ALD Fundamentals
Room Halla Hall - Session AF2-TuA
Plasma ALD

Moderators: Ruud van Ommen, Delft University of Technology, **Seung-Yeul Yang**, Samsung

4:00pm **AF2-TuA-11 Controlling the Crystalline Nature of PEALD Thin Films Through Tuning of Plasma Characteristics**, ***Peter Litwin,*** Naval Research Laboratory, USA; *Marc Currie, Neeraj Nepal, Maria Sales, David Boris,* US Naval Research Laboratory; *Michael Johnson,* Naval Research Laboratory, USA; *Scott Walton, Virginia Wheeler,* US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) utilizes a plasma-based reactant step increasing the complexity of the deposition process compared to thermal ALD. The plasma-based reactant step introduces a flux of energetic particles (ions, fast neutrals, electrons, photons, etc.) directed towards the surface of the growing thin film, which helps reduce the energetic barriers to high growth rates or crystallinity at low temperatures. Understanding the role that these energetic species play in the deposition process potentially enables better tunability of the growth conditions for a given application. For example, during the plasma step, careful control of the power, pressure, gas flow mixture, and substrate bias all enable control over the magnitude of the ion energy flux density delivered to the sample surface. The consequence of this is a greater level of control over the properties of the deposited material. This has been experimentally observed in previous studies, namely in the control of the crystalline phase of various compounds. For example, through alteration of the gas chemistry, flow rate, and pressure used during the reactant half-step it has been shown that the rutile and anatase phases of TiO_2 and the α- and β-phases of Ga_2O_3 could be selectively deposited [1, 2].

In this work, we investigate methods to vary the properties of the plasma in our PEALD system. We use a suite of characterization techniques, including optical emission spectroscopy (OES) and Langmuir probe measurements, to examine how various plasma conditions (power, pressure, and gas flow ratio) impact the ion flux, plasma potential, and atomic O concentrations produced in our Kurt J. Lesker 150 LX PEALD system. As a testbed, we deposit vanadium oxide and report on how the changing properties of the plasma impact the properties of the deposited thin films. We find that through alteration of the pressure in the system during the plasma process, the films can be selectively deposited in an amorphous or crystalline manner. We correlate this change in crystallinity with the change in the energy flux density delivered to the material surface during deposition. From this, we estimate the critical energy flux density necessary for crystallization of vanadium oxide films deposited in our PEALD system. Lastly, we discuss these results more broadly and consider the applicability of these findings to other material systems.

[1]V. D. Wheeler *et al.*, *Chemistry of Materials*, vol. 32, no. 3, pp. 1140–1152, Feb. 2020

[2]J. R. Avila *et al.*, *Chemistry of Materials*, vol. 31, no. 11, pp. 3900–3908, Jun. 2019

4:15pm **AF2-TuA-12 Comparative Study of CeO_2 Thin Films Prepared by Plasma-Enhanced and Thermal Atomic Layer Deposition Using a New Liquid Ce Precursor**, ***Yewon Seo,*** *Sang Bok Kim, Soo-Hyun Kim,* Graduate School of Semiconductor Materials and Devices Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea

Cerium oxide (CeO_2) has been widely studied for applications such as optical waveguides, solid oxide fuel cells (SOFCs), and gas sensors. In particular, it is considered a promising gate dielectric material for complementary metal-oxide-semiconductor (CMOS) devices due to its high dielectric constant (23–52), high refractive index (2.2–2.8), excellent dielectric strength (25 MV/cm), moderate bandgap (3.0–3.6 eV), and thermodynamic stability in contact with silicon [1]. So far, research on ALD CeO_2 films, especially plasma-enhanced ALD (PEALD) of CeO_2, has been very limited, mainly due to the lack of suitable precursor-reactant combinations; thus, more detailed investigations are required. In this study, CeO_2 thin films were deposited by ALD using a new liquid Ce precursor with O_2 molecule or O_2 plasma as reactants. The deposition process was conducted at temperatures ranging from 150 to 350 °C, and both thermal ALD (Th-ALD) and PEALD exhibited self-limiting surface reactions at 250 °C.In addition, increases in peak intensities for PEALD CeO_2 film as compared to that of Th-ALD one were confirmed through XRD analysis (figure 1), indicating the improvement of the film crystallinity by using plasma as a reactant. Film properties varied with deposition conditions such as growth temperature, plasma power, reactant pulsing time, etc..and were characterized by SEM (thickness), TEM (step coverage, microstructure), XRR (density, thickness, roughness), XRD (crystallinity), and XPS (composition and impurity) etc. Electrical properties were evaluated via Metal–Oxide–Semiconductor capacitors, focusing on dielectric constant and leakage current. The detailed results will be presented at the conference.

