ALD Fundamentals
Room Tamna Hall BC - Session AF-WeA
Material Growth II

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, **Erwin Kessels**, Eindhoven University of Technology, Netherlands

1:30pm **AF-WeA-1 ALD of Nitride Semiconductors*, Henrik Pedersen,*** Linköping University, Sweden **INVITED**

The group 13 nitrides, AlN, GaN, InN and their alloys, is an important class of semiconductors, forming the backbone for technologies such as light emitting diodes (LEDs) and high electron mobility transistors (HEMTs). Chemical vapor deposition (CVD) at high temperatures, 800-1200 °C, is the typical way of depositing these materials. But CVD of indium nitride (InN) is severely limited by the low thermal stability of the material,[1] and can thus only tolerate relatively low deposition temperature. As ALD is intrinsically low temperature, it is a logical path for InN films and has been demonstrated to deposit epitaxial InN films with excellent crystalline quality.[2,3] The two chemically and structurally closely related materials aluminium nitride (AlN) and gallium nitride (GaN) has been deposited by both plasma and thermal ALD, with ammonia (NH_3) as nitrogen precursor in thermal processes.

In this talk I will describe ALD of these semiconducting nitrides, with focus on the fundamental understanding of the ALD chemistry. ALD has been shown to be an enabler for the metastable InN and $In_xGa_{1-x}N$ with x close to 0.5.[4] By combining quantum-chemical density functional theory (DFT) calculations[5] and *in-situ* techniques such as mass spectroscopy[6], we can present a detailed surface chemical model for the ALD processes. I will also present results from our efforts understand the surface chemistry by *in operando* ambient pressure XPS. Finally, I will discuss limitations to thermal ALD of these nitrides and why plasma activation seems to be needed.

References

(1) Ivanov, S. V.; Shubina, T. V.; Komissarova, T. a.; Jmerik, V. N. *J. Cryst. Growth* **2014**, *403*, 83–89.

(2) Hsu, C.-W.; Deminskyi, P.; Martinovic, I.; Ivanov, I.; Palisaitis, J.; Pedersen, H. Appl. Phys Lett. **2020**, *117*, 093101.

(3) O'Brien, N. J.; Rouf, P.; Samii, R.; Rönnby, K.; Buttera, S. C.; Hsu, C.-W.; Ivanov, I. G.; Kessler, V.; Ojamäe, L.; Pedersen, H. *Chem. Mater.* **2020**, *32*, 4481–4489.

(4) Pedersen, H.; Hsu, C.; Nepal, N.; Woodward, J. M.; Eddy, C. R. *Cryst. Growth Des.* **2023**, *23*, 7010–7025.

(5) Rönnby, K.; Pedersen, H.; Ojamäe, L. *J. Mater. Chem. C* **2023**, *11*, 13935–13945.

(6) Mpofu, P.; Hafdi, H.; Niiranen, P.; Lauridsen, J.; Alm, O.; Larsson, T.; Pedersen, H. *J. Mater. Chem. C* **2024**, *12*, 12818–12824.

2:00pm **AF-WeA-3 Low-Temperature Atomic Layer Deposition of (00l)-Oriented Elemental Bismuth*, Amin Bahrami,*** *Jorge Luis Vazquez-Arce, Alessio Amoroso, Nicolas Perez,* Leibniz Institute for Solid State and Materials Research, Germany*; Jaroslav Charvot,* University of Pardubice, Czechia*; Dominik Naglav-Hansen,* Ruhr-University Bochum, Germany*; Panpan Zhao, Jun Yang, Sebastian Lehmann, Angelika Wrzesińska-Lashkova,* Leibniz Institute for Solid State and Materials Research, Germany*; Fabian Pieck, Ralf Tonner-Zech,* Leipzig University, Germany*; Filip Bureš,* University of Pardubice, Czechia*; Annalisa Acquesta,* University of Napoli Federico II, Italy*; Yana Vaynzof, Anjana Devi, Kornelius Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

This study presents the first successful demonstration of growing elemental bismuth (Bi) thin films via thermal atomic layer deposition (ALD) using Bi(NMe2)3 as the precursor and Sb(SiMe3)3 as the co-reactant. The films were deposited at a relatively low temperature of 100 °C, with a growth per cycle (GPC) of 0.31-0.34 Å/cycle. Island formation marked the initial growth stages, with surface coverage reaching around 80% after 1000 cycles and full coverage between 2000 and 2500 cycles. Morphological analysis revealed that the Bi grains expanded and became more defined as the number of ALD cycles increased. This coalescence is further supported by X-ray diffraction (XRD) patterns, which show a preferential shift in growth orientation from the (012) plane to the (003) plane as the film thickness increases. X-ray photoemission spectroscopy (XPS) confirmed the presence of metallic Bi with minimal surface oxidation. Temperature-dependent sheet resistance measurements highlight the semimetallic nature of Bi, with a room temperature resistivity of ≈200 µΩcm for the 2500 cycles Bi. Temperature-dependent sheet resistance was also associated with a transition in carrier-type dominance from electrons at higher temperatures to holes at lower temperatures.

