ALD Fundamentals
Room Grand Ballroom A-C - Session AF-TuA

Plasma ALD: Growth and Characterization

Moderators: HyeongTag Jeon, Hanyang University, Korea, Jiyoung Kim, University of Texas at Dallas

1:30pm **AF-TuA-1 Low Temperature High Quality Silicon Dioxide by Neutral Beam Enhanced Atomic Layer Deposition**, ***Hua-Hsuan Chen***, *D Ohori, T Ozaki,* Tohoku University, Japan*; M Utsuno, T Kubota, T Nozawa,* ASM Japan K.K., Japan*; S Samukawa,* Tohoku University, Japan

Atomic layer deposition (ALD) has shown to have high control of conformality on thin films in recent decades. Instead of conventional deposition technique, such as physical vapor deposition and plasma-enhanced chemical vapor deposition, it is usually used to deposit thin layers on complex structures due to its thickness control ability. Plasma-enhanced ALD (PEALD) and thermal ALD are the examples. However, there are some serious problems. For instance, plasma irradiation and charge accumulation existed in PEALD [1] can cause defects in thin films; high temperature is also needed in thermal ALD. In previous studies, neutral beam technology has shown advantages on depositing high quality films, such as low-k SiOCH film [2] and nitrogen doping diamond-like carbon film [3]. Here, we demonstrated the atomic layer growth of SiO_2 film on Si using novel neutral beam-enhanced deposition (NBEALD) technique, which was deposited at room temperature, and serves as an important material in various applications.

Neutral beam enhanced atomic layer deposition system consists of a large-radius ALD process chamber and an inductively coupled plasma source. We used Aminosilane as the precursor and O_2 as the neutral beam source to deposit films on the Si substrate. The stage temperature was controlled at 30℃. After the ALD cycle which was composed of: precursor feed, precursor purge, O_2 injection, neutral beam irradiation and O_2 purge, the SiO_2 film was grown on silicon wafers. We used spectroscopic ellipsometry to measure film thickness; the atomic force microscope was used to investigate the surface morphology; the X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR) and secondary ion mass spectrometry (SIMS) were used to analyze the chemical composition of the films for investigating the SiO_2 film quality.

The ALD cycle shows the thickness is linearly dependent on the number of cycles with growth per cycle comparable to that of PEALD [4]. The uniformity of the film was obtained by measuring thickness on different places of 8 inch wafer, and the result shows the film has good uniformity. For the XPS, XRR and SIMS results, high quality and high density SiO_2 film composition was confirmed. Furthermore, the excellent surface morphology could be seen on SiO_2 films as no difference for thickness discrepancy. Therefore, we succeeded to make high quality SiO_2 films using NBEALD technique under room temperature.

[1] H. B. Profijt et al, *J. Vac. Sci. Technol. A* 29, 050801 (2011)

[2] Y. Kikuchi et al, *J. of Phys. D: Appl. Phys.* Vol. 46 (2013)

[3] S. Yasuhara et al, *J. of Phys. D: Appl. Phys.* Vol. 43 (2010)

[4] S. J. Won et al, *IEEE Elec. Dev. Lett*. Vol. 31, No. 8 (2010)

1:45pm **AF-TuA-2 Radical Surface Recombination Probabilities during Plasma ALD of SiO_2, TiO_2 and Al_2O_3 Determined from Film Conformality**, ***Karsten Arts***, Eindhoven University of Technology, Netherlands*; M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University, Finland*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, UK

This work addresses the growth of conformal films on high aspect ratio (AR) structures by plasma ALD, which can be challenging due to loss of the reactive radicals through surface recombination. Using plasma ALD of SiO_2, TiO_2 and Al_2O_3 as case studies, we show that the AR up to which film growth is achieved gives quantitative insight into the recombination probability r of plasma radicals on given material surfaces. Such quantitative information on r is often not available in the literature and difficult to obtain by conventional methods, while it is essential for predicting and understanding the conformality achieved by plasma ALD. Applications of plasma ALD such as the conformal growth of SiO_2 spacers for self-aligned patterning can thus benefit from this work.

