ALD Fundamentals
Room Grand Ballroom A-C - Session AF3-TuM

Growth and Characterization II

Moderators: Jolien Dendooven, Ghent University, Belgium, Henrik Pedersen, Linköping University, Sweden

10:45am **AF3-TuM-12 Enabling Nucleation Phenomena Studies of ALD Deposited Films by In-situ High-Resolution TEM***, **Stephanie Burgmann**, A Dadlani, A Bin Afif,* Norwegian University of Science and Technology, Norway*; J Provine,* Aligned Carbon*; A van Helvoort, J Torgesen,* Norwegian University of Science and Technology, Norway

Understanding the nucleation stage and growth characteristics of atomic layer deposition (ALD) is indispensable for the fabrication of quantum dots or very thin films of just a few nanometers thickness. The tools for analyzing such small features and films are limited and often include post deposition characterization failing to capture the initial nucleation step. Enabling ALD processes in a closed gas-cell system inside a transmission electron microscope (TEM) allows manufacturing and characterization during film evolution at working conditions, a significant component in optimizing the nucleation phase.

In-situ characterization of deposition processes could be performed in an environmental TEM (ETEM) or a separated closed gas-cell holder system in a TEM preserving all analytical signals and TEM imaging capabilities as well as possible. A gas-cell reactor promises benefits in terms of versatility, controllability, and a defined deposition area. A successful implementation of ALD in a closed gas-cell system necessitates a gas-cell rector, a microscale heating system, a heated gas injection system, and an evacuation system to be placed into the limited space of a TEM holder.

An *in-situ* gas-cell holder system allowing deposition of different materials in a TEM has to be tailored to the delicate temperature sensitive ALD processes. To avoid contamination due to outgassing of sealing components, a gas-cell is designed based on a single wafer process, using the “Sandbox” process as basis. A layered structure employing ALD Al_2O_3 as etch stop layer and window material gives the opportunity to create a buried channeling system. Precursor gases will be injected from the back side of the chip using the two outer openings as inlet and exhaust. The central opening is the area where the electron beam is transmitted through the chip for imaging purposes. Al_2O_3 layers are used as functional windows with only a few atomic layers in thickness to achieve best possible high-resolution imaging and serve as a substrate for deposition. The design of the gas cell on a single wafer enhances the possibility to use characteristic x-ray signals for compositional analysis due to higher signal yield and simplifies the preparation for TEM studies involving environmental conditions.

The *in-situ* gas-cell reactor system is currently prototyped and will be tested thoroughly before its application inside the TEM. Ultimately, we envision that it enables controlled deposition inside any TEM, opening up new opportunities in nucleation studies for various researchers working on functional thin films around the world, opportunities not necessarily limited to ALD only.

11:00am **AF3-TuM-13 *In-situ* ellipsometric analysis of plasma assisted ALD grown- stoichiometric and crystalline AlN films***, **Adnan Mohammad**, D Shukla, S Ilhom, B Willis,* University of Connecticut*; B Johs,* Film Sense LLC*; A Okyay,* Stanford University*; N Biyikli,* University of Connecticut

