

ALD Applications

Room Hall 3E - Session AA3-WeM

Other Emerging Applications

Moderators: Sumit Agarwal, Colorado School of Mines, Parag Banerjee, University of Central Florida

10:45am AA3-WeM-12 Tunable Superconducting Nb_xTi_{1-x}N by Fast Plasma-enhanced ALD for Quantum Applications, Silke Peeters, L. Nelissen, Eindhoven University of Technology, Netherlands; D. Besprozvanny, Oxford Instruments Plasma Technology, UK; M. Verheijen, Eindhoven University of Technology, Netherlands; M. Powell, L. Bailey, Oxford Instruments Plasma Technology, UK; E. Kessels, Eindhoven University of Technology, Netherlands; H. Knoops, Oxford Instruments Plasma Technology, UK

Superconducting films ranging from a few to hundreds of nanometers are at the basis of a wide range of quantum devices, and are therefore key in advancing quantum technology to an era of widespread utility. The further development of quantum technologies hinges on improvements in materials and their interfaces. With its atomic-scale growth control, plasma-enhanced ALD (PEALD) could become an enabling technique for the growth of superconducting thin films with high-quality interfaces. High-throughput processes will facilitate the growth films beyond 100 nm, broadening the application perspective for ALD of superconducting films.

We demonstrate PEALD of superconducting Nb_xTi_{1-x}N films ranging from 5 to 100 nm thickness at a high throughput of >50 nm/hour on the Plasma Pro ASP system. The depositions consist of NbN and TiN supercycles using the TBTDEN and TDMAT precursors and an Ar/H₂/N₂ plasma at a table temperature of 320 °C. The RF-driven remote capacitively coupled plasma source is combined with RF substrate bias functionality allowing for ion-energy control.

The Nb_xTi_{1-x}N films show critical temperatures of superconductivity from 3 K at x=0 to 13 K at x=1 for 25 – 50 nm films. High film quality is confirmed by low O impurity contents ~ 5 at.% or lower and room-temperature resistivities increasing with Nb content from 160 μΩ cm (41 nm TiN) to 284 μΩ cm (25 nm NbN). Accurate composition control of Nb_xTi_{1-x}N is demonstrated from x=0 to x=1, with the C content increasing from 5 at.% to 16 at.% and the N content correspondingly decreasing from 48 at.% to 36 at.%. EDX mapping confirms homogeneous mixing of Ti and Nb, and XRD measurements show all prepared films are fcc polycrystalline. Tuning of the ion energy indicates a stable composition, while the crystallinity and conductivity can be influenced. TEM imaging of the most conductive 49 nm Nb_{0.5}Ti_{0.5}N film reveals a disordered polycrystalline film in agreement with XRD measurements. A relatively high sheet kinetic inductance of 24 pH/sq is found for 38 nm film thickness. In addition to lowering resistivity, substrate biasing provides the ability to enhance film disorder, making these films attractive for applications such as microwave kinetic inductance detectors. The high throughput and tunability of the Nb_xTi_{1-x}N deposition process puts forward PEALD as a promising technique to tackle material challenges in quantum technologies.

11:00am AA3-WeM-13 Atomic Layer Deposited Metal Nitrides (TiN and InN) and Metal Semiconductor Heterojunctions for Quantum Applications, Neeraj Nepal, J. Prestigiacomo, M. Sales, P. Litwin, T. Growden, V. Wheeler, US Naval Research Laboratory

Direct integration of III-N semiconductors with superconductors are beneficial for quantum technologies such as superconducting qubits, secure quantum communications, and superconducting radio-frequency circuits [1]. To-date direct integration has been achieved using III-N/NbN grown at >600 °C [1]. Atomic layer deposition (ALD) provides a path towards integration at lower temperatures with wafer scale uniformity, conformality and subatomic thickness control. Titanium nitride (TiN) is a favorable, superconductor (T_c ~5.6 K [2]) to integrate with III-N materials. In fact, ALD TiN has been used as a Schottky gate metal in III-N devices for improved electrical and thermal performance [3]. Also, kinetic inductance is one of the highest in TiN [4] and increases with decreasing thickness. High quality InN semiconductor with high carrier concentration has been demonstrated by ALD [5]. Thus, integrating high quality, crystalline ALD deposited TiN metal with InN semiconductor could provide metal-semiconductor heterojunctions (HJ) for various quantum applications.

