ALD Fundamentals
Room Tamna Hall BC - Session AF-WeM

Material Growth I

Moderators: John Conley, Oregon State University, **Gregory N. Parsons**, North Carolina State University

10:45am **AF-WeM-12 High Crystallinity Yttrium-Doped ZrO2 under 2 nm Through Atomic Layer Modulation***, **Ngoc Le Trinh**, Bonwook Gu, Wonjoong Kim, Minhyeok Lee,* Incheon National University, Republic of Korea*; Byung-ha Kwak,* Ajou University, Republic of Korea*; Hyun-Mi Kim, Hyeongkeun Kim,* Korea Electronics Technology Institute, Republic of Korea*; Youngho Kang,* Incheon National University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea*; Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

The rapid miniaturization of integrated circuits poses significant challenges for various silicon-based devices, such as DRAM capacitors and 3D transistors, which demand both high capacitance density and low leakage current density. As the device dimensions shrink further, the thin films used in these devices must become even thinner, making it increasingly difficult to preserve their physical properties at such reduced thicknesses. In this work, we studied high crystallinity dielectric thin films with Y-doped ZrO_2 (YZO) less than 2 nm of film thickness. Atomic layer modulation (ALM) based on atomic layer deposition (ALD) was utilized to achieve better compositional uniformity both in-plane and out-of-plane direction at atomic level. In the ALM process, the surface was sequentially exposed to precursors with an intervening purging step between each exposure, followed by a reaction with a counter-reactant, resulting in the growth of the YZO film within a single atomic layer. The ratio of Y and Zr in ALM film was determined by steric hindrance and chemical reactivity of the precursors. To design and interpret the experiment, two theoretical approaches, density functional theory (DFT) and Monte Carlo (MC) simulation were used. The formation energy of the crystalline phase in the ALM films was expected to be lower than in the ALD film. In the ALM film, Y atoms are formed closer to Zr atoms, with Y−O−Zr bonds forming both laterally and vertically within a few atomic layers. Consequently, the ALM film requires a lower energy barrier for diffusion to form theYZO crystalline phase, which enhances film density and improves crystallinity. It was revealed that doping ZrO_2 with Y induces a crystal structure change, leading to a phase transformation from monoclinic to a cubic (111)-plane-dominant phase. Consequently, YZO prepared via ALM shows approximately 250 times lower leakage current density compared to conventional YZO fabricated through ALD at a thickness of 2 nm. This key finding highlights that that YZO achieves both increased dielectric constant and reduced leakage current density at low thicknesses, demonstrating its potential as a promising material for future silicon device applications.

11:00am **AF-WeM-13 ALD Outstanding Presentation Award Finalist: Ultrahigh Purity Plasma-Enhanced Atomic Layer Deposition and Electrical Properties of Epitaxial Scandium Nitride***, **Bruce Rayner**, Noel O'Toole,* Kurt J. Lesker Company*; Bangzhi Liu, Jeffrey Shallenberger,* The Pennsylvania State University*; Jiadi Zhu, Tomas Palacios, Piush Behera, Suraj Cheema,* Massachusetts Institute of Technology*; Blaine Johs,* Film Sense*; Nicholas Strnad,* DEVCOM Army Research Laboratory

Scandium nitride (ScN) by plasma-enhanced atomic layer deposition (PEALD) was demonstrated on silicon (100), sapphire (0001) and magnesium oxide (001) substrates under ultrahigh purity conditions using a new Sc precursor, bis(ethylcyclopentadienyl)scandium-chloride [$ClSc(EtCp)_2$]. Out-of-plane x-ray diffraction patterns indicated single-crystal, cubic phase ScN deposited at 215°C on sapphire (0001) and magnesium oxide (001) substrates; phi-scans confirmed epitaxial growth. The ScN thin films grown on silicon with native oxide were polycrystalline with no preferential orientation. The ScN films showed a nitrogen-to-scandium ratio of approximately 1:1 measured by x-ray photoelectron spectroscopy, with ultra low levels of elemental impurities including 2.5 at.% chlorine, 0.9 at.% carbon and 0.4 at.% oxygen. $ClSc(EtCp)_2$ and N_2-H_2 plasma were evaluated as a ScN co-precursors at substrate temperatures ranging from 200-300°C, where we identified an ALD window between 200–215°C. Images by field emission scanning electron microscopy (FESEM) on 43 nm-thick films grown on untreated silicon revealed columnar grains with lateral sizes ranging from 16-28 nm. ScN conformality across 4:1 aspect ratio silicon trench structures with 312 nm-wide openings was also imaged by FESEM showing a top-to-bottom thickness ratio of 75%. ScN electrical properties were evaluated by performing Hall measurements to determine mobility, free electron concentration and resistivity. For ScN PEALD on magnesium oxide (001), the average mobility was 298 cm^2/Vs with a carrier concentration of 2.35×10^{19} cm^{-3}. The average resistivity was 1.01 mΩ·cm.

