at least 20 nm under the GaAs surface if one wants to avoid the problems caused by surface states [1]. Therefore, it is important to find a technology to prevent the surface states when the dimensions of the components are decreasing. Atomic layer deposition (ALD) is a promising technology for the GaAs surface passivation. The main benefits of ALD are 1) large range of materials, 2) Large growth areas and 3) low process temperatures.

In this study, suitability of ALD TiN for GaAs surface passivation is investigated. A 2-6 nm thick titanium nitride (TiN) film was grown at 275 °C on top of near surface InGaAs/GaAs quantum wells (NSQWs) by using titanium tetrachloride (TiCl₄) and ammonia (NH₃) as precursors and trimethylaluminum (TMA) as a reducing agent between the TiCl₄ and NH₃ pulses. The TiN recipe used in this study has been published earlier in ref. [3]. The liquid precursors (TiCl₄ and TMA) were kept at 20 °C and ammonia tank was at room temperature. It has been earlier shown that the PL intensity and the decay time of NSQW increase when the number of surface states decreases [2]. These two parameters were used to indicate the passivation efficiency in this paper. The thickness, growth rate, surface roughness and mass density of TiN were studied using X-ray reflectivity (XRR) measurements. X-ray diffraction (XRD) measurements were executed to see the crystallinity of the film and tension in the GaAs/TiN boundary. The optical properties of TiN were also studied with transmission and reflectivity measurements.

According to the XRR measurements the growth rate for TiN at 275 °C was 0.045 nm/cycle which is close to the result in ref. [3]. XRD measurements showed that the TiN film was amorphous and that there was no tension at the TiN/GaAs boundary. In passivation studies it came out that the TiN film decreased clearly the number of surface states. The PL intensity of the TiN coated NSQW was 15 times higher compared to the unpassivated reference NSQW. The decay time of the TiN passivated NSQW increased also by 42 %. Both transmission and PL measurements of NSQWs indicated that the TiN films also absorb light. This study shows that atomic layer deposited titanium nitride is a promising material for the GaAs passivation.

Atomic layer deposition has recently been applied on depositing inorganic thin films on nanostructured biological templates such as viruses\(^1\) and butterfly wings\(^2\). The properties of the biological templates can be preserved and combined with the durability and added functionality of the inorganic thin film. The reported structures include nanotubes, interconnected tube networks and periodical layers with optical interference.

The aim of this work was to study the effect of combining the hydrophobic surface of the cicada wing with the ultraviolet-switchable wettability of ZnO. As-deposited ZnO is hydrophobic, but it can be made hydrophilic by UV illumination.\(^3\) Cicada wings have a superhydrophobic surface morphology consisting of 250-nm-high pillars close to one another.

ZnO thin films were deposited from diethylzinc and water at 120 °C on cicada wings. In some depositions an Al\(_2\)O\(_3\) seed layer was deposited from trimethylaluminum and water at the same temperature. It is seen from SEM images that the ZnO layers deposited directly on the cicada wings did not follow conformally the microstructure of the wings (Figure 1). With a 2-nm-thick Al\(_2\)O\(_3\) seed layer, however, conformal growth was achieved (Figure 2). The contact angle of water was measured from as-deposited and UV-illuminated films. The maximum contact angles of 140° decreased by 40-80° upon UV illumination.

---

TOUGHNESS AND ADHESION OF ALD Al₂O₃: A COMPARISON BETWEEN THERMAL AND PLASMA DEPOSITED THIN-FILMS ON POLYCARBONATE

B. Latella, G. Triani, E. Langereis, M. Creatore, P.J. Evans, J Davis, M James, and W.M.M. Kessels

a Australian Nuclear Science and Technology Organisation, PMB 1, Menai NSW 2234, Australia
b Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
gtx@ansto.gov.au

The deposition of inorganic barrier coatings on polymer surfaces has the potential to improve the lifetime performance of organic functional materials that may be susceptible to degradation. In particular, the ingress of moisture and atmospheric gases as well as the abrasion and thermal cycling can significantly diminish a polymer’s suitability in cases where its bulk properties meet all other requirements.

In recent years, the coating of polymers has been extensively investigated as a means of improving their performance. The thermal degradation of many polymers limits deposition temperatures <150°C which restricts the methods suitable for producing high quality films. Thermal and plasma enhanced atomic layer deposition (ALD) are both capable of meeting the criteria of an effective barrier layer, as evidenced by recent reports describing the successful deposition of Al₂O₃ films on polymeric substrates [1-2]. In the present study, the mechanical properties of thermal and plasma-enhanced ALD Al₂O₃ films on polycarbonate substrates have been investigated. All films were deposited using an Oxford Instruments FlexAL™ reactor at the temperatures of 25 or 100°C. In addition, the effect of surface pre-treatment with an oxygen plasma was also examined. All films were subjected to micro-tensile testing from which the adhesion and toughness of the alumina films was determined. The films were also characterised with several analytical techniques including scanning electron microscopy, X-ray reflectivity and Rutherford backscattering which permitted an assessment of the as-deposited and tensile-loaded films.

References

NEGATIVE CHARGE AND CHARGING DYNAMICS IN Al₂O₃ FILMS ON Si CHARACTERIZED BY OPTICAL SECOND-HARMONIC GENERATION

J.J.H. Gielis, B. Hoex, N.M. Terlinden, M.C.M. van de Sanden, and W.M.M. Kessels

Dept. of Applied Physics, Eindhoven University of Technology, The Netherlands
j.j.h.gielis@tue.nl

Thin films of Al₂O₃ synthesized by plasma-assisted ALD provide an excellent level of surface passivation of c-Si and III-IV compound semiconductors, which is vital for the performance of devices such as nanocrystal or wafer-based light emitting diodes, photodetectors, and high-efficiency solar cells. Recently, it was demonstrated that the surface passivation properties of Al₂O₃ thin films arise after a postdeposition anneal.¹ In general, surface passivation can be achieved by a reduction of surface defects or by electrostatic shielding of charge carriers by internal electric fields (i.e. field-effect passivation). In this contribution the nonlinear optical technique of second-harmonic generation (SHG) has been applied to study Al₂O₃ thin films before and after anneal. SHG is a surface and interface specific technique that is extremely sensitive to internal electric fields. Spectroscopic SHG, carried out with a femtosecond Ti:sapphire laser tunable in the 2.66-3.50 eV SHG photon energy range [see Fig. 1], has revealed the presence of negative fixed charge in the Al₂O₃. For as-deposited Al₂O₃ films the negative fixed charge density was found to be on the order of 10¹¹ cm⁻², which increased to 10¹² - 10¹³ cm⁻² after anneal. The corresponding internal electric field most likely accounts for the surface passivation properties of Al₂O₃ thin films after anneal. The important role of the negative fixed charge density in the passivation properties of Al₂O₃ was confirmed by carrier lifetime spectroscopy and capacitance-voltage measurements. In addition, real time SHG experiments causing multiple photon induced charge trapping suggest a reduction of recombination channels after anneal, which could play an additional role in the surface passivation mechanism by Al₂O₃. The results directly show the feasibility of SHG for contactless characterization of charge and charging dynamics in c-Si/high-κ dielectric structures in situ and during processing, which are important applications inaccessible by conventional techniques such as capacitance-voltage measurements. The application of SHG during processing of c-Si/high-κ structures provides not only relevant information on field-effect passivation but also for nonvolatile memory and CMOS applications.

