Emerging Materials
Room Evergreen Ballroom & Foyer - Session EM-MoP
Emerging Materials Poster Session

EM-MoP-1 Conformal ALD of Ferromagnetic ε-Fe2O3 Thin Films*, T. Jussila,* Aalto University, Finland*; **Anish Philip**, J. Kinnunen, M. Utriainen,* Chipmetrics Oy, Finland*; M. Karppinen,* Aalto University, Finland

Magnetic and multiferroic thin films are vital for next-generation electronic and spintronic devices. For instance, strong room-temperature ferromagnets are required for high-density magnetic data storage while multiferroic materials could enable ultra-fast electrical writing and non-destructive magnetic reading of memory devices. However, the state-of-the-art magnetic and multiferroic materials typically have complex chemical composition including critical elements and their functional properties do not meet the requirements of the next-generation applications. Fortunately, there is a highly promising material, ε-Fe_2O_3, which possess a unique combination of multiferroic properties including ultra-hard room-temperature ferromagnetism and magnetoelectric coupling of the ferromagnetic and ferroelectric properties.[1] Moreover, this simple iron oxide is composed of Earth-abundant, low cost, and biocompatible elements. The only drawback is metastability of the ε–Fe_2O_3 polymorph; it is easily transformed to more stable α-Fe_2O_3 and γ-Fe_2O_3 polymorphs. Therefore, the synthesis of phase-pure ε-Fe_2O_3 has been notoriously challenging which has hindered its potential for practical applications. Excitingly, atomic layer deposition (ALD) has turned out to be superiorly suited for the deposition of in-situ crystalline and amazingly stable ε–Fe_2O_3 thin films from simple precursors ($FeCl_3$ and H_2O) in the temperature range of 260 – 300 °C.[2]Here we show the high quality of our ALD-grown ε–Fe_2O_3 thin films through ^{57}Fe Mössbauer spectroscopy, magnetic and crystallographic analyses.[3] Then, most inspiringly, we demonstrate excellent suitability of the robust ε–Fe_2O_3 ALD process for high-aspect ratio substrates using PillarHall LHAR4 structures.[4] The conformality is shown using various methods such as optical microscopy, SEM, and Line scan optical reflectometry. Deposition of ε–Fe_2O_3 over complex surfaces creates exciting possibilities in terms of nanostructuring (magnetic 3D nanodevices) and modification of the fine magnetic properties through dimensional effects.

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EM-MoP-3 In-situ FTIR Analysis of Molecular Atomic Layer Deposited Hybrid Thin Films for EUV Resist Applications*, **Dan Le**, S. Hwang, J. Veyan, T. Park, J. Kim,* University of Texas at Dallas*; R. Choi,* Inha University, Republic of Korea*; W. Lee, A. Subramanian,* Stony Brook University*; N. Tiwale, C. Nam,* Brookhaven National Laboratory*; J. Kim,* University of Texas at Dallas

The progression of lithography technology has enabled the downscaling of device feature size, prolonging Moore's law over decades. However, this has also necessitated the development of novel photoresist systems to keep pace with advancements in patterning technology. Thus, the lack of appropriate photoresist materials for EUV (λ=13.5 nm) lithography is still a pressing challenge in the current race toward the 1 nm node. In recent years, molecular atomic layer deposition (MALD) has emerged as an innovative route to synthesize highly homogenous hybrid inorganic-organic photoresist systems with the ability to control the material thickness at the atomic-scaled level. However, as these photoresist systems have only recently been proposed, there is a gap in our fundamental understanding of the chemical reactions induced by EUV exposure.

Herein, we demonstrate a unique methodology to examine the chemical reactions that occur within MALD inorganic-organic hybrid thin films composed of trimethylaluminum (TMA) and hydroquinone (HQ) under EUV-like exposure conditions. Specifically, we have employed an in-situ Fourier-transform infrared (FTIR) spectroscopy system equipped with an electron flood gun to examine various crosslinking mechanisms of MALD TMA/HQ hybrid thin film. Since various reported studies suggested the generation of secondary electrons during EUV exposures,[1] this study focuses on the interaction between electrons with energy ≤80 eV and the hybrid thin films. In addition, a residual gas analyzer (RGA) was also used to monitor the byproducts produced during the low-energy electron exposures. The obtained RGA and IR absorbance spectra revealed the role of low energy electrons in the crosslinking mechanisms responsible for the solubility switching of the MALD TMA/HQ hybrid thin films in the developer solution. Furthermore, we also studied the effects of thermal annealing on the MALD hybrid thin films before and after low-energy electron exposures. While pre-exposure baking showed no effectiveness, the post-exposure baking process demonstrated an improvement in pattern quality in terms of thickness contrast as well as edge roughness. The detailed experimental procedure and results will be discussed.

