ALD Applications
Room Grand Ballroom H-K - Session AA2-TuA

Emerging Materials

Moderators: Joel Molina Reyes, Instituto Nacional de Astrofísica, Óptica y Electrónica (INAOE), Tero Pilvi, Picosun Oy

4:00pm **AA2-TuA-11 Unfolding the Challenges to Prepare Epitaxial Complex Oxide Membranes by Chemical Methods***, **Mariona Coll**, P. Salles,* ICMAB-CSIC, Spain **INVITED**

Epitaxial transition metal complex oxides have raised enormous interest to be integrated in next-generation electronic devices envisaging distinct and novel properties that can deliver unprecedented performance improvement compared to traditional semiconductors. However, this step demands for ease heterointegration in mature semiconductor device technology including bendable, wearable and light-weight devices. The possibility to fabricate free-standing single crystal complex oxides has revolutionized this field stimulating new research from synthetic procedures and uncommon combination of materials to fundamental physics, foreseeing an even broader spectrum of applications.[1]

Motivated by the use of cost-effective chemical deposition approaches to prepare high quality complex oxide epitaxial films and investigate the influence of defects on its properties, here it is presented our most recent studies towards the fabrication of epitaxial complex oxide membranes using the sacrificial layer approach. First, it will be introduced a facile chemical route to prepare $Sr_3Al_2O_6$ (SAO) sacrificial layers [2] and how to overcome its instability in air. Then, it will be discussed the preparation of bendable and magnetic $CoFe_2O_4$ [3] and $La_{0.7}Sr_{0.3}MnO_3$ membranes with special focus on the influence of the sacrificial layer composition on the membrane crystallinity and physical properties. Advanced X-ray diffraction analysis (XRD), reflection high energy electron diffraction (RHEED) and scanning transmission electron microscopy combined with electron energy loss spectroscopy (STEM-EELS) are used to unfold and start solving the challenges to prepare free-standing epitaxial membranes by chemical methods. This approach here presented offers a new opportunity to work with crystalline oxide membranes, easy manipulate them and fabricate new artificial heterostructures allowing future investigations of novel physical phenomena that can bring new opportunities for high-performance oxide electronic devices.

[1]*Synthesis of freestanding single-crystal perovskite films and heterostructures by etching of sacrificial water-soluble layers*, Di Lu, Harold Y Hwang et al. **Nature Materials**, 15, 11255-1260 **(2016)**

[2] *Facile Chemical Route to Prepare Water Soluble Epitaxial $Sr_3Al_2O_6$ Sacrificial Layers for Free-Standing Oxides* Pol Salles, Ivan Caño, Roger Guzman, Wu Zhou, Mariona Coll* et al.**Advanced Materials Interfaces**, 8, 2001643 **(2021)**

[3]*Bendable Polycrystalline and Magnetic $CoFe_2O_4$ Membranes by Chemical Methods P*ol Salles, Roger Guzmán, David Zanders, Anjana Devi, Mariona Coll* et al. **ACS Applied Materials Interfaces***.* 14,10 12845-12854**(2022).**

4:30pm **AA2-TuA-13 Tailoring Lattice Match by Cation Substitution in a Functional Ternary Oxide***, M. Rogowska, L. Rykkje, **Henrik Sønsteby**,* University of Oslo, Norway

Integration of functional complex oxide thin films can push the boundaries of electronic device performance. Functionality can be enhanced by implementing materials with tailored properties, or completely new functionality may be achieved by *e.g.* making use of ferroic characteristics. Model systems have been predicted, designed, and found to be interesting, but their realization often comes to a halt due to the difficulty of preparing samples under conditions feasible for ICT industry.

One example is the integration of $SrTiO_3$ (STO) as a high-κ material in transistor architectures. The dielectric constant of defect-free STO is among the highest known, but integration of the material very often leads to structural defects that hamper its functionality. High-quality STO can be deposited by high-temperature techniques, but these are seldom compatible with device manufacturing. Furthermore, the properties of STO are sensitive to strain and the quality of epitaxy at the interface, which is often hard to control when applying a high thermal budget. A functional template layer deposited under industrially relevant conditions, that can mitigate strain effects while working as an electronic conductor, would be a significant step towards harnessing the attractive properties of STO.

One such material could be $LaNiO_3$ (LNO). LNO is structurally similar to STO while being a metallic conductor and ALD epitaxy has already been shown. Unfortunately, LNO imposes a 1.7 % strain on STO, which again hampers the dielectric properties by inducing structural defects and pinholes.

In this work, we use the unique strengths of ALD to deposit a lattice matched and conductive material that may act as a template for implementation of STO. The material is based on $LaNiO_3$, but utilizes substitution of Sc on B-site to increase the lattice size to match STO. We show that the lattice parameters can be continuously tailored from those of $LaNiO_3$ to $LaScO_3$, albeit exhibiting a critical substitution level at which the metallic properties of are lost. Luckily, at lattice matched substitution levels (a_{pc} = 3.905 Å), low resistivity is maintained. We show that direct epitaxial integration of this quarternary compounds is achievable by ALD, and that the interfacial quality towards STO is of high quality. We also pinpoint a crucial advantage of the low thermal budget of ALD: The mixed compound seems to be metastable and decomposes into binary/ternary constituents at higher temperatures.