FIG. 1 SHG intensity as a function of SHG photon energy for an 11 nm Al₂O₃ film on Si(100), both as-deposited (open symbols) and after anneal (solid symbols). The strong increase in SHG intensity after anneal directly reflects the strong increase in the negative fixed charge density in the Al₂O₃. The inset illustrates the principle of SHG; generation of photons at twice the incident photon energy.

We investigated the atomic layer deposition of RuO₂ films for application as electrode layers of the next generation DRAM capacitors. These capacitors will be built up from ultra thin films of higher-k materials like SrTiO₃ or (Ba, Sr)TiO₃ in order to decrease the equivalent oxide thickness. In metal-higher-k materials-metal structured capacitor, the effective dielectric constant of the insulating layer decreases with decreasing film thickness due to interfacial effects. However, adoption of conducting oxide electrodes such as RuO₂ can increase the capacitance density of such integrated capacitors. In case that also structural compatibility is achieved as it is obtained for TiO₂ on RuO₂, the TiO₂ layer is shown to crystallize in the higher-k rutile phase structure (k ~ 100).[1] However, three-dimensional structured capacitor in DRAM devices is indispensable for satisfying required cell capacitance in spite of their high dielectric constant. In order to have a conducting oxide electrode also available for 3D integrated capacitor structures, we investigated the ALD growth process for RuO₂ thin films in detail.

In this study, RuO₂ films were deposited using traveling wave type ALD reactor. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(III) (Ru(C₁₁H₁₉O₂)₃, Ru(TMHD)₃) dissolved in ethylcyclohexane was used as a metal source. The Ru-solution was pulse injected and evaporated in a vaporizer at a temperature of 200 °C. The growth behavior of the ALD RuO₂ films was studied as a function of the substrate temperature and the type of oxidant. The films were characterized with respect to their structural, morphological and resistance properties.

The high dielectric constant TiO₂ thin films were deposited by an atomic layer deposition (ALD) using the Ti(O-i-C₃H₇)₄ (TTIP) and O₃ as metal and oxygen sources, respectively. TiO₂ is well known as a material having several polymorphs: rutile and anatase. Dielectric constants (k) of anatase are 45 and 25 along the a- and c-axis, respectively. Rutile structured TiO₂ has larger k values: 170 and 90 along the c- and a-axis, respectively. The authors reported that rutile TiO₂ thin films having a k value of 83-100 are grown on Ru electrodes by using ALD at a growth temperature of 250°C although the rutile TiO₂ is stable form at temperatures > 700°C.[1] The structural compatibility between the rutile TiO₂ and RuO₂ that was in-situ formed by the strong oxidation power of O₃ was the main reason for obtaining rutile TiO₂ on Ru at such a low temperature. However, Ru is a very expensive material and it is difficult to form the extreme 3 dimensional (3D) electrode structure in future dynamic random access memories (DRAM) using the Ru single layer. Therefore, in this study, Ru/TiN composite electrodes are used. It is expected that 3D TiN electrode could be formed using the well-matured process technology in DRAM, and thin Ru layer (< 5 nm) could be deposited on top by ALD. The thin Ru layer may enhance the rutile TiO₂ growth. In experiment, ALD-Ru films with varying thicknesses were grown at 250°C using the DER (2,4-(Dimethylpentadienyl)(ethylcyclopentadienyl)Ruthenium) and O₂ as the metal source and reactant, respectively, on sputtered TiN substrates. The growth behaviors of ALD-Ru film were studied by SEM, AFM, XRD and XRF. The TiN substrates were in-situ Ar-plasma pretreated to reduce nucleation barrier of Ru before the Ru ALD. It was reported that the Ar-plasma treatment selectively removes N ions from the surface of TiN, which makes the TiN surface more metallic or ionic (due to the residual Ti-O bonding) and reduces the nucleation barrier.[2] TiO₂ films were grown on the Ru/TiN substrates having different Ru thicknesses ranging from 0 to 10 nm. The structure and electrical properties of top Pt/TiO₂/Ru/TiN MIM capacitor will be presented. The k value of TiO₂ was increased from the k-value corresponding to anatase to that corresponding to rutile as Ru layer thickness was increased. A critical layer thickness of Ru at which the TiO₂ structure changes will be reported. In addition, the merits and demerits of Ru/TiN stack compared to Ru as a DRAM capacitor electrode will be discussed.

Ruthenium finds a variety of applications in semiconductor industry. It has been considered as metal electrode material in DRAM application in combination with SrTiO₃ dielectric and as p-type gate metal in transistor applications. One interesting new application is also the potential use of Ru metal as seed layer for Cu plating. Ru thin films are typically deposited by physical vapor deposition (PVD) or metal organic chemical vapor deposition (MOCVD). Due to the changes in the future semiconductor devices towards high aspect ratios and 3D structures the interest in the utilization of the atomic layer deposition (ALD) method for the growth of Ru thin films is growing.

The issue with either the Ru ALD or Ru CVD process has been the non-reactivity of the Ru precursors toward the starting oxide surfaces. In particular, the use of the most familiar precursors, RuC₂ and Ru(EtCp)₂, has shown to lead to long growth incubation time and at the same time to a production of poorly nucleated film [1]. Recently S. K. Kim et al. have shown that the growth of Ru can be started without any extensive incubation period when Ru[(CH₃)₂(C₅H₅)]EtCp (DER) compound is used [2].

To understand the difference in reactivity between the various Ru compounds on oxide surfaces, their reactions were studied on porous high surface area silica and alumina. The high surface area enables a highly detailed study of the very first ALD reaction of the metal compound with the starting oxide surface. The compounds studied included Ru(thd)₃, Ru(hfac)₃, Ru(EtCp)₂, Ru[(CH₃)₂(C₅H₅)]EtCp (DER) and Ru[(CH₃)₂(C₅H₅)]₂. The samples were characterized by elemental analysis and FTIR spectroscopy. Ru was determined by instrumental neutron activation analysis (INAA) and carbon with Leco carbon analyzer.