2:15pm **AF-WeA-4 High-Quality ALD-Ru Process Using Thermally Stable ALD Ru Precursor*, Hideaki Nakatsubo,*** TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd. / UNIST, Japan*; Jeongha Kim, Soo-Hyun Kim,* UNIST, Republic of Korea

Ruthenium (Ru) is expected to be a promising alternative material for copper (Cu), due its better scaling performance resulting from a shorter electron mean free path and possibility of the barrierless interconnectes scheme. Until now, many atomic layer deposition (ALD) processes have been developed to achieve a high-quality Ru film with a low resistivity as possible (bulk resistivity of Ru: 7.4 μΩ·cm), but many reported values have not yet achieved the desired low resistivity one. In this study, a novel Ru precursor, trimethylenemethane (p-methylisopropyl benzene) ruthenium [Ru(TMM)(p-cymene)], was synthesized and investigated for a high-quality ALD-Ru process. Since this precursor has a thermal stability up to 400 ℃, one can adopt a high process temperature for ALD, giving a lower resistivity than those obtained many previous ALD processes typically performed lower than 300 ℃ due to the poor thermal stability of Ru precursors. For developing ALD-Ru process, O2 was used as a reactant, and substrates used included SiO2, TiN, and Ru. The ALD-Ru process nicely shows a typical self-limiting behavior of ideal ALD with a growth per cycle (GPC) of ~1.28Åon TiN and a negligible incubation cycle at the deposition temperature of 300 oC. Interestingly, on SiO2, there was no Ru deposition even after 1000 cycles. The resistivity decreased with increasing process temperature, reaching ~14 μΩ·cm at 300℃ and ~11 μΩ·cm at 375℃, comparatively lower than those of previously reported Ru ALD processes. Annealing the Ru film in H2 gas further reduced resistivity to 8.65 μΩ·cm at 700℃, close to the bulk Ru resistivity. XRD and SEM analysis showed increased grains size and improved crystallinity with annealing, resulting in the decrease in the resistivity. In conclusion, the present study demonstrates high-performance and versatile ALD-Ru process with a very low resistivity, high GPC, and extremely high selectivity can be achieved using a newly synthesized Ru precursor.

2:30pm **AF-WeA-5 The Development of Ultralow-Dielectric Constant Boron Nitride Film by Novel Plasma Atomic Layer Deposition*, Kazuki Goto,*** *Yoshihiro Kato, Shuichiro Sakai, Hiroki Murakami, Yamato Tonegawa,* Tokyo Electron Technology Solutions Ltd, Japan

The miniaturization of electronic devices has intensified challenges related to electrical signal propagation delays, primarily due to increased wiring resistance and capacitance. As a response, there is a rising demand for low dielectric constant (low k) materials to enhance device performance. Silicon oxide-based dielectrics (SiCOH) are conventionally known as a low k material. However, the thermal and mechanical stability of these materials are significantly compromised due to their low film density. In this context, boron nitride (BN) films have emerged as promising candidates due to their low dielectric constant and high stability [1]. Hexagonal BN (*h*BN) is characterized by its layered structure and wide band gap (5.2 – 5.9 eV), and it is expected to exhibit low k values, particularly along the c-axis [2].

In this study, we explored the film formation process of *h*BN using a borazine-based precursor with N_2 and NH_3 plasma to achieve high-quality BN films with low k, high density, and high conformality. Deposition was conducted at 400 ℃ on a 300 mm Si substrate, resulting in an ideal *h*BN layered structure clearly revealed by cross-section TEM (Fig. 1a). It was possible to deposit even thicker layers while maintaining the *h*BN structure. Moreover, we have successfully deposited conformal *h*BN on a trench pattern for the first time (Fig. 1b), expanding the applicability and versatility of *h*BN. C-V measurements indicated a low k value of <3 for our *h*BN. Analysis through XPS and IR spectroscopy confirmed a stoichiometric BN composition containing a significant amount of B-N sp^2 bonds. By applying additional plasma treatments, we observed a reduction in k value along with increased density due to the promotion of sp^2 B-N bonding. The resulting *h*BN films exhibited a low k value at higher density than can be achieved with Si-based films (Fig. 2).

