Emerging Materials
Room On Demand - Session EM11
Emerging Materials Poster Session

EM11-1 Strategies for High-Quality Nitride and Oxide Stacks by Plasma ALD*, **Yi Shu**, Oxford Instruments Plasma Technology, UK; F. McGuire, Oxford Instruments Plasma Technology; A. Kurek, O. Thomas, Oxford Instruments Plasma Technology, UK; H. Knoops, Oxford Instruments Plasma Technology, Netherlands*

Many applications in industry require the deposition of nitrides and oxides with high purity and with high-quality interfaces. The focus of most atomic layer deposition (ALD) studies is on the deposition of a single layer in a dedicated deposition chamber. This contribution highlights a set of strategies for high-quality nitride and oxide stacks deposited by ALD in a single run in a single chamber. As an example, an HfO_2/SiN_x multilayer is demonstrated with <5% oxygen in the nitride.

Low oxygen content is a challenge for nitride deposition, especially when lines and chambers might contain oxygen and water traces from a previous deposition. To demonstrate a high-quality oxide and nitride stack, HfO_2 using TDMAHf and O_2 plasma and SiN_x using BTBAS and N_2 plasma are employed. The depositions are carried out in a FlexAL system in a single run and to get the best SiN_x the residence time was minimized by a combination of turbo pumping, chamber heating and pressure and flow control.[1] For other ALD nitride processes substrate biasing could be employed to lower oxygen content, but in the case of SiN_x this is less effective.[2] When switching from oxide to nitride deposition, the following strategies are employed:

1. Strong purging and pumping of any gas lines that could contain oxygen or oxygen byproducts.
2. TDMAHf precursor pulses to scavenge possible oxygen by-products.
3. Plasma treatment of the chamber and wafer surface.

After the subsequent deposition of the nitride the surface is exposed to a plasma post-treatment to further densify the material and protect it against oxidation. Using this strategy an alternating stack of HfO_2 and SiN_x was deposited with individual layer thicknesses of 20 nm. XPS depth analysis indicated that even with this relatively fast switching, oxygen content levels <5% were obtained for SiN_x (XPS analysis by Dr. Shihong Xu, nanoFAB Centre, University of Alberta). This example and general strategies for such oxide and nitride stacks will be presented.

1. Knoops et al.,*Appl. Phys. Lett.***107**, 014102 (2015)
2. Faraz et al., *Plasma Sources Sci. Technol.***28**, 024002 (2019)

EM11-2 Compositionally Graded Laminate ALD Films*, **Alexandru Pavel**, V. Vorsa,* Greene Tweed, Inc.

To prevent contamination of microelectronic devices during semiconductor processing, chamber components of semiconductor tools are often coated with high purity ceramic coatings such as alumina or yttria that exhibit high resistance to plasma erosion in halogen environments.However, even these materials exhibit erosion over time leading to lower yield and costly down time, especially as the industry moves to smaller node sizes.

To overcome these limitations, there has recently been a major effort to find new coating materials and processes leading to improved plasma erosion resistance. There are now emerging plasma-resistant coatings deposited by atomic layer deposition (ALD). Advantages of ALD include conformal, dense, and pinhole-free film that can coat complex 3D shapes and high-aspect ratio holes.

One weakness with many coatings, including ALD, is the transition from one material composition to another.For example, the transition from substrate to film or from one film composition to another.Typically, in ALD, the film-substrate interface transitions abruptly within an atomic spacing of 1-2 Å.This can lead to high stress gradients confined to a narrow planar region potentially leading to poor film adhesion, especially where smooth surfaces and large CTE mismatches are present.

To overcome this drawback, ALD films can be deposited in such a way (US20200131632A1) that the composition is smoothly transitioned from one material to another, thus avoiding narrowly confined stress gradients.In this work, we present plasma resistant multi-layer coatings that exhibit excellent bonding of films to substrates formed by gradually varying the chemical composition from substrate to film and from one film type to another in a technique called Compositionally Graded Laminates (CGL).Examples of Compositionally Graded Laminate films of Y2O3-Al2O3, Y2O3-SiO2, and Y2O3-ZrO2 systems will be presented.

In addition to the semiconductor industry, this technique may be used to prepare and/or to coat substrates that form components useful in a variety of industries, especially those where components may be exposed to high temperatures and/or corrosive chemicals. For example, Compositionally Graded Laminates may be used on components that are found in equipment or devices used in aerospace, energy storage, pharmaceutical production, food processing, oil field applications, military and/or maritime applications, industrial manufacturing, and scientific and/or diagnostic instrumentation.