In this paper it is shown for instance that the most reactive precursor toward the oxide surfaces is Ru[(CH₃)₂(C₅H₅)]₂. DER precursor was the next most reactive and far more reactive than the other Ru precursors. In case of DER the amount of Ru deposited was found to depend on the number of Si-OH groups on the surface and the reaction temperature. At 300°C the amount of Ru deposited on silica heat treated at 350°C was 1.6 Ru atoms/nm². The (CH₃)₂(C₅H₅) ligand was released in the reactions and at 250°C the remaining EtCp ligand on Ru stayed intact as confirmed by FTIR spectra. At 300°C the EtCp ligand was decomposed, which led to very air sensitive Ru/silica sample. It started burning when in contact with ambient air. Ru(EtCp)₂ was shown not to react with Si-OH groups even at 350°C. It is concluded that the EtCp or in general the Cp ligands when bonded to Ru are very stable and not reactive towards OH groups, which explains the long incubation times observed.

During the 30 years of development of the Atomic Layer Deposition method, the technology has matured to a level meeting the demanding requirements of advanced microelectronics and nanotechnology manufacturing. Major development has been performed for well controlled surface reactions essential to successful ALD processes in the precursor chemistry. An essential part of the progress comes also from advances in ALD reactor design. Modern ALD reactors allow the use of a wide variety of precursor chemicals, fast sequencing, low particular and impurity levels, and high throughput.

Picosun Oy develops and manufactures Atomic Layer Deposition (ALD) reactors for scientific and industrial production purposes.

SUNALE™ Picobatch ALD tool by Picosun has a footprint of less than 1 m$^2$, and is able to coat 25 – 50 pieces of 4-inch or 6-inch wafers in a single run. Repeatability of Al$_2$O$_3$ process of 0.3% 1-sigma and uniformity of 0.6% 1-sigma have been reached in production. Added particle count of 4 pieces larger than 0.2 micrometers per a single 50 nm film deposition run, including loading and unloading steps has been achieved.

Loading of the batch can be done manually or automatically with preloaded holders and a Robotic handler. Fast cycle times are enabled by efficient purging of the reaction chamber. Maintenance of the reactor is easy and fast. Low precursor, gas, and power consumption combined with a very high uptime through reliable industrial software and electronics lower the cost-of-ownership of the SUNALE™ Picobatch ALD tool far below the usually accepted level.
ZrO₂ is an extensively studied high permittivity material for a wide range of applications. For example it is a candidate for replacing Al₂O₃ as the high k dielectric in DRAM and embedded DRAM (eDRAM). Polycrystalline films may be preferable to amorphous films due to their higher density and higher dielectric constant. The dielectric constant values in the literature vary from 18 to 35[1] depending on degree of crystallinity or crystaline phase. Among the various techniques to deposit ZrO₂ films atomic layer deposition (ALD) is already well known. Due to a self-limiting growth mechanism the method provides layer-by-layer growth with accurate thickness control, high conformality and precise composition control. To enhance reactivity between adsorbed precursor and the reactant gas on the surface radio frequency (RF) plasma is introduced. This method is called Plasma Enhanced ALD (PEALD). Using O₂ plasma enhances the growth rate and improves properties of thin films.

Typical metal precursor selection criteria include physical state, vapor pressure, thermal stability and purity. Preferably precursors should be liquid, thermally stable at high temperatures and yield stoichiometric and impurity-free films. Halides like ZrCl₄ or ZrI₄ were used in the past but residual halide in the film limits the usage of these precursors [2,3]. Recently other commonly used precursor groups are alkyl amides and cyclopentadienyls. In this poster we discuss physical and electrical characterization results from three different metal precursors, tetrakis (ethylmethylamino)zirconium (TEMAZr), bis(methylcyclopentadienyl)methoxymethyl zirconium (IV) (ZrD-04) and (ZyALD.0). Physical and electrical data will be presented for each precursor for both PEALD mode (with O₂ plasma) and thermal mode (with ozone).

Figure 1 – Jg as a function of EOT for TEMAZr and ZyALD.0

References
Photo Electron Spectroscopy is one of the methods widely used to investigate important properties of various materials, which could be correlated to their performances in electronic devices. Anyway, the interpretation of the photoemission experiments could become very complex if one compares samples produced with different methods and/or parameters.

For the purpose of clarify which information can be get by the material analysis with photoemission, we have investigated various HfO$_x$ layers grown onto Si substrate by ALD, by means of Synchrotron Radiation X-ray Photoemission Spectroscopy (SR-XPS) observing the dependence of the O1s, Si2p, and Hf4f spectra on the different sample preparations. From the experimental results we could determine the O/Hf ratio, the film thickness, and the silicate content of the samples, finding that the O/Hf ratio and the amount of silicate depend on the ALD parameters and on the precursors used, while the VBM and other spectroscopic features are almost independent. Finally, we discuss possible explanations of our findings.
IN-SITU FORMATION OF TRANSITION METAL AMIDO COMPOUNDS

J. Strickler, a F-J Wu, a T. Stoll b

a Albemarle Corporation, Gulf States Road, Baton Rouge, LA 70805
b Albemarle Corporation, 451 Florida St. Baton Rouge, LA 70801
jamie_strickler@Albemarle.com

Homoleptic transition metal amido compounds have several synthetic uses as reactive intermediates. They can be used to prepare metallocenes, 1-2 as catalysts for asymmetric intramolecular hydroamination, 3 catalysts for hydroaminoalkylation, 4 and as precursor compounds to metal oxides and nitrides in high k dielectric applications. 5 The synthesis of these compounds has traditionally been through the reaction of a metal halide and a preformed lithium amide (see example below). 6-7

\[
\text{ZrCl}_4 + 4 \text{LiNMMe}_2 \xrightarrow{\text{solvent}} \text{Zr(NMe}_2)_4 + 4 \text{LiCl}
\]

This synthesis works well, but has some limitations for industrial practice. This reaction has been done two ways; (1) the metal halide can be added to the preformed lithium amide or (2) the preformed lithium amide can be added to the metal halide. In the first route, a metal halide, which is typically a solid of low solubility (ie. \text{ZrCl}_4), is added to the slurry or solution of the lithium amide in a hydrocarbon solvent. It is difficult to control the addition rate and the reaction stoichiometry with solids. This raises safety and quality/yield issues. The second route requires two reactors and, depending on the amine and solvent, may involve a slurry transfer that is also difficult to control on industrial scale.

A new route has been developed which is flexible across many metal salt and amine combinations and has all the desirable features of an industrial process. This one-pot reaction produces metal amides \textit{in-situ} from metal halides, an amine, and a base (eg. \text{n-BuLi}) in a solvent. The metal halide and the amine are premixed to form a soluble intermediate. The solution of the base is then added in a controlled fashion to produce the desired product in good yields. Several examples will be presented.

\[
\text{MCl}_4 + 4 \text{HNR}_2 \xrightarrow{\text{solvent}} \text{MCl}_4(\text{HNR}_2)_2 + \frac{4 \text{n-BuLi}}{4 \text{LiCl}} \rightarrow \text{M(NR}_2)_4
\]

A side reaction between \text{HfCl}_4, a secondary amine, and tetrahydrofuran will also be described.

