Area Selective ALD
Room Plaza Exhibit - Session AS-MoP
Area Selective ALD Poster Session

AS-MoP-1 Area-selective ALD using Vapor and Solution-Phase Synthesized Perfluorodecyltrichlorosilane (FDTS) SAMs as Growth Inhibition Layers, ***Ali Haider***, Bilkent University, Turkey; *S Altuntas,* TOBB University of Economics & Technology, Turkey; *P Deminskyi, T Khan,* Bilkent University, Turkey; *F Buyukserin,* TOBB University of Economics & Technology, Turkey; *N Biyikli,* Utah State University

One of the main type of organic materials used for growth inhibition in area-deactivated selective atomic layer deposition (AS-ALD) is self-assembled monolayers (SAMs). SAMs are made up of long organic molecules consisting of three elements: the head group, chain as the backbone, and a tail group. The tail groups of SAM molecules transforms the surface from an OH-terminated hydrophilic surface into a chemically saturated $C-H_3$ or $C-F_3$ hydrophobic surface. When compared with the conventional C-H terminated SAM chemistries, an organic back bone chain made up of fluorine (CF_2) and CF_3 tail groups might provide an enhanced hydrophobic character and potentially may result in an improved film-growth inhibition performance with higher nucleation initiation threshold ALD-cycle numbers. Moreover, the vast majority of the reported SAM-based AS-ALD work in literature utilizes SAMs which are synthesized in wet-solution phase to modify the substrate surface. Such wet processing features low-compatibility with main-stream device fabrication technology and suffers from long processing times and unavoidable defect sites leading to imperfections in growth inhibition. Vapor phase grown SAMs for AS-ALD could provide additional advantages such as faster processing, eliminating wet processing, topographical selectivity, and facile integration with ALD reactors and other fabrication equipments.

In this work, we report an experimental study for AS-ALD using perfluorodecyltrichlorosilane (FDTS) SAM molecules, which are deposited on Si(100) substrates using both vapor-phase and solution-phase synthesis approaches. A comparison between vapor and solution-phase grown SAMs will be provided in terms of growth inhibition performance. FDTS monolayer terminated surfaces formed via vapor and solution phase synthesis methods demonstrated exhibit both high-degree of hydrophobicity (contact angle ~120°) owing to long CF_2 organic back bone chain and CF_3 tail groups. Contact angle, scanning electron microscope (SEM), spectroscopic ellipsometer, and X-ray photoelectron spectroscopy (XPS) measurements results will be presented to demonstrate the effectiveness of FDTS molecules against thin film growth blockage. Finally, we will present micro-scale patterning of thin films using a photolithography patterned SAMs substrate.

AS-MoP-2 Nanoscale Patterning of C_4F_8 Plasma Polymer Blocking Layers via Femtosecond Pulsed Laser Processing for Selective Deposition of Noble Metals, ***Petro Deminskyi***, *I Pavlov, S Ilday, O Tokel,* Bilkent University, Turkey; *H Eren,* Delft University of Technology, Netherlands; *A Haider, F Ilday,* Bilkent University, Turkey; *N Biyikli,* Utah State University

Area-selective ALD (AS-ALD) is a promising technique for low-temperature self-aligned nanoscale device fabrication by reducing or eliminating lithography/etch process steps. Several methods have been reported for the patterning of ALD-grown films: (1) patterning based on lithography and lift-off; (2) AS-ALD by area-deactivation; (3) AS-ALD by area-activation; and (4) the ideal but highly challenging inherently selective AS-ALD. Though numerous of techniques of surface patterning for AS-ALD have been reported (optical/e-beam lithography), cost-effective alternative solutions are highly attractive.