EM11-3 *In Situ* Electrical Conductance to Measure Vapor Phase Infiltration (VPI) Doping Kinetics of Semiconducting Polymers*, **Kristina Malinowski**, S. Gregory, O. Hvidsten, A. Jungreis, M. Losego,* Georgia Institute of Technology

This poster will show our development of *in situ* electrical conductance measurements during vapor phase infiltration (VPI) of polyaniline (PAni) thin films with titanium tetrachloride ($TiCl_4$) to achieve electrical doping. *In situ* measurements during vapor phase processes provide abundant information about reaction kinetics and mechanisms that could not be acquired with *ex situ* data alone. The field of vapor doping semiconducting polymers lacks a robust understanding of doping mechanisms and their respective kinetics. Therefore, the vapor doping community stands to benefit from the implementation of *in situ* measurements. Here, we demonstrate how *in situ* conductance correlates with *ex situ* characterization and propose a sequence of *in situ* doping mechanisms. Dosing and holding $TiCl_4$ in a chamber where hydroxyl groups are present can lead to both oxidative and acid doping of PAni films. The$TiCl_4$ vapor can directly oxidatively dope PAni while the HCl byproduct of $TiCl_4$+ -OH can lead to acid doping. During the first dose and hold of $TiCl_4$, *in situ* conductance measurements show that varying the $TiCl_4$ dose pressure changes the rate and total conductance. Then, purge, pump and isolate steps remove unentrapped $TiCl_4$ from the chamber. Dosing and holding H_2O allows further acid doping, oxidative dedoping and oxide formation. Acid doping is in competition with dedoping and oxide formation to increase and decrease conductance, respectively. The *in situ* conductance measurements show decreasing conductance rates with increasing initial $TiCl_4$ pressures, suggesting that acid doping dominates at low pressures and dedoping and oxide formation dominates at high pressures. The *ex situ* characterization of the thin films validates these suggested mechanisms. Opposite pressure-conductance correlations between the $TiCl_4$ dose and H_2O dose present an opportunity for optimizing PAni conductivity, aided by a thorough understanding of *in situ* kinetics. PAni doping can be further controlled by managing the reactor wall chemistry. If the reactor is first exposed to a precursor reactive towards hydroxyls but does not create an acid byproduct (for example trimethyl aluminum, TMA), then the walls can be passivated. Consequently, when $TiCl_4$ is dosed, it does not react with the passivated walls, and HCl is not formed, so only oxidative doping occurs. During the subsequent water dose, the potential for acid doping is reintroduced through HCl formation within the film. *In situ* measurements demonstrate that this effectively isolates the two doping mechanisms. Thus, *in situ* measurements show promise in aiding design of complex processes for vapor doping of conductive polymers.

EM11-4 Atomic Layer Deposition of Yttrium Oxide using a Liquid Yttrium Precursor, Y-08*, M. Kim,* EMD Performance Materials, Korea (Republic of)*; S. Lee,* EMD Electronics, Korea (Republic of)*; M. Fang, J. Aldo, J. Woodruff, R. Kanjolia,* EMD Performance Materials*; **Bhushan Zope**,* EMD Electronics, USA*; S. Ivanov,* EMD Performance Materials

Yttrium Oxide (Y_2O_3) films deposited by ALD have been extensively studied as a promising high-k material for future device manufacturing such as in MOSFETs or memory applications due to its wide band gap (~5.5 eV), high permittivity (>10), and high thermal stability. Pure or doped Y_2O_3 containing films have also been used in other applications such as in solid oxide fuel cells, protective coatings, photonics, and quantum information processing.

Herein, we report the studies of atomic layer deposition (ALD) of Y_2O_3 thin films using a newly developed volatile, scalable, liquid yttrium precursor, Y-08, with ozone and/or water as co-reactants.

A comparison of oxygen sources shows that "ozone followed by water" leads to a higher growth per cycle {0.81 Å/cycle} compared to either ozone-alone {0.51 Å/cycle}, or water-alone {0.16 Å/cycle}. The ALD window starts at 310 °C on the system tested, and the growth/cycle is 1.09 Å/cycle when saturation is achieved with both the Y-08 and oxygen sources doses.The refractive index ranges from 1.90 to 1.95. XPS analysis confirms that the bulk of film consists of exclusively oxygen and yttrium; but there was some carbon contamination on the film surface.