The self-limiting aluminum nitride (AlN) plasma-assisted ALD (PA-ALD) growth process is monitored in dynamic real-time mode by in-situ multi-wavelength ellipsometry. AlN thin films are deposited on Si(100) substrates by PA-ALD reactor featuring a capacitively-coupled hollow-cathode plasma source and using trimethyl-aluminum (TMA) and Ar/N2/H2 plasma as metal precursor and coreactant, respectively. The temperature range for the saturation experiments is 100 – 250 °C, while each growth parameter variation is carried out for 10-cycle sub-runs. The sensitivity of the multi-wavelength ellipsometry has provided sufficient resolution to capture not only the subtle changes in the growth-per-cycle (GPC) parameter, but as well the single chemical surface reactions including precursor adsorption and plasma-assisted ligand removal and nitrogen incorporation. GPC values showed a slight increase with temperature slope within 100 – 200 °C, followed by a stronger surge at 250 °C, signaling the onset of thermal decomposition of TMA. The real-time dynamic in-situ monitoring depicted mainly the following perceptions into the HCPA-ALD process of AlN: (i) The GPC and TMA chemisorption amount showed plasma-power dependent saturation behavior which was also correlated with the substrate temperature; (ii) The cycle dependent refractive index profile shows a faster increase within the first ~100 cycles followed by a slower increase as the AlN film gets thicker; (iii) The crystallinity is improved particularly when substrate temperature exceeded 200 °C. In terms of additional materials characterization, optical, structural, and chemical properties are studied via ex-situ measurements on 500-cycle grown AlN films as a function of substrate temperature. The single-phase wurtzite polycrystalline character was confirmed for all AlN samples with no detectable carbon and relatively low (< 5%) oxygen content within the bulk of the films. Moreover, the highly stoichiometric (~1:1) elemental composition was also noticed as well for all AlN samples, regardless of the substrate temperature. A detailed comparative analysis with previously published reports on PA-ALD grown AlN will be presented.

11:15am **AF3-TuM-14 Film Properties of ALD SiNx Deposited by Trisilylamine and N_2 Plasma***, **Markus Bosund**, E Salmi, K Niiranen,* Beneq Oy, Finland

Silicon nitride is a widely used material in semiconductor applications, such as gate dielectrics, III/V surface passivation and etch stop layer.

PEALD SiNx films have been previously grown using aminosilanes like BTBAS with N_2 plasma [1]. These processes generally have a relatively low growth rate of 0.15 - 0.21 Å/cycle and high film quality can only be reached at above 300 °C deposition temperatures. Trisilylamine (TSA) has been previously combined with N_2/H_2 plasma at 300–400 °C [2], NH_3 plasma at 50–400 °C [3] and N_2 plasma at 250 – 350 °C [4] to grow PEALD SiNx films. However, in these works the low temperature range has remained either inaccessible or uncharted.

In this work we explored the PEALD TSA-N2 plasma process with a wide deposition temperature range from 50 to 350 °C. Focus was given to the electrical and optical properties of the films. A Beneq TFS 200 capacitively coupled hot wall plasma ALD reactor was used at direct plasma mode. It was found that reactor temperature, and plasma power and time had the highest impact on the film properties. Film deposition was observed at temperatures as low as 50 °C. Metal insulator semiconductor (MIS) structures were used to determine the breakdown field and leakage current at different temperatures. Films were dipped in 1 % HF solution for etch rate determination.

[1] KNOOPS, Harm CM, et al. Atomic layer deposition of silicon nitride from Bis (tert-butylamino) silane and N2 plasma. ACS applied materials & interfaces, 2015, 7.35: 19857-19862.

[2] TRIYOSO, Dina H., et al. Evaluation of low temperature silicon nitride spacer for high-k metal gate integration. ECS Journal of Solid State Science and Technology, 2013, 2.11: N222-N227.

[3] JANG, Woochool, et al. Temperature dependence of silicon nitride deposited by remote plasma atomic layer deposition. physica status solidi (a), 2014, 211.9: 2166-2171.

[4] WEEKS, Stephen, et al. Plasma enhanced atomic layer deposition of silicon nitride using neopentasilane. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 2016, 34.1: 01A140.

11:30am **AF3-TuM-15 Comparison of Properties of Conductive Nitride Films Prepared by PEALD using Quartz and Sapphire Plasma Sources***, I Krylov, X Xu, K Weinfeld, **Valentina Korchnoy**, D Ritter, M Eizenberg,* Technion - Israel Institute of Technology, Israel