EFFECTS OF ANNEALING TIME ON ZnO THIN FILM GROWN BY REMOTE PLASMA ALD


hhryu@inje.ac.kr

Department of Nano Systems Engineering, Center for Nano Manufacturing, Inje University, Obang-dong, Gimhae, Gyeongnam 621-749, Korea

Atomic layer deposition has been proposed as a promising method to deposit thin film because it is available to grow uniform and high quality nano-scale thin films on large area, and atomic level thickness is controlled very simply by adjusting the number of deposition cycles. However, due to low deposition temperature, annealing treatment is demanded to get a high quality of ZnO thin film.

In this experiment, we investigated the effects of annealing time on the properties of ZnO thin film grown by remote plasma atomic layer deposition (RPALD). For ZnO thin film, DEZn and O2 plasma gas were used as reactants and the growth temperature of ZnO thin film was 150℃. After that, the samples were annealed at various time (30sec. ~ 60min.) with annealing temperature of 800℃. The properties of ZnO thin film depended on the annealing time greatly. The structural and optical properties were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), and photoluminescence (PL) measurements.
Differences of interfacial characteristics between HfO$_2$/GaAs (100) substrate

C. Y. Kim, C. J. Yim, C. N. Whnag, M. –H. Cho*

Institute of Physics and Applied Physics, Yonsei University, Seoul, 120-749 Korea.

Y. Yi

Advanced Technology Group, Korea Research Institute of Standard and Science, Daejeon, 305-600 Korea

Abstract

The interfacial characteristics between HfO$_2$ film/n-GaAs (100) substrate, which is chemically treated with or without buffered oxide etchant (BOE), formed by atomic layer deposition was investigated. With combination of high resolution x-ray photoelectron spectroscopy and reflection electron loss spectroscopy measurements, we evaluated the energy band alignment at the HfO$_2$/GaAs interfaces, which indicates that values of valence band maxima and band gaps were deduced to be 2.76 eV and 5.71 eV for HfO$_2$ on BOE-cleaned GaAs and to be 2.69 eV and 5.59 eV for HfO$_2$ on oxide-covered GaAs, respectively. The difference in band alignments was related to the interfacial chemical states in As-O bonding on the initial interface states. In addition, As 3d and Ga 3d+Hf 4f core-level spectra taken by HRXPS has examined interface chemical bonding states.

* E-mail: mh.cho@yonsei.ac.kr
The wurtzite-structure II-VI semiconductor ZnO has currently gained substantial interest because of its attractive properties for possible applications in UV laser, thin film gas sensor, varistor, and LEDs. Atomic Layer Deposition is applied in many advanced technologies that require precise control of film properties in the nanometer or sub-nanometer scale.

In this study, we used two different buffer layers (Al$_2$O$_3$ and ZnO), to compare the effects of buffer layers on ZnO thin film grown by ALD. X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to examine the structural property and surface morphology. Photoluminescence (PL) measurement was also done for optical properties.
Zinc oxide (ZnO) films have been recently studied as a promising material for optoelectric devices because ZnO has a wide band gap of 3.37 eV at room temperature and large exciton binding energy of 60 meV. However, ZnO grown on mismatched substrate, like silicon, showed low quality of optical and structural properties. So, many kinds of buffer layer were inserted between Si substrate and ZnO film.

In this experiment, we studied the effects of the Al₂O₃ buffer layer thickness on ZnO thin film grown by remote plasma ALD. The structural properties were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). And for optical and electrical properties, photoluminescence (PL) and hall effect measurements were used, respectively.
EFFECTS OF $\text{Al}_2\text{O}_3$ BUFFER LAYER ANNEALING ON ZnO THIN FILM GROWN BY REMOTE PLASMA ALD


hhryu@inje.ac.kr

$^a$Department of Nano Systems Engineering, Center for Nano Manufacturing, Inje University, Obang-dong, Gimhae, Gyeongnam 621-749, Korea

$^b$Major of Nano Semicon., Korea Maritime University, #1 Dongsam-dong, Yeongdo-ku, Busan 606-791, Korea

$^c$Department of Mechatronics Engineering, Korea Maritime University, #1 Dongsam-dong, Yeongdo-ku, Busan 606-791, Korea

$^d$Department of Electronic Materials Engineering, Silla University, Gwaebep-dong, Sasang-gu, Busan 617-736, Korea

ZnO thin film on Si substrate has many attractive features including wide band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV. However, there is a problem near the interface due to lattice mismatch between Si substrate and ZnO film. So buffer layer is usually adopted to release the defects from lattice mismatch, and to get a high quality ZnO thin films.

In this study, the properties of ZnO thin film on annealed $\text{Al}_2\text{O}_3$ buffer layer with different annealing temperatures were investigated. The annealing temperatures for $\text{Al}_2\text{O}_3$ buffer layer were from 450°C to 900°C. ZnO thin film was grown on annealed $\text{Al}_2\text{O}_3$ buffer layer by remote plasma ALD. X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to examine the structural property and surface morphology. ZnO thin film was characterized by photoluminescence (PL) and hall effect measurement for optical and electrical properties, respectively.
Advances in the Use of Near-IR Tunable Diode Laser Spectroscopy as a Real-Time Probe of ALD Processes

I. M. Povey, A. O’Mahony and M.E. Pemble

Tyndall National Institute, University College Cork, Lee Maltings, Cork, Republic of Ireland
ian.povey@tyndall.ie

The monitoring of CVD, and its variant ALD, by in-situ spectroscopic methods is well established and has been used to elucidate many important details of the dynamics, kinetics and mechanisms of these complex processes. However, the lack of temporal and spatial resolution offered by many of the methods employed can often be a hurdle to reliable interpretation. To overcome these limitations we have been developing an in-situ optical monitoring system for ALD processes, based on the use of near infrared tunable diode laser spectroscopy (NIR TDLS), which is capable of both spatial and temporal resolution of spectral information [1]. We illustrate recent advances in the development of this approach in two configurations; firstly as a gas phase probe of reaction products and secondly in conjunction with an attenuated total internal reflectance element to study the surface chemistry of the ALD process. Data is presented for several growth systems including; i) Al₂O₃ from Al(CH₃)₃ and H₂O and; ii) HfO₂ from Hf(NR₂)₄ and H₂O.