In this study we use microscopic lateral-high-aspect-ratio structures[1] supplied by VTT (PillarHall® LHAR4) to assess the conformality of plasma ALD processes. As these chips have extremely high AR trenches (AR<10000) deposition is typically limited up to a certain penetration depth. For the first time, we demonstrate that this penetration depth can be used to quantify r during plasma ALD.

By carrying out plasma ALD of SiO_2 using $SiH_2(N(C_2H_5)_2)_2$ and different O_2/Ar plasma exposure times, we have observed that the penetration depth increases logarithmically with the plasma time used in the ALD cycle. This relation is well described by a simple analytical model which can be used to calculate r. For plasma ALD of SiO_2 this gives $r=(6\pm3)\cdot10^{-5}$, which compares well to reported literature values.[2] Using a long plasma exposure, deposition of SiO_2 is achieved up to an AR as high as 900. Similarly, growth of TiO_2 using $Ti(N(CH_3)_2)_4$ reaches AR>250. In contrast, plasma ALD of Al_2O_3 using $Al(CH_3)_3$ shows a surprisingly low penetration (AR~80) compared to the thermal ALD process, even with long plasma exposure, which indicates the impact of a relatively high surface recombination probability. Estimations of the corresponding values of r and additional insights will be provided in this contribution. These results demonstrate that our method is a powerful and straightforward way to gain knowledge on surface recombination during plasma ALD and its strong effect on film conformality.

1. Arts, Vandalon, Gao, Utriainen, Puurunen, Kessels and Knoops, 18th Int. Conf. At. Layer Depos. ALD 2018 – Proc., (2018)

2. Kim and Boudart, Langmuir 7, 2999 (1991)

2:00pm **AF-TuA-3 A Robust Method for In-situ Gas Monitoring of ALD Processes using Optical Emission Spectroscopy of a Pulsed Remote Plasma**, ***Joe Brindley***, *B Daniel, V Bellido-Gonzalez,* Gencoa Limited, UK*; R Potter, B Peek,* University of Liverpool, UK

Effective and robust monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behavior as well as being an important step in the eventual wide-spread industrialization of the ALD technique.

Conventional quadrupole residual gas analyzers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. For these reasons monitoring of precursor gas concentrations during the ALD process is not often undertaken, especially at the production stage.

An alternative gas sensing technique that operates directly at pressures above $1E^{-4}$ mbar has been built around remote plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor's plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species. Importantly, this plasma, generated inside the sensor, has a sole function as a gas detector and does not affect the ALD process itself.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Previous work had demonstrated the usefulness of this technique but limitations were encountered when using a DC voltage to generate the sensor's plasma as contamination and reduced sensitivity developed when used with certain precursors. This work will describe a novel method of generating the detector plasma using a high peak power, low duty cycle pulsed voltage. It will be demonstrated that the pulsed power technique is more effective than DC in preventing contamination of the sensor's electrodes as well as improving the detection sensitivity of common ALD precursors and their reaction by-products.

Examples of this sensing technique's practical uses for Al_2O_3 and TiO_2 ALD processes are discussed; this includes detection of contaminants, optimizing purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption and reaction by-products.

2:15pm **AF-TuA-4 Near Room Temperature Plasma Enhanced Atomic Layer Deposition of Gold Metal**, ***Michiel Van Daele***, Ghent University, Belgium*; M Griffiths,* Carleton University, Canada*; A Raza,* Ghent University - IMEC, Belgium*; M Minjauw,* Ghent University, Belgium*; S Barry,* Carleton University, Canada*; R Baets,* Ghent University - IMEC, Belgium*; C Detavernier, J Dendooven,* Ghent University, Belgium

Currently only two Au ALD processes exist, using two different precursors. The first Au ALD process, reported by Griffiths et al. [1], is a three step process using Me_3AuPMe_3 as the precursor in combination with an oxygen plasma and water vapour as the reactants. The deposition of metallic gold was reported at a deposition temperature of 120°C, with only some carbon and oxygen impurities present in the film (6.65% C and 1.83% O). A growth per cycle of 0.05 nm per cycle was achieved. The Au ALD process, reported

by Mäkelä et al. [2], uses $Me_2Au(S_2CNEt_2)$ as the precursor and ozone as the reactant. Deposition between 120-180°C was reported with self-limiting growth at 180°C and a growth rate of 0.09 nm per cycle. The deposited films had low resistivity values (4-16μΩ cm) and were chemically pure with few impurities, O (2.9%), H (0.9%), C (0.2%), and N (0.2%).