11:15am **AF-WeM-14 Microwave Enhanced (ME) ALD of HfO_2***, Jessica Haglund-Peterson, **John Conley**,* Oregon State University

The low temperatures typical of ALD can allow incorporation of impurities from unreacted ligands leading to sub-optimal physical, optical, and electrical properties. Although post deposition annealing (PDA) can help drive off impurities, the temperatures required may exceed thermal budget limits. To maintain low temperature while maximizing film properties, adding energy in-situ *during* each ALD cycle (energy enhanced, EE-ALD) can help drive/speed reactions and reduce impurity incorporation. Indeed, in-situ every cycle rapid thermal annealing improved the density, stoichiometry, electrical, and optical properties of ALD films that could not be achieved by PDA alone.[1-3] Other EE-ALD methods include flash lamp, plasma, UV, laser, and electron beam exposure.[4-9] It has been shown that *post*-deposition microwave annealing (MWA) can improve ALD films,[10] and recently, we introduced *in-situ* microwave enhanced (MWE) ALD.[11] Here we investigate low temperature MWE-ALD of HfO_2.

A Picosun R200 was equipped with a custom MW antenna (MKS) and an MKS SG 1024 solid state MW generator. HfO_2 was deposited at 150˚C using 1/30/0.1/30 sec TEMA-Hf/N_2/H_2O/N_2 ALD cycles. Film thickness and refractive index were modeled using a Film Sense FS-1 mapping ellipsometer. As compared to a control sample without MW exposure, adding 30 s in-situ 400 W MW exposures (*without* plasma generation) during the H_2O purges of each ALD cycle had no significant impact on growth. However, the same MW exposures during the TEMA-Hf purge were found to increase film thickness by ~50% and increase refractive index from 1.9 to 2.1 over the control sample. The impact during the precursor purge as opposed to H_2O purge is consistent with our previous results on TMA/H_2O Al_2O_3.[11] This work demonstrates quality ALD deposition at a temperature normally below the standard "window" for this process, allowing for a decrease in thermal budget. Additional electrical and analytical data will be presented, including density, crystallinity, stoichiometry, roughness, as well as leakage and capacitance of MOS and MIM device structures.

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8. Liu and Chang. J. Chem. Phys. 116, (2002).
9. Becher *et al.*, Adv. Eng. Mater. 2300677 (2023).
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11:30am **AF-WeM-15 Atomic Level Engineering of Dy-doped HfO2 Ultra-thin Films via Controlling Lateral and Vertical Mixing***, **Byung-Ha Kwak**,* Ajou University, Republic of Korea*; Ngoc Le Trinh,* Incheon National University, Viet Nam*; Bonwook Gu, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea

We investigate the effects of Dy doping in HfO_2 thin films using two distinct atomic arrangement strategies: lateral mixing, known as atomic layer modulation (ALM), and vertical mixing, known as supercycle ALD. Lateral mixing can control atomic concentration by sequentially exposing two precursors (Dy and Hf) in a first-half cycle of ALD process and exposing a single reactant that reacts both precursors at the second-half cycle, determined by chemical reactivity and steric hindrance of two precursors.[1] This method allows precise controlling of atomic-level doping even in ultrathin films under 5 nm thickness. In contrast, the vertical mixing method, where a few cycles of Dy_2O_3 deposition are followed by multiple cycles of HfO_2, has limitations[2], as it requires a minimum thickness to maintain a consistent concentration across the film.