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EM-MoP-4 Exploring the Benefits of Reduced Cycle Time in Molecular Layer Deposition (MLD) of Metal-linked 7-(trioxysilyl)heptanoeate (M-TOSH)*, **Jesse Kalliomäki**, J. Binte Mariam, R. Ritasalo, T. Sarnet,* Applied Materials, Finland

Molecular layer deposition (MLD) is being increasingly adopted by industries, like organic electronic manufacturing and medical technology. Increased interest is driven by the versatility MLD adds to he more established sister technique, Atomic Layer Deposition (ALD). Similarly with ALD, after the adoption to industrial process flow, effort must shift to increase its performance, which is measured with metrics such as throughput (wafers per hour). The principal way to increase throughput in the atomic layer processing family is to either increase the growth per cycle (GPC) or decrease cycle time. For high-GPC MLD processes, such as M-TOSH, decreasing the cycle time is an obvious low hanging fruit.

For the M-TOSH process, the literature values for cycle times in a research environment ranges from in excess of one minute [1] up to 416 s (7min) [2]. Our previously reported values in batch ALD chamber were 205 s [3].For this work, we have studied the effect of cycle time optimization on different varieties of M-TOSH (Al, Hf, Ti) films deposited in Picosun R&P-series tools on 200 mm wafers at 90°C. The impact of decreased cycle time was studied using a range of measurement tools, including XPS, FTIR, DSA, ellipsometer.

As a result, we found out that several key process steps could be decreased by >95%. Specifically in the case of O_3, reduction was found to be beneficial. Overexposure to the oxidant lead to decreased C-content, lower GPC and compromised moisture barrier properties. By adopting the reduced cycle time, M-TOSH growth rate (Å/min) was increased more than 200% and uniformity (1σ WiW) improved by almost 50%

This work aims to strengthen the general perception of MLD as an industrially viable deposition method and signal MLD's graduation from a research to a useful tightly optimized nanostructure engineering tool beside putting it more closely on par with other thin film deposition methods.

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EM-MoP-5 Low-Temperature Atomic Layer Annealing Deposition of Crystallized Gallium Nitride on Oxide-Free Si (111)*, **SeongUk Yun**, A. Kummel, P. Lee, A. Mcleod, J. Fammels, J. Watson, H. Kashyap,* University of California at San Diego*; J. Spiegelman,* RASIRC*; W. Aigner, T. Metzger,* Qualcomm Germany RFFE GmbH, Germany

Gallium nitride (GaN) has gained interest due to its wide band gap 3.39 eV and as a buffer layer for other III-V deposition with applications in power electronics operated at high voltage and high temperature [1]. Ueda et al. and Shih et al. showed that atomic layer annealing (ALA) improved the crystallinity of the epitaxy layers of III-V compounds (aluminum nitride) at low temperatures as compared to the conventional thermal ALD [3,4]. Rouf et al. reported that the ionized NH_3 or N_2 could deposit GaN epitaxial layers below 250°C by using typical plasma-enhanced ALD [5]. 100 nm of SiO_2 and sapphire substrates were reported to deposit the crystallized GaN ALA films using krypton by UCSD. However, crystallized GaN ALA films have not been widely studied to deposit on inert, oxide-free Si (111) due to the lattice mismatch (~16%) and coefficient of thermal expansion mismatch (~54 %) between Si and GaN [2].

Thermal ALD and ALA processes were investigated for the low-temperature GaN ALD films on oxide-free Si (111). The native Si oxide was removed by dipping in 2 wt.% HF solution. The self-limiting ALD growth was achieved at 800 ms of N_2H_4 (Rasirc), 100 ms of TDMAGa (EMD), and 400°C (Figure 1a-c). However, a significant CVD process was observed at 150 ms of TDMGa and 430°C. Lower O contents (below 3.3 at.%) were observed in four GaN ALA films on Si (111) as compared to the GaN thermal ALD film (4.6 at.%) (Fig 2a). The higher N/Ga atomic ratio in the GaN ALA films than those in the thermal ALD suggested the ALA process improved the quality of GaN thin films. It is noted the low N/Ga ratio is an artifact of the AES sensitivity factors and ex-situ XPS confirmed a nearly stoichiometric N/Ga ratio.