We believe this is a large step towards integration of functional complex oxides in future ICT, while at the same time showcasing the fantastic opportunities of using ALD to deposit complex oxides.

4:45pm **AA2-TuA-14 *In situ* Atomic Layer Doping of Epitaxially Grown β-Ga_2O_3 Films via Plasma-enhanced ALD at 240 ℃***, S. Ilhom,* Univerisity of Connecticut*; A. Mohammad, N. Ibrahimli, J. Grasso, B. Willis,* University of Connecticut*; **Ali Okyay**,* Stanford University*; N. Biyikli,* University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. However, the relatively complex growth reactors and typical growth temperatures around 1000 °C lead to increased production costs and limited application space. Gallium oxide (Ga_2O_3) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environments (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for Ga_2O_3 would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Hence, we report on the low-temperature as-grown crystalline β-Ga_2O_3films on Si, glass, and sapphire via hollow-cathode plasma-enhanced atomic layer deposition (HCPA-ALD). The films were deposited using triethylgallium (TEG) and Ar/O_2 plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed in situ atomic layer doping to n-type dope β-Ga_2O_3films where tris-dimethylaminosilane (TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, eachunit ALD-cycle was followed by an *in situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both in-situ and ex-situ ellipsometry were employed to measure the thickness and optical properties of the films. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial Ga_2O_3 films with monoclinic β-phase. On the other hand, GIXRD of the samples grown on Si and glass displayed polycrystalline β-Ga_2O_3 films. HR-STEM imaging and EDX elemental analysis confirmed the epitaxial relationship of the β-Ga_2O_3films grown on sapphire substrates and displayed successful incorporation of dopant elements. Preliminary electrical conductivity measurements showed highly resistive samples. Therefore, *ex situ* thermal annealing studies are ongoing to explore possible dopant activation. Further studies from our XPS characterizations will provide additional insight about the chemical bonding states of the dopant species. A significant effort will be devoted for the comparison of Si and Sn-doping strategies and potential suggestions will be provided to overcome the challenges in achieving device quality undoped and doped β-Ga_2O_3 layers at low growth temperatures.

5:00pm **AA2-TuA-15 Plasma Enhanced Atomic Layer Deposition of Niobium Nitride for Scalable Quantum Device Fabrication**

Yi Shu, Oxford Instruments Plasma Technology, UK*; C. Lennon,* University of Glasgow, UK*; Z. Ren,* Oxford Instruments Plasma Technology, UK*; H. Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands*; F. Morini, A. Kurek, T. Hemakumara,* Oxford Instruments Plasma Technology, UK*; R. Hadfield,* University of Glasgow, UK

Superconducting niobium nitride (NbN) thin film has gained extensive attention in quantum computing and quantum communication applications[1,2] due to its high transition temperature (T_c) and high critical current. Highly uniform NbN films over whole processed wafers are essential to improve device scalability and fabrication yield. Moreover, superconducting through silicon vias (TSV) is one of the key technologies enabling 3D quantum integration where highly conformal NbN liners inside TSVs are required for interconnection between quantum and control/readout circuits[3]. Plasma enhanced atomic layer deposition (PEALD) of superconducting NbN is a promising option to meet all these requirements.

In this work, we firstly present PEALD NbN films grown at 250 ºC on 200 mm Si wafers, utilizing (t-butylimido)-tris(diethylamido) niobium (TBTDEN) and H_2/Ar plasma, carried out on an Oxford Instruments Plasma Technology FlexAL ALD tool equipped with an independent-controlled RF-biased electrode table (13.56 MHz, substrate biasing up to 100 W power, -350 V resulting DC bias voltage). By optimizing the substrate bias used in plasma steps, NbN films were produced at much faster speed (plasma exposure time in each ALD cycle was reduced from 60 s[4] to 5 s) with excellent film quality and uniformity. Characterization of T_c with a series thickness of NbN thin films (5 nm, 8 nm, 15 nm, 20 nm, and 30 nm) has demonstrated excellent film quality: T_c was as high as 10.2 K with the ultrathin 5 nm film and approached 13.5 K with the 30 nm film, as illustrated in Figure 1. Also, uniformity of the 8 nm NbN film was explored by investigating the thickness and superconducting properties spread up to a wafer size of 200 mm. Unparalleled uniformity over the whole 200 mm wafer was observed for both film thickness (±2.8%) and transition temperature T_c (±3.1%), as illustrated in Figure 2 and 3. A comparison of our parameter spread with literature data[4] is summarized in Table I.