A new plasma enhanced ALD process has been developed using Me_3AuPMe_3 and H_2 plasma as the precursor and reactant, respectively. Both precursor and reactant exhibit saturating behaviour, with a growth per cycle of 0.03 nm per cycle. A temperature window between 50°C and 120°C is achieved, with decomposition of the precursor above 120°C. The as-deposited gold films are polycrystalline and pure, with no phosphorous present in the film and very few carbon impurities (0.3%). Measured resistivity values (5.85μΩ cm) were close to the expected bulk value of gold (2.44 μΩ cm).

The surface chemistry and growth mechanism were investigated using in-situ RAIRS measurements, optical emission spectroscopy, and mass-spectrometry, pointing to an abbreviated growth cycle, instead of a complete one [3]. The initial growth starts off with the nucleation of gold particles on the surface. The formed gold nanoparticles grow and coalesce during the ALD process, as characterized using SEM measurements. The spacing of the gold particles makes this process interesting for surface enhanced Raman spectroscopy (SERS). Free space Raman measurements were performed on some of the samples and these showed excellent surface enhancement of the Raman signal. As far as we know this is the first report of an ALD gold film that shows SERS properties. In contrast to other SERS substrate fabrication methods, often involving lithography, this ALD process provides a direct way to fabricate SERS substrates without the need for a lot of process steps.

[1] M. B. E. Griffiths, P. J. Pallister, D. J. Mandia, and S. T. Barry, Chem. Mater. 28(1) (2016) 44-46

[2] M. Mäkelä, T. Hatanpää, K. Mizohata, J. Räisänen, M. Ritala, and M. Leskelä, Chem. Mater. 29(14) (2017) 6130-6136

[3] S. Elliott, G. Dev, and Y. Maimaiti, J. Chem. Phys. 146(5) (2017) 052822

2:30pm **AF-TuA-5 Low-Temperature Deposition of Gallium Oxide and Aluminum Oxide with Arrays of Microcavity Plasma Enhanced Atomic Layer Deposition***, **Jinhong Kim**, A Mironov, S Park, J Eden,* University of Illinois at Urbana-Champaign

A new atomic layer deposition (ALD) technology has been developed with an array of microcavity plasma devices which enable to grow the atomic layers at low temperature and enhance the growth rate with less defects and contamination. Confining low temperature plasmas to an array of microcavities yields uniform, glow discharges operating at pressures of 1 atmosphere and beyond. Not only are electron densities above 10^{16} cm^{-3} now routine, but the plasma electron temperature (T_e) and the ratio of the local electric field strength to the gas number density (E/N) are also increased significantly relative to conventional (macroscopic) plasmas. All of these characteristics are ideal for plasma chemical processing to generate oxidants efficiently compared to conventional RF or others existing source technology. A compact ALD system of which volume reduced by at least a factor of five was realized thanks to the minizturized microplasma source operating in lower frequency ac waveform. The uniform and conformal gallium oxide (Ga_2O_3) and aluminum oxide (Al_2O_3) thin films were deposited at low temperatures (< 50 °C) on silicon, quartz, and even polyethylene terephthalate (PET). Due to the complete reaction between precursors, the stoichiometric value of films presents ~ 1.5 in crystalline state, indicating the presence of negligible levels of impurities. MOSCAP was fabricated to analyze the electrical characteristic of 30 nm thickness of Al_2O_3 film. This MOSCAP exhibits higher breakdown electric field of 6.1 MV than conventional Al_2O_3 thin film . Hysteresis width from the sweep bias voltage was measured to less than 1 mV which is close to ideal MOSCAP electrical characteristics. In addition, Ga_2O_3 films deposited on PET were used to fabricate for transparent and flexible solar-blind photodetector with metal-semiconductor-metal junction structure. The crystallinity of films was analyzed using Transmission electron microscope (TEM) and X-ray diffraction (XRD). Post annealing (> 800 C) with argon environment was essential to produce polycrystalline β-Ga_2O_3. Bandgap was calculated by optical characteristics of the films from UV spectrophotometer. The photoresponse properties of photodetectors were investigated by the current-voltage characteristics and time-dependent photoresponse curves. Various thin film grown by microplasma enhanced ALD demonstrates improved optical and electrical properties. The scientific inspiration of this new deposition technology as well as the prospect for commercial application will be discussed in this presentation.