In this study, we show that by using the pulsed-laser processing technique it is possible to achieve nanoscale patterned surfaces for AS-ALD of nobel metals. To develop this alternative methodology, we have used: an ultrafast Yb-fibre laser, operating at a central wavelength of 1,030 nm which has a 170-fs pulse duration, 1 MHz repetition rate with adjustable laser power levels. For Pt ALD growth, we used trimethyl (methylcyclopentadienyl) platinum (IV) and ozone as Pt and O_2 precursors, with N_2 as the carrier gas. Samples have been characterized using HR-SEM, contact angle measurements, EDX-analysis, and XPS for elemental composition analysis.

Our study consists of the following steps:

- C_4F_8 plasma polymerization on Si(100) substrate surface in an ICP etch reactor;
- Micro- and nanoscale patterning of C_4F_8 plasma polymer by femtosecond (fs) laser pulses;
- Si surface patterning by nonlinear laser lithography (NLL);
- AS-ALD of Pt thin films on patterned C_4F_8/Si interface;
- Plasma polymerization of C_4F_8 on Pt thin film;
- Hydrophobicity study of dielectric/metal/substrate stack.

We'll present our experimental results on surface patterning via *fs* laser pulses and NLL for Pt AS-ALD. Here we speculate about the transparency of C_4F_8 polymer to ~1 μm wavelength. In this regardsTherefore, due to substrate heating, polymer can be removed from specific areas. Patterned structures with diameters as small as 250 nm have been achieved.

This new capability could pave the way for cost-effective lithography-free patterning technique. For future work, (1) surface patterning with smallest possible features; (2) super-hydrophobic surfaces with metal contacts underneath are under development of which the latest results will be presented as well.

AS-MoP-3 Feasibility Study of Single and Multi-layered Graphene as Plasma-compatible Deactivation Layers for Selective Deposition of III-Nitride Materials, ***Petro Deminskyi***, *E Kovalska, A Haider, C Kocabas,* Bilkent University, Turkey; *N Biyikli,* Utah State University

Plasma-assisted atomic layer deposition (PA-ALD) is a promising method for low-temperature growth of III-nitride materials. However, selective film deposition using PA-ALD is quite challenging mainly due to the plasma-incompatibility of conventional deactivation/blocking layers including SAMs and polymers. The main motivation of this work was to explore alternative growth inhibition materials which could withstand plasma environment.

Towards this goal, we investigated single-layer graphene (SLG) and multi-layered graphene (MLG) as an effective lift-off mask for AlN, GaN, and InN grown via low-temperature PA-ALD. We achieved crystalline III-nitride thin films on graphene blocking layer and Si substrate surface. As far as SLG and MLG possess relatively weak Van der Waals forces between (1) graphene/substrate and (2) graphene/graphene interfaces, here, we gauge the importance of those forces for selective deposition of III-nitride materials. This strategy could be mainly used as an alternative patterning approach based on the graphene-assisted lift-off technique.

To evaluate the selective deposition studies, GaN, AlN, InN, and graphene have been removed from Si surface and were characterized using SEM and XPS. Spectroscopic ellipsometry measurements were performed to measure the film thickness on Si substrate surface and graphene-masked area. An extensive comparative study has been carried out with some successful results for certain binary III-nitride alloys. Possible blocking, nucleation, and graphene-penetration mechanisms will be discussed in conjunction with possible future strategies to further develop selective deposition methods for plasma-assisted film growth recipes.

AS-MoP-4 Electroless Noble Metal Deposition - A New Approach for Highly Selective Surface Controlled Deposition Process, ***Stanko Brankovic***, Universtiy of Houston; *D Solanki, D Wu,* University of Houston; *Y Dordi, A Joi,* Lam Research

The improved understanding of nucleation kinetics has led to various discoveries in which the thin film growth was manipulated to enhance the evolution of atomically flat epitaxial overlayers. Exploiting some of these results has led to invention of several new methods and protocols for electrodeposition where underpotentially deposited (UPD) monolayer (ML) is used as a mediator, surfactant or sacrificial template. The one successful example is so called “*Deposition via Surface Limited Redox Replacement (SLRR) of UPD ML*” which gained a lot of applications for synthesis of noble metal thin films with different functionalities. This protocol/method represents the combination between the potential controlled step – formation of UPD ML and electroless step – SLRR of UPD ML by more noble metal ions (galvanic displacement). However, our studies show that there is still a lot of room left for improvements and further simplifications. They should expand application of this deposition protocol in many areas where traditional ALD process has been used.