In addition, superconducting TSV with conformal NbN coating was also explored by respectively depositing 50 nm PEALD NbN films on frontside and backside of a perforated TSV sample. Preliminary tests on such sample have revealed superconducting interconnections between the frontside and backside NbN films, provided by the NbN coated TSVs at ~10.7 K.

1. Yan et al., Supercond. Sci. Technol. 35, 065004 (2022)
2. Taylor et al., Appl. Phys. Lett. 118, 191106 (2021)
3. Yost et al., npj Quantum Inf 6, 59 (2020)
4. Knehr. et al., J. Vac. Sci. Technol. A 39, 052401 (2021)

5:15pm **AA2-TuA-16 Superconducting NbN Thin Films Deposited by Plasma Enhanced Atomic Layer Deposition**

Jakob Zessin, SENTECH Instruments GmbH, Germany*; M. Hagel, T. Reindl, L. Freund,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany*; P. Plate,* SENTECH Instruments GmbH, Germany*; J. Weis,* SF Nanostructuring Lab, Max Planck Institute for Solid State Research, Germany

Niobium nitride (NbN) is a superconductor with a critical temperature up to 16 K[1]. The application of NbN as a superconductor has already been demonstrated in superconducting nanowire single-photon detectors in the near infrared range[2] and resonators[3].

Atomic layer deposition (ALD) is an advanced technique used to deposit thin films with precisely controlled thickness in the sub-nanometer range, high conformality on complex 3D structures and the possibility of uniform deposition for large area fabrication.

With the Nanostructuring Lab of the Max-Planck-Institute for Solid State Research Stuttgart, we developed a plasma-enhanced ALD (PEALD) process of NbN. The depositions have been carried out in a SENTECH PEALD tool. Tris(diethylamido)(tert-butylimido)niobium(V) (TBTDEN) was used as a precursor and H_2 and Ar as plasma gas mixture. The influence of the most critical process parameters, such as temperature and plasma exposure time on room temperature resistance and critical temperature will be discussed. The highest achieved critical temperature was 9.6 K.

[1]Hazra et al. *Supercond. Sci. Technol.***2016**, 29, 105011.

[2]Cheng et al. *Appl. Phys. Lett.***2019**, 115, 241101.

[3]Sheagren et al. *J. Low Temp. Phys.***2020**, 199, 875.

5:30pm **AA2-TuA-17 Work-Function Modulation using Atomic Layer Deposited TaN and Ternary TaAlN Metal Gate**

Moonsuk Choi, *B. Ku, S. Kim, C. Chung, C. Choi,* Hanyang University, Republic of Korea

With the disruptive scaling in semiconductor technology, high-k/metal gate (HKMG) stacks have been introduced to overcome direct tunneling in gate leakage current and reliability issues associated the conventional poly-Si/SiO_2 stacks. To implement a wide range of threshold voltage (V_{TH}) in MOS devices, work-function modulation is required. There are several factors that govern V_{TH}, which is significantly influenced by metal gate. The selection of suitable metal electrodes to modulate their work function remains still a challenging task. Considering 3D structure in FinFET and Gate-all-around FET (GAAFET) with the narrow dimensional margin, atomic layer deposition (ALD) is the promising process to form the advanced gate electrodes due to the excellent thickness control, outstanding film quality, and applicable complex structure with high aspect ratio.

In this study, we characterized ALD TaN and TaAlN and their relevant work functions were investigated. The different metal precursors were used such as metal-organic (tertbutylimide tris-diethylamido tantalum, TBTDET) and metal-halide (tantalum(V) chloride, $TaCl_5$) precursors as Ta source and tri-methylaluminium (TMA) as Al source, respectively, with reacting ammonia (NH_3) gas and deposition temperature was 350 °C. The chemical structures of the metallic precursors as well as the specific sequence in the ALD process are illustrated in Figure 1 (a)-(b). After the deposition process, the films were treated by forming gas annealing (FGA) treatment to confirm the effects of the thermal budget. Figure 2 (a)-(b) shows the resistivity of these metal gates. Their low values are a promising feature even at the thinner thickness as well as the increased amounts of Al element. MOS devices in the structure of p-Si/HfO_2/metal gate electrodes (TaN and TaAlN)/capping metal (either W or Al) were fabricated. The capacitance-voltage (C-V) characteristics are estimated in Figure 3 (a)-(b). The increase of sub-cycle ratios and pulse time of TMA in ALD induces the positive flat band voltage (V_{FB}) shift with enhancing Al incorporation into TaN films. In figure 4 (a)-(b), the work function of both films was summarized V_{FB} as a function of parameters. The effect of Al incorporation into TaN can provides the modulation of the work function from the mid-gap to the valence band of Si. The FGA process presents another option for tuning the work function in both thin films by reducing the amounts of carbon under a hydrogen ambient. These results can contribute to a better understanding to a feasible application for HKMG stacks with improved electrical properties such as engineering of the work function as well as multiple V_{TH}.

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