

## Area Selective ALD

### Room On Demand - Session AS1

#### Selective ALD by Area-Activation

**AS1-1 Area-Selective Atomic Layer Deposition Patterned by Electrohydrodynamic Jet Printing for Additive Nanomanufacturing of Functional Materials and Devices, Tae Cho, N. Farjam, C. Allemang, C. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. Peterson, K. Barton, N. Dasgupta, University of Michigan, Ann Arbor**

Personalized health care has led to an increase in demand for customization of integrated nanosystems. However, existing additive nanomanufacturing techniques are often restricted by long processing times and/or strict material requirements. For instance, electrohydrodynamic jet (EHD) printing allows for fast and versatile printing down to 30 nm feature sizes, but requires special attention to the physical/chemical properties of the ink. To expand on this nanoprinting approach, we have demonstrated that by patterning polymer geometries, EHD can be used to locally activate/deactivate ALD growth [1,2].

In this study, we combined area-selective atomic layer deposition (AS-ALD) and EHD to pattern inhibitor polymers with sub-micrometer resolution and high line speeds [2]. This allows patterning of ZnO, Al<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and their ternary combinations with tunable geometry and elemental composition. With additive EHD printing, polyvinylpyrrolidone was printed with an average linewidth of 312 nm to deactivate the surface to ALD growth. Furthermore, using solvent-based subtractive EHD printing to dissolve polymethylmethacrylate [1], an average linewidth of 9 μm region was patterned to activate the surface.

Using this technique, a bottom-gate, top-contact thin-film transistor, with an on/off current ratio of greater than 10<sup>5</sup>, was fabricated using zinc-tin-oxide (ZTO) as the semiconductor and aluminum-doped zinc oxide as the source and drain electrical contacts. We have also demonstrated that by combining thermal and plasma-enhanced ALD processes, ZTO film density can be increased, which resulted in the highest reported  $\mu_{FE}$  of ~22 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> after post-deposition anneal at 400 °C [3]. However, due to the thermal budget of the inhibitor polymers used in AS-ALD-EHD process, a low ALD deposition temperature was used, yielding lower mobility compared to the thermal-plasma ALD device. Therefore, to improve device performance, we have studied the effect of the oxidant (H<sub>2</sub>O, O<sub>3</sub>, and plasma) and deposition temperature on the ALD selectivity and device performance. This technique can be further used to print on nonplanar and/or flexible substrates, without the need for traditional lithography.

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[1] N. Farjam, T. H. Cho, N. P. Dasgupta, K. Barton, *Appl. Phys. Lett.* **117**, 133702 (2020)

[2] T.H. Cho, N. Farjam, C. R. Allemang, C. P. Pannier, E. Kazyak, C. Huber, M. Rose, O. Trejo, R. L. Peterson, K. Barton, N. P. Dasgupta, *ACS Nano* **14**, 17262 (2020)

[3] C. R. Allemang, T. H. Cho, O. Trejo, S. Ravan, R. E. Rodríguez, N. P. Dasgupta, R. L. Peterson, *Adv. Electron. Mater.* **6**, 2000195 (2020)

**AS1-2 Surface-Activated Area-Selective Atomic Layer Deposition of Palladium, Himamshu Nallan, X. Yang, University of Texas at Austin; B. Coffey, Lam Research Corporation; J. Ekerdt, University of Texas at Austin**

Flexible electronics and next-generation roll-to-roll nanomanufacturing rely on the use of polymeric substrates, which constrain processing temperatures. In addition to typically operating a low thermal budget, ALD can provide atomic-level control, making it a suitable method of deposition for these applications. In this work, we present an area-selective ALD (AS-ALD) route to grow difficult-to-nucleate metals that promises to mitigate the need for post-deposition removal of any metal that grows non-selectively.

The area-selective deposition of palladium metal uses palladium(II) hexafluoroacetylacetonate and H<sub>2</sub> at low temperature (≤150 °C). There is a significant nucleation delay during the deposition of Pd with these coreactants on various metal-oxide substrates due to the low reactivity of the H<sub>2</sub> molecule with Pd(hfac)<sub>2</sub> as well as the Hhfac reaction product inhibiting oxide surface sites. Typically, a high deposition temperature or hydrogen plasma is employed to facilitate Pd film growth. Here we report an alternative route to enhancing palladium deposition and conferring selectivity by employing a pre-patterned metallic seed layer. First, AS-ALD