ALD TiN and InN films (40 nm), were deposited as single and bilayer structures on resistive Si and c-sapphire in a Veeco Fiji Gen2 ALD reactor. TDMAT and TMI precursors were used to grow TiN and InN, respectively. An Ar/N₂ plasma at 300W was used for both layers. ALD process windows were

monitored and optimized on Si substrates using *in-situ* ellipsometry and *ex-situ* characterizations. Both materials were determined to have a common ALD window at 250 °C allowing bilayers to be deposited at these temperatures with abrupt interfaces.

40 nm TiN films grown on c-sapphire and resistive Si(100) exhibited a T_c of 3.85 K and 3.45 K, respectively. This is similar to previously reported 50 nm TiN films on resistive Si with a T_c of 4.05 K [4]. XRD revealed a more crystalline TiN film on sapphire than Si, which could account for the higher T_c measured. ALD InN films exhibited a high electron carrier concentration of ~4x10²⁰ cm⁻³. Bilayer semiconductor-superconductor HJ of 40 nm TiN/40 nm InN on and 40 nm InN/40nm TiN were then deposited on sapphire at 250 °C. XRD shows that individual layers in these HJ are crystalline with both InN (0002) and Ti(111) peaks present. Detailed ALD growth and characterization results will be presented for all layers and discussed in context of use in quantum applications.

References

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11:15am AA3-WeM-14 Ceramic Thin-Film Composite Membranes with Tunable Subnanometer Pores for Molecular Sieving by Atomic Layer Deposition, X. Zhou, Yale University; R. Shevate, A. Mane, Jeffrey Elam, Argonne National Laboratory; J. Kim, M. Elimelech, Yale University

Membranes with tunable, sub-nanometer pores are needed for molecular separations in applications including water treatment, critical mineral extraction, and recycling. Ceramic membranes are a promising alternative to the polymeric membranes typically used in such applications due to their robust operation under harsh chemical conditions. However, current fabrication technologies fail to construct ceramic membranes suitable for selective molecular separations. In this presentation, we describe a ceramic thin film composite (TFC) membrane fabrication method that achieves sub-nm pore size control using atomic layer deposition (ALD) by incorporating a molecular-scale porogen. By co-dosing alkyl alcohols along with the H₂O coreactant during Al₂O₃ ALD, we incorporate alkoxide species in the film which create a continuous network of pores upon calcination. Varying the alkyl alcohol (methanol, ethanol, isopropanol) tunes the pore size. We use Fourier transform infrared absorption spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy to elucidate the surface chemistry and growth during the alcohol-modulated ALD as well as the subsequent pore formation. We evaluate the transport and separations properties of the ALD TFC membranes using a two-chamber diffusion cell with aqueous salt solutions. We measured a remarkable enhancement in the transport of Cl⁻ compared to SO₄²⁻ (8.6 times faster) matching the selectivity of state-of-the-art polymer membranes. We attribute this selectivity to the dehydration of the large divalent ions within the subnanometer pores. In addition, permeation studies using neutral adsorbates revealed average pore sizes of ~7Å, 13Å, and 19Å for ALD TFC membranes prepared using methanol, ethanol, and isopropanol, respectively. This work provides the scientific basis for the design of ceramic membranes with subnanometer pores for molecular sieving using ALD.

11:30am AA3-WeM-15 Recent Developments and Emerging Applications in Atmospheric-Pressure Atomic Layer Deposition of High-Porosity Materials, M. Chen, TU Delft, China; M. Nijboer, A. Kovalgin, A. Nijmeijer, University of Twente, The Netherlands; F. Roozeboom, University of Twente and Carbyon B.V., Netherlands; Mieke Luiten-Olieman, University of Twente, The Netherlands

Atomic layer deposition (ALD) is a widely recognized technique for depositing ultrathin conformal films with excellent thickness control at Ångström or (sub)monolayer level. Atmospheric-pressure ALD is an upcoming ALD process option with a potentially lower reactor ownership cost.