2:45pm **AF-TuA-6 The Effects of Varying Plasma Conditions on Plasma Assisted Atomic Layer Epitaxy***, **David Boris**, V Wheeler, N Nepal, S Rosenberg, J Avila, J Woodward, V Anderson, S Walton, C Eddy, Jr.,* U.S. Naval Research Laboratory

Plasma assisted atomic layer deposition (PA-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user.

In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the inductively coupled plasma source used in a Fiji 200 (Ultratech/CNT) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface, spatial variation of plasma properties, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow fractions in context of PA-ALD of AlN, InN, TiO_2 and Ga_2O_3 films. Changes in plasma parameters are then linked with changes in film characteristics.

3:00pm **AF-TuA-7 Plasma-Enhanced Atomic Layer Epitaxy of Ultra-wide Bandgap Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ Films***, **Virginia Wheeler**, N Nepal, D Boris, S Walton, S Qadri, J Avila, D Meyer, B Downey, V Gokhale,* U.S. Naval Research Laboratory*; L Nyakiti,* Texas A&M University*; M Tadjer,* U.S. Naval Research Laboratory*; M Goorsky,* University of California Los Angeles*; C Eddy Jr.,* U.S. Naval Research Laboratory **INVITED**

Ga_2O_3 has emerged as a promising material for next generation power electronics. While β-Ga_2O_3 (monoclinic) is the most stable and studied of five Ga_2O_3 polymorphs, the slightly less energetically favorable α- and ε-Ga_2O_3 phases have unique characteristics that can be exploited. α -Ga_2O_3 (rhombohedral, corundum) has the largest bandgap of 5.3 eV and can be alloyed with α-Al_2O_3 and α-In_2O_3 for bandgap engineering. ε-Ga_2O_3 phase (hexagonal, wurtzite) is polar, with a predicted polarization strength that is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron channels formed at heterojunctions, which would improve the viability of Ga_2O_3 electronic devices. Plasma-enhanced atomic layer deposition (PEALD) is a popular, conformal, energy-enhanced synthesis method for thin films due to its many advantages, including: deposition at reduced growth temperatures, access to metastable phases and improved crystallinity, and increased growth rates. In this work, we use PEALD to produce high-quality heteroepitaxial Ga_2O_3 and $(Al_xGa_{1-x})_2O_3$ (AlGO) films, and investigate phase selectivity as a function of substrate, growth temperature (T_g), plasma gas phase chemistry and gas pressure.

All Ga_2O_3 films were deposited in a Veeco Fiji G2 reactor equipped with a load lock and turbo pump using trimethygallium and O_2 plasma. Initial studies on c-plane sapphire substrates at 350°C and 8 mTorr, show the phase could be altered from β to α by a varying the O_2 flow during plasma pulse from 5-40 sccm. Optical emission spectroscopy indicate that the O^*/O_2 ratio is crucial for phase selectivity while the high ion flux to the surface can contribute to the crystallinity at low T_g. To grow ε-Ga_2O_3 on c-plane sapphire required going to much higher temperature (500°C), pressure (100's mTorr), and O_2 flow (100sccm) . Under no conditions was pure ε-Ga_2O_3 on sapphire achieved. Using optimum growth conditions for the three phases on sapphire, films were deposited on GaN and diamond to determine the effect of substrate structure. While films on diamond resulted in mixed β/ε phases, pure ε-phase films were attained on GaN and the strain varied with pressure and T_g. To investigate favorable heterojunctions for 2DEG formation, AlGO films were developed. While the full stoichiometric range could be reached using a PEALD digital alloying method, crystallinity was lost above ≈30 %Al, independent of phase. Initial electrical results on breakdown voltage and heterojunctions will be shown in order to establish the feasibility of these films in device applications.

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