In this talk we present results demonstrating electroless (e-less) ALD process where deposited Pb monolayer is used as a reducing agent and sacrificial material in SLRR reaction with noble metal ions such as Pt, Pd, Ru etc…. The full deposition cycle involves sequential exposure of the substrate to the solution for Pb ML deposition and then to solution for SLRR reaction and noble metal deposition. This results in an overall

deposition of controlled amount of noble metal which is the function of the areal density of deposited Pb monolayer and stoichiometry of the SLRR reaction. Therefore, the process mimics to great extend the standard ALD cycle where adsorption of the metal precursors and surface catalyzed reaction are replaced by e-less Pb monolayer deposition and SLRR reaction. If two-step SLRR cycle is repeated an arbitrary number of times a highly compact, smooth and conformal noble metal thin film is grown. The deposition process is highly selective to the metal substrates at which Pb forms an UPD monolayer providing an advantage when certain integration requirements are considered. The process is designed (but not limited) for aqueous solutions with fairly simple and stable chemistry that can be easily scaled up to any size and shape of the substrate surface. Results demonstrating details and underlying phenomena controlling this process will be discussed. In addition, an example of a high quality of Pt, Pd and Ru films grown on Cu substrate will be shown as well as the applications of this process for metallization of structures relevant to semiconductor device fabrication.

AS-MoP-5 Inherently Selective Plasma-assisted ALD: A Feasibility Study for III-Nitride Materials*, **Necmi Biyikli**,* Utah State University*; A Haider, P Deminskyi,* Bilkent University, Turkey

ALD processes featuring inherent selectivity without using any area deactivation/blocking layers or area-activation/patterned seed layers, is an almost unexplored field, but is a highly challenging method with enormous potential to revolutionize the nanoscale processing technology. As ALD processes strongly depend on the chemistry of substrate surfaces and precursor molecules, there is significant potential for the development of selective chemistries and reactions possessing large kinetic barriers. Selective atomic layer deposition/epitaxy of nitride materials has not yet been reported mainly due to the plasma-incompatibility of utilized blocking layers. Likewise, inherently selective atomic layer etching is still challenging with there being very limited success and no reports yet on nitrides.

In this work, we aim to develop inherently selective PA-ALD recipes for the nitride material family. To realize this objective, individual deposition reactions featuring selective chemistry with large kinetic barriers for III-nitride materials against major surfaces will be investigated. This unique bottom-up fabrication tool-box for nitride materials would enable the self-aligned fabrication of critical nanoscale structures minimizing the need for expensive and complex lithography-based top-down processing. Current state-of-the-art selective atomic layer processes include selective-area deposition of oxides and metals only, by using various blocking layers which need to be removed afterwards via additional process steps. Our strategic goal isto achieve the major breakthroughs necessary to enable not only selective ALD for III-nitrides, but also the making of this selectivity inherent, i.e., chemically favorable, to eliminate the use of blocking layers and extra processing steps. The highly-challenging task of developing inherently selective nitride-ALD will be embraced through a systematic study featuring extensive materials characterization efforts to gain a full understanding of the material growth dynamics on various surfaces and carefully monitoring the self-limiting surface reactions.

Our initial investigation on the influence of several critical parameters which might lead to the development of inherently selective plasma-assisted surface reactions show that the choice of substrate material and reactor pressure have a considerable impact on the properties of the deposited film. The key achievement sought in our studies is to obtain a certain nucleation delay between different surfaces including metallic (Pt, Cu), oxide (SiO_2, Al_2O_3), and conventional substrates (Si). We would like to share our critical experimental findings thorughout the presentation.

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