Wednesday Afternoon, August 1, 2018

ALD Fundamentals
Room 113-115 - Session AF2-WeA
Process Development

Moderators: Woojin Jeon, Dankook University, Harm Knoops, Eindhoven University of Technology

4:00pm **AF2-WeA-11 Water Assisted ALD Process for Y_2O_3 Thin Films and Evaluation of the Y_2O_3 Containing Metal-insulator-capacitor Structures***, **Nils Boysen**, L Mai, E Subasi, C Bock, A Devi,* Ruhr-University Bochum, Germany

The development of new ALD processes involving promising metal-organic precursors and mild process conditions is important to gain advances in creating ultra-thin films with superior functional properties for various micro- and optoelectronic applications. ALD is the method of choice for these functional applications, as the deposition of conformal, dense and pure films at low temperatures and mild oxidizing conditions is possible, which renders ALD as an indispensable method for modern microelectronic devices. In this context, the development of a new ALD process for the material Yttrium(III) oxide is highlighted, as Y_2O_3 exhibits a large band-gap of 5.5 – 5.8 eV with a dielectric constant of k = 14-18, while also possessing a high thermal stability and a high mechanical strength, which makes this material a suitable choice for application as high-k gate dielectric in metal-oxide-semiconductor field-effect transistor (MOSFET) based devices. Among the reported precursors for the ALD of Y_2O_3 there are certain drawbacks, which include a narrow ALD-window, high deposition temperatures and low growth rates. To tackle some of these issues, we developed a new water assisted ALD process for the fabrication of ultra-thin Y_2O_3 films under mild process conditions involving the highly reactive precursor Tris(*N*,*N'*-diisopropyl-2-dimethylamido-guanidinato) Yttrium(III) [$Y(DPDMG)_3$]. Furthermore, detailed film characterization with a special focus on the functional properties of the Y_2O_3 thin films were performed and the results are highlighted. The Y_2O_3 thin films were deposited in a self-limiting ALD growth mode ranging from 175°C to 250°C (Figure 1) resulting in smooth, polycrystalline and oxygen-rich thin-films with low level of contamination (Figure 2). To prove the functionality of the yttria thin films in terms of dielectric applications, 20 nm Y_2O_3 thin films were used as the insulating material in Au/Ti/Y_2O_3/n^+-Si(100) capacitors which revealed a very high breakdown field between 4.0 and 7.5 MV/cm accompanied by a low leakage current density of about 10^{-7} A/cm² at 2 MV/cm (Figure 3)[1]. The dielectric permittivity in this capacitor stack was estimated to be k =11. The oxygen-rich features on the surface of the thin-films render this material promising as a passivation layer for metal oxide thin film transistors (MOTFT), to enhance their stability and electrical performance. The promising performance of our yttria films renders the new ALD process as a potential alternative to other established ALD processes for the deposition of yttria by successfully lowering the deposition temperature, while retaining growth rate and thin-film purity.

4:15pm **AF2-WeA-12 New Plasma-enhanced Atomic Layer Deposition Process for SnO_2: Process Development and Evaluation of SnO_2 for TFT Applications***, **David Zanders**, L Mai, E Subasi, C Bock, A Devi,* Ruhr-University Bochum, Germany

Tin (IV) oxide (SnO_2) is a promising n-type semiconducting material with excellent electrical and optical properties.[1,2] Hence, thin films of SnO_2 are employed in a broad range of devices such as photovoltaic cells[3] and thin film transistors (TFTs)[4]. With respect to TFTs, SnO_2 as a channel layer material is exceptionally attractive due to its high mobility and transparency. As the properties of metal oxide semiconductor thin films for optoelectronic applications are highly dependent on the deposition process, a wise choice must be made to this effect. Atomic layer deposition (ALD) and plasma enhanced ALD (PEALD) are favourable for such applications owing to the low processing temperatures, precise control of thickness as well as dense and conformal coverage over complex device geometries.

Herein we report a new and promising PEALD process using a new tin alkyl precursor for the deposition of SnO_2 thin films. The liquid precursor is volatile and thermally robust as evidenced by thermal analysis (Fig. 1) and temperature dependent NMR studies. The application of this precursor in a PEALD process using oxygen plasma resulted in high quality SnO_2 layers. The self-limiting ALD growth characteristics and the saturation behavior were confirmed at different substrate temperatures ranging from 60 – 150°C (Fig 2). The films were characterized by XRR, AFM, RBS, NRA and XPS to evaluate the structure, morphology and composition. The as-deposited SnO_2 films were amorphous and stoichiometric. The functional properties in terms of optical bandgap was determined to be 3.6 eV from UV-Vis measurements. Finally bottom-gate bottom-contact TFTs were fabricated using the SnO_2 as a channel layer. Mobilities up to 10 $cm^2V^{-1}s^{-1}$ were achieved at low deposition temperatures (T = 60°C) thus making this PEALD process very attractive for flexible electronics. The devices also show a high I_{on}/I_{off} ratio of 10^7, which is more than sufficient for digital circuits.[5]

[1] S. Das, V. Jayaraman,*Progress in Materials Science,***2014**, *66*, 112.