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[1] Woo-Hee Kim et al, "Growth Characteristics and Film Properties of Cerium Dioxide Prepared by Plasma-Enhanced Atomic Layer Deposition", *J. Electrochem. Soc., 2011,158, G169-G172.*

Acknowledgements

This work was also supported by the Technology Innovation Program (Public-private joint investment semiconductor R&D program (K-CHIPS) to foster high-quality human resources) (RS-2023-00232222, High-temperature atomic layer deposition precursors and processes for dielectrics in 3D V-NAND devices) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (1415187363) (RS-2024-00443041, Development of process parts based on atomic layer deposition technology of plasma coating materials) This work was also supported by the Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0023703, HRD Program for Industrial Innovation). The precursor used in this study was provided by UP Chemical Co. Ltd, Korea.

4:30pm **AF2-TuA-13 Tuning Crystallinity of Plasma-Enhanced Atomic Layer Deposited Aluminum Nitride Thin Films using an Electron Cyclotron Resonance Microwave Source**, ***Julian Pilz,*** *Tai Nguyen,* Silicon Austria Labs, Austria; *Paul Dreher,* Evatec AG, Switzerland; *Marco Deluca,* Silicon Austria Labs, Austria

Aluminum nitride (AlN) thin films are widely utilized in microelectronic devices as high thermal conductance heat spreaders, piezoelectric actuators and sensors or high-k dielectrics.[1,2] In most applications, (0002)-textured wurtzite films are required to achieve the desired device performance.[3] While deposition techniques such as metalorganic chemical vapor deposition[4] and reactive magnetron sputtering[5] have demonstrated to produce highly textured/epitaxial films with low mosaic spread, these deposition techniques faces severe issues such as CMOS-incompatibility due to high temperature growth and poor conformality. Atomic layer deposition (ALD) is renowned for precise control of atomic arrangement and excellent conformality. However, achieving AlN with comparable crystal quality by ALD on Si substrates remains challenging and is under investigation [6,7,8], with factors such as oxygen and carbon contaminations shown to decrease the crystal quality.[9,10]

In this work, AlN thin films are deposited on 200mm Si(111) wafers by plasma-enhanced atomic layer deposition (PE-ALD) utilizing trimethylaluminum (TMA) and NH_3-plasma as reactants. A novel ALD module is used for the deposition of the films (Evatec PEALD), which utilizes an electron cyclotron resonance microwave source and is *in-vacuo* connected in a cluster tool to etch and sputtering modules, with the potential to overgrow and surface pretreat wafers without vacuum break, respectively. The focus of this work is to investigate how NH_3 plasma parameters (pressure, power, duration) produced by the microwave source influence the plasma/chemical species during deposition and resulting thin film properties in terms of thickness uniformity, crystallinity, roughness, and chemical composition. For example, while films grown with 2 s NH_3-plasma duration showed similar growth per cycle values as films grown with 5 s plasma duration, they appear amorphous and structurally unstable in atmosphere. Increase of plasma duration up to 20 s significantly improves the crystalline quality of films showing a preferential 0002 orientation even at a substrate temperature of 200 °C. This points to the importance of considering the kinetic effects of plasma-film interactions and their relevance for crystallite formation as well as influence on the composition of the films.

In a nutshell, this work presents effective mechanisms for producing PE-ALD AlN thin films with preferential c-axis orientation on 200 mm wafers, highlighting the importance of plasma source and parameter choice, as well as showing application potentials for growing layer stacks of ALD and sputtered layers without vacuum break in-between deposition.

4:45pm **AF2-TuA-14 Plasma-Enhanced Atomic Layer Deposition of High-Quality InN Thin Films Using a Novel In Precursor and NH_3 Plasma**, ***Yejun Kim**, Chaehyun Park, Minjeong Kweon, Soo-Hyun Kim,* Ulsan National Institute of Science & Technology, Republic of Korea

Indium nitride (InN), a III-V nitride semiconductor, has a narrow bandgap (0.7 eV), high electron saturation velocity (4.2×10^7 cm/s), low electron effective mass (0.07 m_0), and high electron mobility (4400 $cm^2/V\cdot s$). These properties make InN ideal for sensors, optoelectronics, and high-electron-mobility transistors (HEMTs). However, MOVPE and MBE face challenges due to InN's low thermal stability (~ 500 °C decomposition into In and N_2), making them unsuitable for high-aspect-ratio microelectronics. Plasma-enhanced ALD (PE-ALD) enables precise thickness control and low-temperature processing, offering an alternative, though ALD-grown InN research is still in early stages. This study explores InN ALD using a novel ethanimidamidinate-based indium precursor and NH_3 plasma in a showerhead-type PE-ALD reactor (IOV dX1 PEALD, ISAC Research, Korea). The optimal deposition temperature was 275 °C, confirming self-limiting growth with a saturated rate of ~ 0.57 Å/cycle. A linear relationship between thickness and ALD cycles was observed. Film properties were analyzed using a 4-point probe (resistivity), SEM/TEM (thickness, step coverage), XRR (density, roughness), XRD (crystallinity), RBS (In/N ratio, impurities), UV-Vis (optical bandgap), and Hall measurement (carrier density, mobility). Detailed results will be presented at the conference.