This methodology also facilitated control over the crystalline orientation of *h*BN. We found certain processing conditions led to the deposition of both less and highly ordered *h*BN. C-V measurements across varying oriented films demonstrated a decrease in k values correlating with order, while I-V measurements confirmed that order in crystallinity contributed to the reduction of leakage current. We established a relationship between the crystallinity of *h*BN, the k value, and leakage current. This research created high quality conformal *h*BN, demonstrating significant potential for practical applications as low dielectric constant films for high-performance semiconductor devices.

References

[1] C. M. Lin, *et al.*, Adv. Mater. Technol., **2022**, 2200022

[2] Y. Hattori, *et al.*, ACS Appl. Mater. Interfaces, **2016**, 8, 27877-27884

2:45pm **AF-WeA-6 Thermal Atomic Layer Deposition of InN using Hot-wire-activated NH_3 and Hydrazine Reactants***, **Bonwook Gu**, Kwangyong An, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

Indium nitride (InN) possesses high electron mobility, approximately 3000–4000 $cm^2/V\cdot s$) and a low bandgap (~0.7 eV), making it an ideal material for high-speed transistors and RF devices that require low-power, high-performance operation. Additionally, InN exhibits excellent infrared absorption properties, enabling its applications in infrared detectors, high-efficiency solar cells, and optical sensors. Recently, as device sizes have decreased and structures become more complex, research on atomic layer deposition (ALD) for fabricating InN thin films has gained significant momentum. However, previous InN ALD research has primarily focused on plasma-enhanced processes, which pose challenges such as (1) difficulty in achieving uniform film deposition on three-dimensional structures with high aspect ratios and (2) potential substrate damage due to high-energy plasma exposure. To address these limitations, we explored the feasibility of thermal ALD for InN deposition. Thermal ALD for InN is challenging due to the high deposition temperatures required, low reactivity of reactants, and the tendency of indium compounds to oxidize easily, leading to poor film quality and low deposition efficiency. In this research, we employed hydrazine and hot-wire-activated NH_3 as reactants for thermal InN ALD. We conducted a comparative study using trimethylindium (TMI) and InPALA as In precursors. The physical and chemical properties of the deposited InN thin films were characterized using X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

3:00pm **AF-WeA-7 Electron-Enhanced ALD and CVD of Titanium-, Silicon- and Tungsten-Containing Films at Low Temperatures Using Metal Precursors with Various Reactive Background Gases***, Zachary C. Sobell, **Andrew S. Cavanagh**, Steven M. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) (Figure 1a) and electron-enhanced chemical vapor deposition (EE-CVD) (Figure 1b) can be employed for the low temperature deposition of thin films using metal precursors with various reactive background gases (RBGs).EE-CVD expands on the previous report of TiN EE-ALD using alternating $Ti(N(CH_3)_2)_4$ (tetrakisdimethylamino titanium (TDMAT)) and electron beam exposures with NH_3 RBG.During EE-CVD, the electron beam and the RBG are present continuously.Together with the RBG and electron beam incident on the surface, the metal precursor is pulsed into the vacuum chamber to control the film growth.

In this work, the metal precursors were TDMAT, Si_2H_6, and $W(CO)_6$.The RBGs were O_2, NH_3, CH_4, and H_2.The studies demonstrated TiO_2 EE-ALD and SiN, SiO_2, SiC_x, Si, W_2N, WO_3, and WC_x EE-CVD. To illustrate EE-ALD, TiO_2 EE-ALD was performed at T < 80 °C using alternating TDMAT and electron beam exposures together with O_2 RBG.The growth rate for the TiO_2 EE-ALD was ~0.7 Å/cycle.The TiO_2 EE-ALD films were nearly stoichiometric, displayed crystallinity, and were smooth as measured by atomic force microscopy (AFM).

To illustrate EE-CVD, SiC_x EE-CVD was performed at T < 100 °C using repeating Si_2H_6 pulses with continuous electron beam and CH_4 RBG exposures.XPS revealed a 1:1 Si:C stoichiometry for a CH_4 RBG pressure of 0.45 mTorr and C-rich films for higher CH_4 RBG pressures.The SiC EE-ALD growth rate was ~0.4 Å per Si_2H_6 pulse.The stoichiometric SiC EE-CVD films were smooth as measured by AFM.

W_2N EE-CVD was also performed at T < 120 °C using repeating $W(CO)_6$ pulses with continuous electron beam and NH_3 RBG exposures (Figure 2a).The W_2N EE-CVD growth rate was ~0.17 Å per $W(CO)_6$ pulse.The W_2N films had a resistivity of ~450 μΩ-cm.The W_2N EE-CVD films also displayed crystallinity and high purity (Figure 2b).This work shows that EE-ALD and EE-CVD with various RBGs can deposit a broad range of materials at low temperatures including oxides, nitrides and carbides.

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