The intensity of GaN (200) XRD pattern in GaN ALD films on Si was increased with the pulse length of Ar plasma up to 15-20 s (Figure 2b), suggesting the ALA process could improve the crystallinity of GaN epi-layers. The excess ALA plasma (30 s) could damage the crystallized GaN epi-layers. Smooth surface morphologies were observed in the GaN ALD films (RMS = 0.6~1.0 nm) regardless of Ar plasma pulse length (not shown). The Ga-N species in both spectra of Ga $2p_{3/2}$ (Figure 3a) and N 1s (Figure 3b) were dominant after 10 min Ar sputtering and oxide species disappeared after 20 min Ar sputtering, suggesting the formation of good-quality GaN film without Ga-O bonds. These observations suggested that high-quality crystallized GaN ALD thin films with a smooth surface were successfully deposited on oxide-free Si (111) using 15 s of the ALA process at a low temperature (275°C) using TDMAGa and N_2H_4 precursors.

EM-MoP-6 Vapor Deposited MOFs as Low-K Dielectrics for Logic and RF

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The present work investigates metal-organic frameworks (MOFs) as low-k dielectrics used to fill the gaps between vias or interconnects in the semidamascence process. An ALD grown ZnO layer is converted to the MOF ZIF-8 by dosing the ZnO in an organic linker gas at elevated temperature. The present study determined the key factors in maximizing the 12x volumetric expansion which is critical to gap fill: The volumetric expansion is a function of the crystallinity of the ZnO film, which depends on the substrate temperature of the ALD process. Three different MOF reaction processes were compared: sealed isothermal, sealed temperature differential, and unsealed temperature differential which were all in atmosphere. The sealed isothermal method provided materials at least as good as the more complex methods.

Three substrate temperatures for the ALD ZnO process were examined to investigate the effect on crystallinity of the ZnO film and subsequent MOF layer thickness. XRD measurements demonstrate that crystallinity decreases with decreasing ALD temperature (Fig 1a). These films were converted to MOF using the same sealed isothermal process. The volumetric expansions as determined by ellipsometry for the three films in order of lowest to highest ALD temperature was 11.2x, 7.5x, and 7.7x (Fig 1b). It is concluded that low-temperature deposited ZnO has higher MOF conversion due to lower crystallinity.

Incorporating a temperature differential into the MOF conversion reaction with a sealed container resulted in the build-up of organic linker vapor near the cold substrate which caused organic linker crystals to condense on the ZnO.Shown in Figure 2, incorporating the temperature differential with an unsealed container showed equivalent results to that of the sealed isothermal container, with roughly 12.2x conversion after two hours. Since the unsealed temperature differential set-up is less reproducible, it is concluded that running the MOF reaction isothermally in sealed conditions is superior. Running the MOF reaction under vacuum will be investigated. It is also noted that the RMS roughness of the initial ZnO layer was roughly 6% of the ZnO thickness, while the MOF layer's RMS roughness was roughly 20% of the MOF layer thickness. Finally, to demonstrate the gap filling ability of the MOF conversion process, the 0 nm 4patterned trenches will be filled which have a 5:1 aspect ratio (Fig 3).

EM-MoP-8 Towards Sequentially Infiltrated Two-Photon Polymerized 3d Photonic Crystals for Mid-IR Spectroscopic Applications

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Photonic crystals (PhCs) can slow the group velocity of light for enhanced light-matter interaction, enabling applications in mid-infrared (MIR) spectroscopic sensing systems [1]. The photonic bandgap (PBG) is a group of wavelengths that are forbidden to pass through the PhCs. Over planar microfabrication techniques, two-photon polymerization (2PP) allows rapid fabrication of 3D-PhCs. But 2PP materials have a low refractive index, which leads to only partial PBGs. The process of sequential infiltration synthesis (SIS), derived from atomic layer deposition (ALD) [2], allows precursor gases to infiltrate and react deep within the polymer [3], resulting in increased refractive index.

In this work, we present 2PP-fabricated IP-Dip resin-based 3D PhCs and use SIS to achieve broad PBG. The partial PBG was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis. For infiltration testing, 100 µm cubes were fabricated at a 700 nm hatching distance and ZnO SIS was performed. The ZnO-infiltrated cube was focused ion beam (FIB) half-milled, and energy dispersive spectroscopy (EDS) was performed on the milled structure, showing counts of Zn L-shell, confirming infiltration. SIS is further used on 2PP-fabricated PhCs to achieve increased refractive index, making PhCs suitable for applications in MIR spectroscopic sensing.

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