We will present a comprehensive overview of the recent applications and development of ALD applications exclusively working at atmospheric pressure [1]. Spatial ALD (sALD) has been recently introduced for the commercial surface passivation and encapsulation in the large-area production of solar cells, and for the production of 2D displays, in particular organic light-emitting diode (OLED) displays. Atmospheric-pressure temporal ALD (tALD) has found its route for new emerging applications

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such as high-porosity particle coatings, functionalization of capillary columns for gas chromatography, and membrane modification in water treatment and gas purification. The challenges and opportunities in achieving highly conformal coatings on porous substrates by atmospheric-pressure ALD will be discussed.

Typically, each application often requires its own optimized reactor design [1]. For the application of tuning and functionalizing nanopores in tubular ceramic nanofiltration membranes, we will present a new tubular reactor design [2]. In this design, the reactor wall is formed by the industrial tubular ceramic membrane itself, and carrier gas flows are employed to transport the precursor and co-reactant vapors to the reactive surface groups present on the membrane surface, see Fig. 1. The layer growth for atmospheric-pressure ALD, in this case, proceeds similarly to that for state-of-the-art vacuum-based ALD. Moreover, for membrane preparation, this new reactor design has three advantages: i) monolayers will be deposited only at the outer pore mouths rather than in the entire bulk of the porous membrane substrate, resulting in reduced flow resistances for liquid permeation; ii) an *in-line* gas permeation method was developed to monitor the layer growth in the pores during the deposition process, allowing more precise control over the finished membrane (see Fig. 2), and iii) expensive vacuum components and cleanroom environment are avoided. This opens up a new avenue for commercial ceramic membrane functionalization with nanoscale precision by using ALD at atmospheric pressure.

Literature references:

- 1) Dalton Transactions, **52**, 10254 (2023)
- 2) Separations **11**, 24 (2024)

11:45am **AA3-WeM-16 Modulation Acceptor Doping of Silicon Nanowires using a SiO₂-shell doped with ALD Metal Oxide Monolayers**, *Daniel Hiller*, Institute of Applied Physics (IAP), TU Bergakademie Freiberg, Germany; *S. Nagarajan*, Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden, Germany; *I. Ratschinski*, *S. Shams*, Institute of Applied Physics (IAP), TU Bergakademie Freiberg, Germany; *M. Venzke*, Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany; *P. Hönicke*, Helmholtz-Zentrum Berlin (HZB), Berlin & Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany; *T. Mikolajick*, Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden & Institute of Semiconductors and Microsystems, TU Dresden, Germany; *J. Trommer*, Nanoelectronic Materials Laboratory (NaMLab) gGmbH, Dresden, Germany; *D. König*, Integrated Materials Design Lab (IMDL), Australian National University (ANU), Canberra, Australia

Silicon nanowires (Si NWs) or nanosheets are the building blocks for future transistors and efficient doping processes are inevitable for conductivity. Yet, NWs suffer from severe difficulties with efficient impurity doping due to a multitude of physical and technological problems when the diameters are reduced to a few nanometers: diffusion, dielectric and quantum confinement, statistics of small numbers, etc. Junctionless NW-transistors (JNTs) in particular require high conductivities. However, high impurity dopant concentrations are accompanied by a severely decreased mobility, which in turn implicates the need for higher operation voltages and increased electrical energy dissipation into heat. Therefore, alternative doping methods are desirable to separate the dopant atoms from the doping-induced free carriers.

Here, we present a novel modulation doping approach for Si NWs. According to results from density functional theory (DFT) calculations [1,2], we use Al- or Ga-doped SiO₂ as a shell around Si NWs. The trivalent group-III impurities incorporated into the tetravalent SiO₂ network form unoccupied acceptor states with an energy level located below the Si valence band edge (cf. Fig. 1). Such induced acceptor states can capture electrons from Si, creating free holes as majority charge carriers in the process [1-5].

Experimentally, the Al- or Ga-doping of SiO₂ is realized by ALD to form (sub-)monolayers of Al₂O₃ or Ga₂O₃ on an ultra-thin tunnel-SiO₂ and a subsequently deposited capping layer of SiO₂ or HfO₂. Crucial details of the Al/Ga-deposition on a dry-thermal oxide surface during the initial ALD-cycles are obtained via synchrotron-based reference-free grazing incidence X-ray fluorescence spectrometry (GIXRF) [6].

In this presentation, we furthermore demonstrate that Si NWs with modulation-doped SiO₂ shells exhibit up to 6 orders of magnitude lower electrical resistances as compared to NWs with undoped SiO₂-shells, as shown in Fig. 2 [7,8].

References

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