Atomic Layer Deposition of HfO$_2$ Thin Films on In$_x$Ga$_{1-x}$As:
Influence of surface passivation and In concentration

A O’Mahony$^1$, R.Long$^1$, E.O’Connor$^1$, K.Thomas$^1$, I. M. Povey$^1$, P. K. Hurley$^1$ M. E. PEMBLE$^1$
B. Brennan$^2$, G Hughes$^2$, Guy Brammertz$^3$ and V. V. Afanas’ev$^4$.

$^1$Tyndall National Institute, University College Cork, Ireland
$^2$Dublin City University, Dublin, Ireland
$^3$Interuniversity Microelectronics Center (IMEC vzw), Kapeldreef 75, B-3001 Leuven, Belgium
$^4$Department of Physics and Astronomy and INPAC—Institute for Nanoscale Physics and Chemistry, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

The heterogeneous integration of III-V and Ge high-mobility materials onto silicon or SOI platforms is a technology option for future high performance MOS based transistors [1-6]. Power consumption constraints will necessitate the use of high-k/metal gate stacks to minimize gate leakage [7]. A range of scientific and technological challenges are central to the successful fabrication of high-k/metal gate stacks on III-V channels, such as: surface passivation, nucleation and uniformity of high-k growth on Ge and III-V surfaces, understanding of interface defects at high-k/III-V interfaces and the impact and upper limits of post deposition annealing for high-k/metal gate stacks on III-V surfaces. In relation to the area of electrically active interface defects, atomic layer deposition has proved to be the most promising approach for achieving III-V MOS structures with reduced interface state densities [8]. For n channel devices, InGaAs is of particular interest due to its high electron mobility. Recent work has demonstrated HfO$_2$ thin films by ALD on low indium content (13% In) InGaAs grown by MBE on GaAs substrates [9] and HfO$_2$ films deposited on in-situ H$_2$S passivated high indium content (53%) InGaAs [10]. In this present work we build upon these findings and examine the influence of the In concentration on the bulk and interfacial properties of metal-gate/HfO$_2$ on In$_x$Ga$_{1-x}$As substrates. The ALD growth was based on the use of the metalorganic HfO$_2$ precursor Hf(N(CH$_3$)$_2$)$_4$ at 250°C. The deposition was performed on GaAs, In$_{0.15}$Ga$_{0.85}$As/GaAs, In$_{0.3}$Ga$_{0.7}$As/GaAs and In$_{0.53}$Ga$_{0.47}$As/InP substrates. In addition, the work examines the effect of deposition onto the native oxide with no surface preparation and for a three stage clean consisting of treatment in the following aqueous reagents: 3.7% HCl, 3% NH$_4$OH and 1% (NH$_4$)$_2$S.

Transmission infrared spectroscopy is a valuable diagnostic to study several aspects of ALD processes. In this contribution, we will demonstrate the merit of this technique in investigating the ALD surface chemistry by detection of the surface groups and the volatile reaction by-products.

The surface groups created in an ALD process can be revealed by determination of the differential vibrational spectra of the precursor and reactant step. Often large surface area powders are used as substrates and the excellent conformality of ALD results in a large absorption signal in a single pass. This approach is illustrated for the ALD of $\text{Zr}_2\text{N}_4$, where the types of surface groups created upon the zirconium precursor adsorption were detected and the saturation of the precursor adsorption was observed. Another approach is to deposit the films on flat substrates (e.g., Si or KBr). By averaging the data over several infrared measurements or several ALD cycles, a sufficient signal to noise ratio can be obtained to assign the surface species involved. For example, by monitoring the ALD growth on KBr windows, the surface chemistry of plasma-assisted ALD of $\text{Al}_2\text{O}_3$ was unraveled and the amount of impurities incorporated in the $\text{Al}_2\text{O}_3$ bulk could be addressed.

Transmission infrared spectroscopy was also used to determine and quantify the reaction by-products created in ALD surface reactions. To this end, the volatile by-products should be present in the path of the infrared beam from source to detector. In particular, by confining the reaction products in the reactor, the amount of products released can be quantified and this allows the determination of the saturating dose of the precursor/reactant. It was shown that for the thermal ALD of $\text{Al}_2\text{O}_3$ at low temperatures (25-150 °C), the amount of CH$_4$ decreased with lower deposition temperatures. This observation can be related to the decrease in growth rate when going to lower temperatures. Furthermore, it was demonstrated that the H$_2$O surface reaction is difficult to fully saturate and evidence was provided for bi-functional adsorption of the precursor at lower temperatures.

Infrared spectra of the uptake of the Zr precursor on pressed silica powder [1].

Infrared spectrum after a Al(CH$_3$)$_3$ dose during $\text{Al}_2\text{O}_3$ ALD. The CH$_4$ reaction by-product can be observed while the presence of unreacted Al(CH$_3$)$_3$ indicates saturation.

Films of tantalum nitride, titanium nitride and ruthenium can be used as diffusion barriers for copper interconnects. Due to the increasing aspect ratios of the trenches for copper lines, conformal atomic layer deposition (ALD) has become an interesting candidate for the deposition of nanometer thin barrier films.

The metalorganic precursors pentakis(dimethyl)amido-tantalum (PDMAT) and tetrakis(dimethyl)amido-titanium (TDMAT) were used for the deposition of TaN and TiN, respectively. Nitrogen and ammonia inductively coupled plasmas (ICP) were used as reactive gases. The films deposited with N$_2$-plasma had higher impurity contents compared to the ones deposited with NH$_3$-plasma, according to X-ray photoelectron spectroscopy (XPS).

Low resistivity ruthenium films were grown from di(ethylcyclopentadienyl)ruthenium Ru(EtCp)$_2$ and NH$_3$ plasma on Si(100) (figure), TiN and TaN surfaces. The as-deposited Ru films were poly-crystalline. After annealing for 60 s at 600°C, films deposited on Si(100) showed a single, very strong X-ray diffraction (XRD) peak, indicating a fiber texture, with the basal plane of the hexagonal Ru structure preferentially parallel to the surface and interface.

After ALD of various diffusion barrier stacks (e.g. Ru/TaN, Ru/TiN, TaN, TiN), 50 nm Cu was sputter deposited without breaking the vacuum. By following the copper XRD peaks with increasing temperature (ramp rate: 0.2°C/s), the diffusion barrier properties of the ALD films were studied. TiN and TaN deposited with N$_2$-plasma (see figure) are better Cu diffusion barriers than their counterparts deposited with NH$_3$-plasma as a reactive gas.