We report on the properties of various conductive nitrides (TiN, ZrN, TaN) prepared by PEALD using either quartz or sapphire inductively coupled plasma (ICP) sources. Quartz and sapphire are two commonly used ICP source materials. The films were deposited at 300°C in Ultratech/Cambridge Fiji G2 PEALD system using metal-organic precursors and plasma half-cycles, separated by a purge period. Different reactive gases (N2, NH3, and H2) and various pressures during the plasma half-cycle were examined. All deposited films were ~ 30nm thick. TiN deposition rates are higher for the processes with the sapphire ICP source compared to those with the quartz source (Fig.1). The difference in deposition rates increases if the hydrogen based reactive gases are used for deposition. The low deposition rates of H2 plasma-grown TiN obtained using the quartz source may indicate a significant chemical etch of the quartz source by H radicals. Quartz tube etching is manifested by oxygen contamination in the deposited films, especially at processes with high H_2 flow (Fig.2). All deposited TiN films were found crystalline with a strong preferential orientation (XRD data is shown in Fig.3). The ICP source material has a significant role on film morphology if a H_2 plasma is used for deposition.

Films deposited using the quartz source consist of small (a few nm size) grains. Deposition using the sapphire ICP source results in films with large (∼20nm size) columnar grains (Fig.4). The most technologically important parameter of conductive nitrides is film resistivity. At thicknesses significantly higher than the electron mean free path film resistivity is increased due to scattering at grain boundaries and point defects. Therefore, the main parameters determining film resistivity of the deposited 30nm thick TiN films are the grain size and the oxygen contamination. For all examined nitrides, the lowest film resistivity and the highest film density was obtained for the H2 plasma-grown films deposited using the sapphire based ICP source (Fig.5,6). Sapphire source enabled higher deposition rates, better crystallization, lower film resistivity, and lower oxygen contamination. This indicates a superior chemical resistivity of sapphire to etching by hydrogen radicals compared to that of quartz. The advantage of the sapphire based ICP source is pronounced when a H_2 plasma and/or at high reactive gas flow are used for nitride deposition. The influence of ICP source material choice on the nitride film quality may be minimized if nitrogen based reactive gases and low flow conditions are used for nitride deposition. Optimal deposition conditions for both ICP source materials are determined.

11:45am **AF3-TuM-16 Role of Hydrogen Radicals in the Surface Reactions of Trimethyl-Indium (TMI) with Ar/N_2 Plasma in Hollow-Cathode Plasma-Assisted ALD***, **Saidjafarzoda Ilhom**, A Mohammad, D Shukla, N Biyikli, B Willis,* University of Connecticut

In this work we investigate the surface reactions of trimethyl-indium (TMI) with varying nitrogen plasma compositions. Extended 600-cycle long runs were carried out to grow thin films on Si(100) substrates via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD). TMI and variants of Ar/N_2/H_2 plasma (N_2-only, Ar/N_2, and Ar/N_2/H_2) were utilized as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed within 50 - 200 W plasma power range and 120 - 240 °C substrate temperature. Dynamic *in-situ*ellipsometry was employed to monitor the growth-per-cycle (GPC) characteristics and real-time growth behavior. In addition to *in-situ*analysis, *ex-situ*characterizations were done to identify structural, chemical, and optical properties of the grown InO_xN_yfilms. It was found that samples displayed polycrystalline single-phase hexagonal InN only when Ar/N_2-plasma was utilized. However, introducing H_2gas to the nitrogen plasma led to the growth of crystalline indium oxide (In_2O_3) films. In general, all In_2O_3samples displayed polycrystalline character, which exhibited preferred (222) crystalline orientation with peak intensity values changing as a function of RF-plasma power and substrate temperature. Interestingly, in the film grown at 160 °C the dominant crystal orientation shifted towards (321) with additional appearance of two metallic indium crystalline peaks. The role of H_2in possible reaction mechanisms resulting in the replacement of nitrogen with oxygen will be discussed based on the correlation of XRD and XPS results. The analysis of *in-situ*and *ex-situ*ellipsometry data will provide additional insight into the optical properties of the films as well as how the single chemisorption, ligand removal, and nitrogen/oxygen incorporation events possibly occur along the ALD cycles.

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