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Acknowledgements

This work was also supported by the Technology Innovation Program (Public-private joint investment semiconductor R&D program (K-CHIPS) to foster high-quality human resources) (RS-2023-00236667, High-performance Ru-TiN interconnects via high-temperature atomic layer deposition (ALD) and development on new interconnect materials based on ALD) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (1415187401) and(RS-2023-00232222, High-temperature atomic layer deposition precursors and processes for dielectrics in 3D V-NAND devices and RS-2024-00420281, Developed MOCVD equipment technology for single-cluster, 6-inch class nitride high temperature growth for highly uniform LED characteristics).This work was also supported by the Korea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (P0023703, HRD Program for Industrial Innovation). The precursor used in this study was provided by Soulbrain Co., Ltd, Korea.

5:00pm **AF2-TuA-15 Insights Into Tuning TiO_2 Film Property Distribution in 3D Structures During Peald Process**, ***Takashi Hamano**, Nobuyuki Kuboi, Hiroyasu Matsugai, Shoji Kobayashi, Yoshiya Hagimoto, Hayato Iwamoto,* Sony Semiconductor Solutions Corporation, Japan

Plasma-based deposition techniques are widely employed to fabricate cutting-edge electronic devices with vertical and complicated 3D structures. In addition, owing to the increasing demand for various advanced devices with organic films, low temperature deposition processes are required. During deposition processes, precise control of feature profile, i.e., coverage, and film properties is significant. In general, it is difficult to directly measure the film properties in a local area of 3D structures. Therefore, simulation techniques are effective tools to understand the deposition mechanisms in complicated 3D structures. Recently, we have developed a new simulation model based on the statistical ensemble method to predict both coverage and film properties and analyzed the PECVD and PEALD processes [1][2]. In this paper, we improved the simulation model and investigated the TiO_2 film properties in 3D structures during PEALD process.

In the simulation model, gas transportation and surface reactions, such as adhesion/desorption, migration, and binding are expressed by the movement of voxels using a stochastic algorithm. The voxel status indicating the bonding states and crystallinity is determined depending on the total energy flux of ions at each surface voxel solving the ion transportation in 3D structures. The variation in film thickness by ion bombardment is also modeled. The difference in the bonding states and crystallinity of TiO_2 between the planar region and sidewall of the hole structure was predicted. Especially, at lower process temperature, the film property distribution inside the hole structures becomes remarkable reflecting the distribution of incident ions.

To confirm the simulation results, we evaluated TiO_2 film properties inside the hole structures with an aspect ratio of 5 focusing on the wet etching rate (WER) of TiO_2. WER at the sidewall and bottom regions is several times higher than that at the planar region. In addition, the distribution of WER inside the hole structure notably changes depending on the process temperature.

Present results indicate that the process optimization considering both process temperature and ion irradiation (i.e., flux, energy and angular distribution of ions) is key to obtain the desirable film property distribution in 3D structures.

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[2] T. Hamano et al., Proc. Symp. Dry Process, 2024, p. 19.

5:15pm **AF2-TuA-16 Plasma-Enhanced ALD Process for Boron Carbide Films: Towards Tunable B:C Ratio**, ***Catherine Marichy**, Neil Richard Innis, Abdhulhamid Afolabi, Olivier Boisron, Didier Leonard, Colin Bousige, Catherine Journet,* Universite Claude Bernard Lyon 1, France

Boron carbide (B_xC) is a well-known ceramic material with high chemical and thermal stability, super-hardness, and a large neutron absorption cross-section. It is used in various applications such as refractory and cutting tool ceramics and neutron absorbers and detectors. Less explored are its electronic and optoelectronic properties. B_xC is a rather unknown semiconductor with tunable band gap[1,2] as a function of its B:C stoichiometry. Investigating its semiconductor properties requires its deposition as thin films with precise control over thickness, structure and composition. While PVD[3,4] and especially CVD[4–9] have shown potential for fabricating boron carbide thin films, ALD for B_xC remains largely unexplored[10] despite its advantages in terms of thickness control, uniformity and conformality.

In this study, amorphous B_xC thin films with atomic-level thickness control are successfully deposited by PEALD from triethylboron (TEB) and H_2 plasma[11]. A tunable B:C ratio is achieved by adjusting the process parameters. While the deposition temperature does not significantly affect the stoichiometry, special attention is given to the effect of plasma parameters, such as plasma mode (direct vs remote), H_2 flux and plasma power on the film composition. Plasma species not only remove the ethyl groups from TEB, but can also decompose by-products that may lead to additional carbon introduction into the film. A possible surface etching effect must also be considered.

The developed PEALD process of B_xC is discussed with a focus on the evolution of the film composition as a function of the plasma parameters. The plasma composition is monitored by in-situ optical emission spectrometry. The films are characterized in terms of thickness, morphology, structure and composition using various characterization techniques: ellipsometry, SEM and TEM, AFM, XPS, and ToF-SIMS. Attention is also paid to the physicochemical properties of the layers obtained, including their band-gap.

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