An yttrium oxide film deposited on a via with 20:1 aspect ratio (1800-nm deep, and 90-nm wide) shows excellent conformality when characterized by SEM (Figure 1), with film thickness ranging between 22.5 and 26 nm outside the via (Figure 2a), and 23 and 26 nm at the via bottom (Figure 2b).

We demonstrate that the liquid nature and high volatility of our new yttrium precursor promotes easier precursor delivery and more controllable ALD processes for manufacturing good quality Y_2O_3 thin films for future semiconductor applications.

EM11-7 Direct sALD of MOF: An Improvement in the Nucleation Behavior*,*
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Metal organic frameworks (MOFs), can be described as crystalline three-dimensional porous solids, with a high surface area, which have attracted considerable attention in a wide range of applications e.g. in catalysis,hydrogen storage,gas-separations , thermoelectric applications or as chemical sensors.Up to the present time, low-temperature methods had to be used to grow MOFs thin films today by conventional solution-based techniques. However, traditional growing methods from solution like spin-coating, spray-coating or dip-coating generates MOFs thin films with a rather low film quality and an alarming lack of a precise film thickness control under 1 nm, which renders them unsuitable for most industrial applications and severely limits their future application potential.

Atomic layer deposition (ALD) provides this capability, but is limited by the necessity to use gaseous precursors in vacuum conditions at temperatures above 100°C. However hybrid organo-metalic compunds such as the MOFs are not accessible by ALD due sensitivity to temperature.

In this perspective, we have transferred the principles of ALD to precursors dissolved in liquid solvents. The 'solution ALD' (sALD) method can be implemented in a variety of microfluidic or slot-die processing devices. We have demonstrated that the principles of classical, gas-based ALD —self-limiting surface reactions— are reproduced in sALD. sALD shares the fundamental properties of standard 'gas ALD' (gALD), in particular the self-limiting surface chemistry and the ability to coat deep pores in a conformal manner Furthermore, sALD allows the experimentalist to design new, advantageous, reactions of known semiconductors (oxides, heavier chalcogenides), or to deposit materials otherwise inaccessible to ALD altogether, such as polymers, ionic solids, and metal-organic frameworks. They may be obtained in highly pure, crystalline form at room temperature, either as planar films or as conformal coatings of porous substrates. Based on these advances, we have been able to make the first sALD-derived MOFs.

EM11-10 Thermal ALD Growth of Ir and IrOx Films Using (MeCp)Ir(COD) and Oxygen*,*
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Iridium is a noble metal with low oxygen permeability, high chemical stability and high work function. It is one of the most corrosion resistant metals and has a lower bulk resistivity (~5.0 μΩ-cm) than Ru (6.8 μΩ-cm). Due to these unique properties, iridium has been investigated for potential applications in semiconductor devices as gate electrodes, a seed layer or Cu diffusion barrier. On the other hand, IrO_2 can be converted into Ir metal by H_2 reduction, and IrO_2 nanoparticles are some of the best catalysts with potential applications for oxygen evolution in electrolyzers, metal-air batteries, and photoelectrochemical water splitting.

Various Ir precursors have been reported for ALD and CVD growth of Ir and IrO_2 films (1,2). O_2 is the most common oxidizer. Among the known ALD Ir precursors, the cyclodienyl-based (RCp)Ir(COD) (R=Me, Et) have very high thermal stability, and the liquid (EtCp)Ir(COD) precursor has been studied extensively (3,4), while the low melting-point (~40°C) MeCp analogue, (MeCp)Ir(COD), has not received much attention although it is easier to synthesize and has a higher thermal stability than (EtCp)Ir(COD). We have studied the ALD growth behavior of Ir and IrO_2 films using (MeCp)Ir(COD) and O_2 on a number of oxide and metal nitride surfaces in a wide temperature range up to 425°C. High purity Ir films with low O and C have been obtained on oxide and nitride substrates with resistivity down to ~16 μΩ-cm under various deposition conditions as shown in Fig. 1. The growth behavior on oxide surfaces is more complex. IrOx formed under certain conditions with notably higher resistivities. For examples, IrO_x formed at ~ 350°C with O_2 on Al_2O_3 as shown in Fig. 1.

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