In the lateral mixing process, when both precursors were sequentially exposed for their respective saturation times, the Dy concentration in deposited films was measured to be 20.6 % when a Dy precursor was exposed first, whereas it was 12.5 % when a Hf precursor was exposed first. We elucidate growth mechanism of ultra-thin films of lateral mixing by density functional theory (DFT) and Monte-Carlo (MC) simulations with experimental observation. We observe different crystalline structures between lateral mixing and vertical mixing. In single HfO_2 and vertical

mixing films, tetragonal (101) phase was observed after 600 ℃ annealing process. However, no crystalline phase was observed in lateral mixing films at the same annealing process. We also observe that both lateral mixing and vertical mixing films showed lower leakage current density than a single HfO_2 film of same thickness, which will be discussed with growth mechanism and crystalline structure. Interestingly, the lateral mixing case for Hf-precursor-exposed first exhibits leakage currents approximately 180 times lower than Dy-precursor-exposed first. We believe that these approaches will significantly advance the development of high-k materials with optimized properties, supporting the future scaling down of semiconductor devices and enhancing their performance in next-generation electronic applications.

[1] H.-B.-R. Lee et al., Chem. Mater, 2021, 33. 12, 4435-4444 [2] I.-K. Oh and H.-B.-R. Lee et al., Chem. Mater, 2023, 35, 2312−2320

11:45am **AF-WeM-16 Process-Structure-Properties of Atomic Layer Deposited Niobium Nitride and Evolution of Strain with Plasma Chemistry**, *Neeraj Nepal, Joseph C Prestigiacomo,* ***Maria Gabriela Sales****, Peter M Litwin, Vikrant J Gokhale, Virginia D Wheeler,* U.S. Naval Research Laboratory

Niobium nitride (NbN) has exceptional physical, chemical, and electrical properties that can be utilized in a range of applications such as gate metal, superconducting qubits and detectors (T_c ~9-17 K [1]), RF antennas, resonators, and Cu interconnect diffusion barriers. For all these applications, a low temperature growth process with wafer scale uniformity, conformality, and subatomic thickness control is highly desirable. Atomic layer deposition (ALD) provides a path towards integration of NbN at lower temperatures with control over the desired properties. Most reported thin plasma-enhanced ALD (PEALD) NbN films [2-3] to date are either amorphous or polycrystalline. In this talk, we report on highly oriented single phase, PEALD NbN (111) films and discuss the evolution of strain with plasma chemistry.

ALD NbN films were deposited on resistive Si and c-sapphire in a Veeco Fiji Gen2 ALD reactor using (t-butylimido)tris(diethylamido)niobium(V) (TBTDEN) and N_2/H_2 plasma precursors. Similar to previous reports [2], TBTDEN required a boost to enable growth. Growth windows and film morphological, structural, and electrical properties were optimized for TBTDEN temperature (80-100℃), TBTDEN boost (1-2s), TBTDEN pulse (1.5-2.0s), plasma pulse (20-30s), H_2/N_2 ratio (1.5-12.5), and temperature (150-400 ℃). Optimum growth parameters (TBTDEN = 100℃, TBTDEN boost = 1.5s, TBTDEN pulse = 2s, and H_2/N_2 = 60/20sccm) yielded an ALD window from 250-300℃ with a growth rate (GR) of ~ 0.5A/cy. While GR was almost constant for $N_2 \geq 20$ sccm, room temperature resistivity (ρ_{RT}) increased linearly with N_2 flow. High-resolution XRD scans show 1st and 2nd order (111) NbN peaks. Lattice constants obtained from XRD show that strain changes from compressive to tensile with increasing N_2 flow, in which an N_2 flow of 20 sccm provided an almost strain-free film. The compressively strained 12.6 nm thick film at 5 sccm N_2 resulted in lower ρ_{RT} (~139μΩcm) and superconducting critical temperature (T_c~12.26K). Measured T_c is similar or higher than reported T_c (12.10K) of 15nm thick ALD NbN films [3]. For an optimized 30nm thick film, carbon is below the XPS detection limit, RMS surface roughness is 0.52nm, and rocking curve FWHM is 0.69°, which is narrower than previously reported for 30 nm thick films [3]. T_c on all those films were also measured to establish process-structure-property relationships, and results will be discussed in the context of use in quantum and high temperature contact applications.

References

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