Figures: Growth rate and resisivity of Ru film (left) and in-situ XRD spectrum for Cu(50nm)/Ru(5nm)/TaN(5nm)/Si(100) annealed at 0.2°C/s (right). At 660°C, the Cu XRD peaks disappear, indicating the breakdown of the barrier.
INVESTIGATIONS ON LOW TEMPERATURE DEPOSITION OF TITANIUM CARBIDE FILMS BY PLASMA ASSISTED ALD

Gomathi Natarajan, Tommi Kääriäinen, Sanna Lehti and David Cameron

Lappeenranta University of Technology, Mikkeli Unit, Prikkaatinkatu 3E, Mikkeli, FI 50100, Finland.
Gomathi.Natarajan@lut.fi

Titanium carbide has a wide range of applications due to its key properties including high thermo dynamical stability, high hardness, excellent wear and oxidation resistance. There are a few reports on the preparation of TiC thin films by reactive sputtering [1,2] or CVD. However, a high process temperature (as high as 1200°C) [3] used for the film deposition, remains a disadvantage. We have attempted to grow TiC using ALD for the first time. Particularly interesting is that the process temperature was brought down to the range 200-350°C, thanks to the novel plasma assisted ALD (PA-ALD) process. The precursors used were TiCl₄ and methane with argon/nitrogen carrier gas. In our PA-ALD reactor capacitively coupled plasma is generated inside the deposition chamber adjacent to the substrate but can be separated from it by a grid to reduce the ion bombardment while maintaining the flow of radicals directly to the substrate surface. TiCₓ thin films were grown on Si(100) and glass. The presentation will include the compositional analyses using micro Raman spectroscopy and energy dispersive X-ray spectroscopy and the structural characterization with X-ray diffraction and Atomic force microscopy. The influence of growth parameters on the film properties such as growth temperature and plasma power will be discussed.

Possibilities for ALD in 3D integrated all-solid-state batteries

M.E. Donders\textsuperscript{a,b}, H.C.M. Knoops\textsuperscript{a,b}, L. Baggetto\textsuperscript{a}, M.C.M. van de Sanden\textsuperscript{b}, R.A.H. Niessen\textsuperscript{c}, P.H.L. Notten\textsuperscript{b,c} and W.M.M. Kessels\textsuperscript{b}

\textsuperscript{a}Materials Innovation Institute, P.O. Box 5008, 2600 GA Delft, The Netherlands
\textsuperscript{b}Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
\textsuperscript{c}Philips Research, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands

M.E.Donders@tue.nl

To maintain the current societal trend towards portable devices, very small integrated batteries with a high power to volume ratio are required. Li-ion all-solid-state batteries are very attractive as they combine high energy density with a flexible design and longer lifespan than comparable battery technologies [1]. ALD is a powerful technique to deposit thin films with high conformity and controlled thickness at relatively low temperatures. In this work an outlook towards ALD processes of suitable materials for the production of these Li-ion batteries is given.

A 3D integrated solid-state battery is ideally composed of active electrode materials, anode and cathode, separated by a solid-state electrolyte, a diffusion barrier layer for Li and current collectors. Ideally, these thin-films are deposited, layer by layer, using ALD technology in high aspect ratio structured substrates.

In this battery, one of the most important layers is the anode, e.g. a Si thin film. Thin film poly-Si anodes have been thoroughly characterized and indicate many favourable electrochemical properties, such as high energy density and fast charge transfer kinetics and solid-state diffusion [2,3]. This makes Si an excellent anode candidate for 3D integrated, all-solid-state batteries. Using ALD, deposition of Si as a single element material is challenging although some promising results have been reported [4].

Another challenge in this novel battery concept lies in the deposition of active Li containing films, such as the cathode (e.g. LiCoO\textsubscript{2}) and solid electrolyte (e.g. LiPON or Li\textsubscript{3}PO\textsubscript{4}-based). To the best of our knowledge no Li containing layers have been deposited using ALD, yet several CVD processes have been reported for the deposition of LiCoO\textsubscript{2} [5] which could be used as a starting point to design ALD processes of Li materials.

With the prospect of swift implementation in battery technology, the ALD grown Li diffusion barrier layer and the current collector have the largest potential. TiN is a promising candidate for the Li diffusion barrier as it combines a very low response towards Li intercalation with a high electronic conductivity [2,3]. ALD TiN has already been electrochemically investigated for depositions at various temperatures, thicknesses and plasma exposures and these measurements indicate good barrier properties [6]. In addition, Pt is a well suited cathode current collector. Several good results on Pt ALD have been reported, also in high aspect ratio structures [7,8]. These prospects open a promising route towards 3D integrated all-solid-state batteries containing ALD films.

Atomic Layer Deposition (ALD) for barrier layers and thin dielectrics provides excellent control of film thickness and conformality, but has been plagued by low deposition rates, film contamination, and high cost. Many of these deficiencies are due to the limited reactant concentrations used in low-pressure operation, combined with the complex pump / purge cycles conventionally employed. We developed Atmospheric Pressure ALD (AP ALD) that combined with spatial reactants separation (opposite to time reactants separation (cycling) in conventional ALD) that enables a continuous-processing architecture and promises much higher throughput and lower cost. High reactant concentrations ensure saturated-monolayer growth and low contaminant concentrations without unacceptably slow deposition cycles. Modeling results show that reactants can be separated during deposition without mixing when the distance between injectors and substrate about 1 mm and speed of substrate less or comparable with velocity of the gas (< 40 cm/s). We establish special experimental procedure using N\textsubscript{2} and O\textsubscript{2} using trace oxygen analyzer to verify modeling results. Experimental results show that reactants can be separated in space during deposition without mixture (less than 1 ppm) and without escaping in the chamber (10\textsuperscript{-7} magnitude difference) as predicted by the modeling. Results of TiN deposition are presented.
ATOMIC LAYER DEPOSITION OF DIELECTRIC STACKS CONTAINING HAFNIUM-BASED DIELECTRICS FOR FLASH MEMORY APPLICATIONS

Kwangchol Park\textsuperscript{a}, Byoung-Jun Choib, Byeol Han\textsuperscript{b}, Suk-Cheol Jeong\textsuperscript{c}, Won-Deok Yun\textsuperscript{d}, Sa-Kyun Rha\textsuperscript{d}, and Won-Jun Lee\textsuperscript{b}

\textsuperscript{a}Department of Materials Science and Engineering, KAIST, Daejeon, 305-701, Korea
\textsuperscript{b}Department of Advanced Materials Engineering, Sejong University, Seoul, 143-747, Korea
\textsuperscript{c}AET Corp., Yongin-si, Gyounggi-do, 449-822, Korea
\textsuperscript{d}Department of Materials Engineering, Hanbat National University, Daejeon, 16-1, Korea
wjlee@sejong.ac.kr

The key requirements for interpoly dielectric of flash memories are good capacitive coupling from the control gate to the floating gate and minimized leakage current through the dielectric. The current interpoly dielectric technology is based on SiO\textsubscript{2}/SiN/SiO\textsubscript{2} (ONO) stacked layers, and the continuing reduction of the thickness of ONO will cause unacceptable charge retention properties in the near future. Recently, high-k films are being explored as possible candidates to replace the conventional ONO stacks, because it is possible to easily increase the coupling ratio without increasing cell area.