of nickel(II) oxide is carried out on pre-patterned sp<sup>3</sup> carbon-rich resist using bis(N,N'-di-tert-butylacetamidinato)nickel(II) and H<sub>2</sub>O as coreactants at 200 °C to yield conformal, carbon-free oxide films, with high selectivity and no nucleation delay. Subsequently, the nickel(II) oxide films are reduced with atomic and/or molecular hydrogen to nickel(0), which readily facilitates the surface dissociation of H<sub>2</sub> and thereby enhances the deposition of Pd, defining a route to selective deposition. As only surface nickel(0) provides nucleation enhancement for metal-on-metal deposition, partial, superficial reduction of the nickel(II) oxide film is sufficient. In this way, the selectivity of the oxide deposition process is conferred to palladium deposition as well. In-situ x-ray photoelectron spectroscopy is used to determine the presence and oxidation states and film stoichiometry of palladium and nickel. Ex-situ x-ray reflectivity and atomic force microscopy are used to probe the film thickness and surface morphology, respectively.

**AS1-3 In-Situ and in-Vacuo Studies on Area Selective Atomic Layer Deposited Ruthenium Films on Silicon and Silicon Oxide, Sebastian Killge, J. Reif, Technische Universität Dresden, Germany; M. Knaut, M. Albert, Technische Universität Dresden, Institute of Semiconductor and Microsystems (IHM); Chair of Nanoelectronics, Germany; J. Bartha, T. Mikolajick, Technische Universität Dresden, Germany**

We present a thermal activated inherent area selective atomic layer deposition (*thALD*) of ruthenium (*Ru*) on crystalline silicon (*cSi*) wafer and silicon oxide (*SiO<sub>2</sub>*) interfaces.

The selective deposition is based upon the inhibited nucleation of ruthenium on oxide surfaces such as SiO<sub>2</sub> compared to Si and metal surfaces. The ALD ruthenium (5-20 nm thick) deposited with the organometallic precursor ECPR [(ethylcyclopenta-dienyl)(pyr-rolyl) ruthenium(II)] and molecular oxygen [1, 2] on 4 inch silicon [100] wafers with a pattern of cSi dipped by diluted hydrofluoric acid (*HF*), and native silicon oxide (1.8 nm).

In our experiments, the pattern on the wafer was created by lithography with AZ<sup>®</sup> 5214 E resist. A dip with 0.5% HF (30 s) was used to remove the native oxide film on cSi and to create a hydrogen-terminated surface. Immediately afterwards, the resist was stripped by a treatment with acetone, 2-propanol, and clean water (conductivity 0.05 μS/cm). After drying, the wafer was transferred into ALD tool for deposition within less than 5 minutes.

As shown in [2-4], the initially incubating and nucleation periods strongly depend on the deposition temperature. On HF-dipped cSi after a nucleation period of 10 ALD cycles a steady-state Ru-on-Ru(Ox) growth with a GPC of ca. 0.9 Å was observed (Fig. 1) at 180 °C. In the linear steady-state region the GPC was nearly independent on the deposition temperature [2]. On native SiO<sub>2</sub>, only isolated islands of Ru were formed in negligible quantity after 150-180 ALD cycles, consisting of non-stoichiometric Ru / Ru(Ox). Here, growth started after 180 ALD cycles, whereas on HF-dipped Si a 16 nm thick Ru film (Rs= 14,2 Ω/□; ρ= 22,72 μΩ\*cm) has been deposited already (Fig. 2). A higher quality of selectivity became achieved by combining ALD with selective etching using an O<sub>2</sub> or O<sub>3</sub> purge after a certain number of ALD cycles (Fig. 3). As we demonstrated earlier [1, 2], purge steps with molecular hydrogen (H<sub>2</sub>) during Ru-ALD can prevent blister formation.

**AS1-6 Nucleation and Growth in Localized Thermal Atomic Layer Deposition, Bart de Braaf, K. Storm, Eindhoven University of Technology, Netherlands**

We explore the possibility of achieving area selective ALD by modifying the temperature profile on the substrate. The technique keeps the majority of the substrate at a low temperature, suppressing the surface chemical reaction, while a small area is heated to allow the reaction to locally proceed. A practical example of this technique is the ALD process of Si<sub>2</sub>H<sub>6</sub>(1). Controlling the size and the position of the heating spot on the substrate allows for 'writing' on the surface, with potential applications in the bottom-up fabrication of electronic devices like solar panels and OLED displays. We study the feasibility and window of opportunity of this technique by computational modeling. We first model the control of the temperature by various illumination protocols, and then model and simulate the nucleation and growth of spatially localized dots and lines given an inhomogeneous temperature profile. We show that the temperature profile can direct substrate deposition and control the connectivity and size of the domain deposited on the substrate.

Bibliografie

# On Demand

1. *Ar+-laser-assisted subatomic-layer epitaxy of Si.* **Y. Suda, M. Ishida, M. Yamashita.**1996, Journal of Crystal Growth, pp. 672-680.

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