[2] M. Y. Maximov *et al*., *Journal ofElec Materi,***2017**, *46*, 6571.

[3] C. Beneking *et al*., *Thin Solid Films,***1999**, *351*, 241.

[4] P. D.M., R. Mannam .,*Applied Surface Science,***2017**, *418*, 414.

[5] D. Geng *et al. IEEE Electron Device Lett,***2012**, 33, 1012.

4:30pm **AF2-WeA-13 Hollow Cathode Plasma-Enhanced Atomic Layer Deposition of Silicon Nitride using Pentachlorodisilane (PCDS) and Hexachlorodisilane (HCDS)***, **Xin Meng**, H Kim, A Lucero, S Hwang, J Lee, Y Byun, J Kim,* The University of Texas at Dallas*; B Hwang, X Zhou, J Young, M Telgenhoff,* Dow Chemicals

Plasma-enhanced ALD (PEALD) is an attractive method of depositing silicon nitride (SiN_x) due to its ability to grow high-quality films at low temperatures (≤400°C) for various applications [1]. Unlike other silicon precursors, chlorosilane precursors can be applicable to either thermal ALD process in combination with ammonia (NH_3), hydrazine (N_2H_4) or plasma-enhanced ALD process using NH_3 plasma. The use of chlorosilane precursors is also considered a practical approach for high-volume manufacturing (HVM). Among the reported chlorosilane precursors, hexachlorodisilane (HCDS, Si_2Cl_6) is a promising candidate due to its higher surface reactivity as well as the demonstration of a distinct self-limiting growth behavior in ALD SiN_x process [2]. Nevertheless, it is desirable to find an alternative chlorosilane precursor with a higher reactivity and a higher growth per cycle than HCDS.

In this work, a novel chlorodisilane precursor, pentachlorodisilane (PCDS, HSi_2Cl_5), was investigated for the growth of SiN_x via hollow cathode PEALD. Well-defined self-limiting growth behavior was successfully demonstrated over the growth temperature range of 270−360°C. At identical process conditions, PCDS not only demonstrated approximately >20% higher GPC than that of HCDS, but also delivered a better or at least comparable film quality determined by characterizing the refractive index, wet etch rate, and density of the films. Fourier transform infrared spectroscopy (FTIR) spectra suggested that N−H bonds were the dominant hydrogen-containing bonds in the SiN_x films without a significant amount of Si−H bonds originating from the precursor molecules. We contribute the significant improvement in GPC to the enhanced reactivity of the proposed precursor molecular structure simply by a hydrogen atom substitution. The minor change in the molecular structure can render a lower steric hindrance, a higher polarity of the precursor molecule, and an additional precursor adsorption reaction pathway via Si−H bonds cleavage.

[1] Meng, X.; Byun, Y.-C.; Kim, H. S.; Lee, J. S.; Lucero, A. T.; Cheng, L.; Kim, J. Atomic Layer Deposition of Silicon Nitride Thin Films: A Review of Recent Progress, Challenges, and Outlooks. *Materials* **2016,***9* (12), 1007.

[2] Ovanesyan, R. A.; Hausmann, D. M.; Agarwal, S. Low-Temperature Conformal Atomic Layer Deposition of SiN_x Films Using Si_2Cl_6 and NH_3 Plasma. *ACS Appl Mater Interfaces* **2015,***7* (20), 10806−10813.

Author Index

Bold page numbers indicate presenter

— B —
Bock, C: AF2-WeA-11, 1; AF2-WeA-12, 1
Boysen, N: AF2-WeA-11, **1**
Byun, Y: AF2-WeA-13, 1
— D —
Devi, A: AF2-WeA-11, 1; AF2-WeA-12, 1
— H —
Hwang, B: AF2-WeA-13, 1
Hwang, S: AF2-WeA-13, 1
— K —
Kim, H: AF2-WeA-13, 1
Kim, J: AF2-WeA-13, 1
— L —
Lee, J: AF2-WeA-13, 1
Lucero, A: AF2-WeA-13, 1
— M —
Mai, L: AF2-WeA-11, 1; AF2-WeA-12, 1
Meng, X: AF2-WeA-13, **1**
— S —
Subasi, E: AF2-WeA-11, 1; AF2-WeA-12, 1
— T —
Telgenhoff, M: AF2-WeA-13, 1
— Y —
Young, J: AF2-WeA-13, 1
— Z —
Zanders, D: AF2-WeA-12, **1**
Zhou, X: AF2-WeA-13, 1