Multilayer stack formation with various thickness configurations of different materials offers improvements and control over interface states, total dielectric constant, leakage current, and breakdown voltage. In addition, dielectric band diagram considerations with the stack structure can modify the energy barrier to electron injection from the floating gate electrode. VARIOT and reverse-VARIOT concepts explain asymmetrical electron conduction properties related to multilayer stack formation sequence\cite{1}.

In this work, we produced and characterized various high-k interpoly dielectric stacks containing hafnium-based dielectrics. Hafnium-based dielectrics were selected owing to their thermal stability and large band gap. We replaced SiO\textsubscript{2} of ONO with hafnium silicate (HfSiO) as a low-k material and replaced SiN with HfO\textsubscript{2} as a high-k material. Multilayer stacks consisting of HfO\textsubscript{2} and HfSiO provide both high-k value of HfO\textsubscript{2} and good interface quality of HfSiO. In addition, HfSiO/HfO\textsubscript{2} (low-k/high-k) and HfO\textsubscript{2}/HfSiO (high-k/low-k) were also fabricated to confirm VARIOT and reverse-VARIOT concepts. HfO\textsubscript{2} thin films were deposited by alternating exposures of TEMAH and O\textsubscript{3}, and HfSiO films were deposited from the consecutive independent pulse of TEMAH, a Si precursor, and O\textsubscript{3}. Nitridation of film was also performed by the introduction of NH\textsubscript{3} pulse during HfSiO film deposition. The dielectric stacks were characterized by capacitance-voltage (C-V), current-voltage (I-V), and charge to breakdown (Q\text{BD}) measurements, and were compared with ONO and OAO(SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}) stacks.

ALD OF CU SEED LAYER FOR ELECTROPLATING OF CU INTERCONNECT

Byeol Han\textsuperscript{a}, Kwang-Min Park\textsuperscript{a}, Kwangchol Park\textsuperscript{b}, Suk-Cheol Jeong\textsuperscript{c}, Jung-Woo Park\textsuperscript{d}, Won-Deok Yun\textsuperscript{e}, Sa-Kyun Rhae\textsuperscript{a}, and Won-Jun Lee\textsuperscript{a}

\textsuperscript{a}Department of Advanced Materials Engineering, Sejong University, Seoul, 143-747, Korea
\textsuperscript{b}Department of Materials Science and Engineering, KAIST, Daejeon, 305-701, Korea
\textsuperscript{c}AET Corp., Yongin-si, Gyounggi-do, 449-822, Korea
\textsuperscript{d}UP Chemical Corp., Pyeongtaek-si, Gyounggi-do, 459-050, Korea
\textsuperscript{e}Department of Materials Engineering, Hanbat National University, Daejeon, 16-1, Korea

wjlee@sejong.ac.kr

Cu interconnects provide significant advantages over Al interconnects, including higher speed, lower power dissipation, reduced levels of metal required, and higher resistance to electromigration. The dual damascene processes for Cu interconnect formation require a Cu seed layer to enable a high quality electroplating. This Cu seed layer has been deposited using ionized PVD technique. However, it is difficult for PVD to deposit completely conformal Cu seed layers into the complex shaped structures. ALD is the ideal solution for depositing highly conformal Cu seed layers due its self-limiting growth characteristics.

ALD Cu films can be deposited through the reduction of Cu precursors or reduction of ALD CuO films. The direct reduction of Cu precursor showed poor nucleation on barrier metal, and the reduction of CuO induced unexpected oxidation of underlying barrier metal and agglomeration of Cu owing to high thermal budget of reduction process. Recently, the ALD CuN from Cu(I) amidinate and NH\textsubscript{3} was reported to overcome these problems \cite{1}. CuN can be easily reduced at low temperatures because CuN is metastable and readily decompose.

In this work, Cu(II) (diketiminate)\textsubscript{2} was selected as the Cu precursor because of its oxygen- and fluorine-free nature, excellent thermal stability, and feasible volatility. In addition, Cu(II) precursors can avoid the undesirable disproportionation reaction of Cu(I) precursors. CuN ALD films were deposited by alternating exposures of Cu(II) (diketiminate)\textsubscript{2} and NH\textsubscript{3} and then were reduced by various reducing agents. We also performed the ALD of Cu via direct reduction of Cu(II) (diketiminate)\textsubscript{2} and compared with the reduction of ALD CuN. The characteristics of ALD CuN and Cu films were analyzed by various techniques: resistivity (4-point probe), step coverage (SEM), and adhesion force to the barrier metal (Scratch test, pull off test).

\cite{1} Z. Li and R. G. Gordon, Chemical Vapor Deposition 12, 435 (2006).
HIGH CAPACITANCE DENSITY MOS CAPACITOR STACKS IN 3D SILICON USING PLASMA-ASSISTED ALD

D. Hoogeland\textsuperscript{a,b}, K.B. Jinesh\textsuperscript{a}, F. Roozeboom\textsuperscript{a,b}, W.F.A. Besling\textsuperscript{b}, W. Keuning\textsuperscript{b}, M.C.M. van de Sanden\textsuperscript{b}, and W.M.M. Kessels\textsuperscript{b}

\textsuperscript{a}NXP Semiconductors, Research, High Tech Campus 4, 5656 AE, Eindhoven, The Netherlands
\textsuperscript{b}Dept. of Applied Physics, Eindhoven University of Technology, The Netherlands
d.hoogeland@student.tue.nl

For the application in high performance rf decoupling in passive dies with PICS (Passive Integration Connecting Substrate) technology [1], high-density MOS planar capacitors have been fabricated by subsequent deposition of Al\textsubscript{2}O\textsubscript{3} and TiN films using plasma-assisted ALD in a single deposition chamber. Plasma-assisted ALD of Al\textsubscript{2}O\textsubscript{3} at temperatures up to 300 °C has already been investigated in single MOS planar and “trench” capacitors with Al top electrodes [2]. The objective of this study is to optimize the electrical quality of the deposited stacks and to employ plasma-assisted ALD in the same run to deposit the TiN electrodes. The application of ALD deposited films only is considered necessary to fabricate stacks of multiple MIM capacitors in 3D silicon [3].

An Oxford Instruments FlexAL\textsuperscript{TM} reactor was used to subsequently deposit Al\textsubscript{2}O\textsubscript{3} (from Al(CH\textsubscript{3})\textsubscript{3} combined with O\textsubscript{2} plasma, 1.0 Å/cycle) and TiN (from TiCl\textsubscript{4} combined with H\textsubscript{2}-N\textsubscript{2} plasma, 0.55 Å/cycle) on a Si substrate using remote plasma ALD. For the Al\textsubscript{2}O\textsubscript{3}, nominal thicknesses of 10 nm, 20 nm and 40 nm have been selected whereas the nominal TiN thickness was 30 nm. Films have been deposited at 350 °C and 400 °C. The resistivity of the deposited TiN layers was 253 ± 19 µΩ.cm and was found to be independent of the substrate temperature.

For the as-deposited MOS capacitor structures grown at 350°C and 400°C the average electric breakdown field was 8.9 ± 0.4 MV/cm and 8.8 ± 0.4 MV/cm, respectively. Leakage current densities were ~100 nA/cm\textsuperscript{2} at 2 MV/cm. Capacitance measurements of the thickness series grown at 350 °C indicate a dielectric constant of \( k \approx 6.8 \). These results suggest that the layer stack and interface quality is already good without post-deposition annealing. This is also supported by the average measured barrier height of the TiN/Al\textsubscript{2}O\textsubscript{3} interface being 3.63 ± 0.20 eV. Arrhenius and C-V measurements are planned to further demonstrate the quality of the deposited films. In addition, the step coverage of a single MOS TiN/Al\textsubscript{2}O\textsubscript{3}/Si structures is currently investigated in Si-wafers with high aspect ratio (~13) pore arrays.

Figures demonstrating the capacitance as a function of electrode area (left) and the J-E breakdown curves (right) of the MOS capacitors

ATOMIC LAYER DEPOSITION OF LANTHANUM OXIDE THIN FILMS USING WATER (H2O) AND OZONE (O3) CHEMISTRY


aMaterials Science and Engineering, The University of Texas at Dallas, Richardson, TX 75080
bAdvanced Thin-Film Technologies, Microelectronic Technologies, Rohm and Haas Electronic Materials LLC, North Andover, MA 01845
*jiyoung.kim@utdallas.edu

Lanthanum oxide (La2O3) is recently being considered as one of the promising high-k candidates beyond the Hf-based materials because of its superior properties such as, a high dielectric constant (~27) and a large energy band offset (~2.3eV). Until now, there have been many attempts to deposit high quality La2O3 oxide films using physical and chemical deposition method such as, evaporation, molecular beam deposition (MBD), chemical vapor deposition (CVD). In particular, ALD technique offers several advantages which include precise thickness control and excellent conformality. However, there are only a few reports of ALD lanthanum oxide in gate dielectrics since the ALD process for La-oxide appears to be rather unstable compared to other high-k materials (such as HfO2 and Al2O3). Ozone (O3) has rarely been used as the oxidant reactant for ALD derived La oxide films although it has been reported that use of water (H2O) leads to the formation of lanthanum hydroxide which causes permittivity deterioration and increase in film roughness. [1] In this study, we present properties of ALD lanthanum oxide films from an amidinate-type precursor La(iPrfAMD)3 which has not been reported earlier. We discuss the physical and electrical characteristics of the La-oxide films deposited using two different oxidant reactants (H2O and O3).

We deposited La-oxide films on H-terminated p-type Si (100) substrate from tris(N,N'-diisopropylformamidinato) lanthanum, La(iPrfAMD)3 as the La precursor and H2O and O3 as the oxidants, respectively. Since uncapped La2O3 film is considered to be chemically unstable, most work was done in-situ for the La-oxide films with H2O and ex-situ for La-oxide films with O3. The La-oxide films deposited using O3 were additionally capped with ~1nm thick HfO2 layer. In-situ XPS spectra for the La-oxide films with H2O showed a high content of La-O-H component compared to the La-O-Si and La-O-La components. Even after annealing at 400°C in vacuum, the films shows dominant La-silicate bonding characteristics. In contrast to H2O chemistry, the films deposited using O3 were hydroxide-free with no La-O-H components. XPS after Ar ion sputtering showed that the films mainly consisted of La-O-La and La-O-La components. However, these films indicated traces of residual carbon. SIMS measurements were performed for further in-depth characterization of the carbon content. For electrical measurements, all films were capped with TaN as the top electrode so as to minimize the formation of lanthanum hydroxide. Further details on the physical and electrical properties of the La-oxide deposited by ALD will be addressed with respect to the oxidant reactants.

We would like to thank Rohm and Haas Electronic Materials LLC for financial support and providing the La precursor and TMEIC for providing ozone generator.

HYDROGEN STREAM PURIFICATION USING ALD NANOSTRUCTURE COMPOSITES FOR FUEL CELL APPLICATIONS

R.K. Grubbs\textsuperscript{a}  A. Ambrosini\textsuperscript{a}  M.E. Welk\textsuperscript{a}

\textsuperscript{a}Sandia National Laboratories, Albuquerque, NM 87123  
rkgrubb@sandia.gov

The need to purify hydrogen feed stocks from reformate streams for fuel cell applications is crucial to the full cell energy conversion process. Feed stock impurities such as sulfur can poison precious metal catalysts deactivating their surface catalytic properties. As fuel cells are designed and developed for various power applications, localized sources of extremely clean hydrogen will be required. To produce clean hydrogen from hydrocarbon sources, nanostructure composites are being investigated that incorporate both getter materials for sulfur sequestering and extremely thin proton conducting membranes (PCM) for additional hydrogen purification. These nanostructure composites utilize ALD chemistry to deposit both the sulfur getter material and the PCM.

ZnO and MnO$_2$ are known to react with sulfur to make ZnS and MnS$_2$. These materials are attractive as getters because they are easily reoxidized back to their oxide form by heating under oxygen. This reversibility enables the sulfur getter material to be regenerated. ALD of ZnO and MnO$_2$ are investigated for their sulfur getter efficiency and their ability to undergo multiple cycles of regeneration. Sulfur and oxygen uptake, BET surface analysis and phase change monitoring via x-ray are performed on conventional alumina supports coated with ALD ZnO and MnO$_2$. Preliminary results indicate that complete conversion is observed in both the sulfur and oxygen reactions with a slight increase in crystallinity of the material as the number of regeneration cycles is increased. A minimal surface area change is also observed in the nanostructure as a function of regeneration cycle.

Many perovskite materials are known to be efficient proton conductors\textsuperscript{1}. Plasma ALD of PCM materials is the ideal deposition method due to the limited conformality of plasma ALD and the ability to make ultra thin films. The lack of conformality allows a thin PCM to be deposited on top of a porous nanostructure and the ability deposit such thin layers increases the proton diffusion across the membrane allowing higher concentrations of ultra pure hydrogen to be generated. Plasma assisted ALD is used to create to create proton conducting perovskites of SrTiO$_3$ and SrCeO$_3$. The plasma ALD chemistries of these materials is presented and the ability to deposit non-conformal thin films on porous nanostructures is quantified and discussed.