Thin Films Division
Room 316 - Session TF+AP-ThM

Novel ALD CVD Precursors, Processes, Deposited Morphologies and Substrate Architectures

Moderators: Parag Banerjee, University of Central Florida, **Richard Vanfleet**, Brigham Young University

11:00am **TF+AP-ThM-10 The Electrical and Magnetic Properties of Nonstoichiometric Nickel Oxide Thin Films***, **Mari Napari,*** University of Southampton, UK **INVITED**

Nonstoichiometric nickel oxide (NiO_x), a p-type oxide semiconductor, has gained significant attention due to its versatile and tunable properties. It has become one of the critical materials in wide range of electronics applications and highly sensitive and selective sensors. In addition, the wide band gap and high work function, coupled with the low electron affinity, have made NiO_x widely used in emerging optoelectronics and p-n heterojunctions [1,2]. Also, it is a commonly applied material in heterogenous catalysis. The properties of NiO_x thin films depend strongly on the deposition method and conditions. Efficient implementation of NiO_x in next-generation devices will require controllable growth and processing methods that can tailor the physical, electronic, and magnetic properties of the material.

In this presentation I discuss our work that links together the fundamental electronic properties of NiO_x thin films with the chemical processing methods, and how these can be used in device applications. I discuss how the p-type nature of NiO_x arises and how its stoichiometry affects its electronic properties, and present results that show how the antiferromagnetic nature of the NiO prevails also in the non-stoichiometric films. I will present examples of NiO_x thin films grown by the chemical deposition techniques, including CVD, ALD, and solution processing approaches, and show how these films can successfully be used in a range of devices and applications, including perovskite solar cells and photoelectrocatalysis [3,4].

[1] Napari et al. "Antiferromagnetism and p-type conductivity of nonstoichiometric nickel oxide thin films" InfoMat 2 (2020) 769-774

[2] Napari et al. "Nickel oxide thin films grown by chemical deposition techniques: Potential and challenges in next-generation rigid and flexible device applications" InfoMat 3 (2021) 536-576

[3] Zhao et al. "In Situ Atmospheric Deposition of Ultrasmooth Nickel Oxide for Efficient Perovskite Solar Cells" ACS Appl. Mater. Interfaces 10 (2018) 41849-41854

[4] Innocent et al. "Atomic scale surface modification of TiO_2 3D nano-arrays: plasma enhanced atomic layer deposition of NiO for photocatalysis" Mater. Adv. 2 (2021) 273-279

11:40am **TF+AP-ThM-12 Al_2O_3 Thin Films with Controlled Nanoporosity Prepared by Low Temperature Thermal ALD***, **Marceline Bonvalot**, S. Hekking,* LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY POLY, Albany

Because Al_2O_3 is a cheap and abundant material with a very high hardness and inertness to numerous chemicals, porous alumina thin films find a great variety of applications as a filtering material of liquids in the food industry, oil and gas industry, pharmaceutical industry and in biotechnologies as well. In this work, we describe an original experimental route, which leads to the production of Al_2O_3 thin films with controlled nanoporosity. The deposition is carried out by thermal ALD with trimethyl aluminum (TMA) as precursor and at low temperatures (between 50°C and 80°C). The process temperature is deliberately set below the precursor temperature window, so that a significant amount of carbon-rich contaminants remain in the produced thin film, due to poor decomposition of the precursor at low thermal energy. An intermediate O_2 plasma step is then inserted within the thermal ALD cycles, which helps for the degassing of these contaminants leaving behind nanoscale porosities within the thin film under growth. The process optimisation will be presented by discussing the impact of incident plasma power and duration on carbon-rich contamination levels. The frequency of the occurence of the O_2 plasma step inserted within the thermal ALD process will also be investigated, and discussed in regards to imperfectly perfect materials strategies.

12:00pm **TF+AP-ThM-13 Thermal ALD Process of NiO Based on $Ni(^tBu\text{-}MeAMD)_2$ Precursor***, **Cristian van Helvoirt**, N. Phung, M. Creatore,* Eindhoven University of Technology, Netherlands

The applications of NiO thin films have increased over the last years, especially in the fields of electrocatalysis for water-splitting [1] and metal halide perovskite photovoltaics [2]. Previously, we reported an ALD-process for NiO based on bis-methylcyclopentadienyl-nickel as precursor and O_2-plasma as the co-reactant [3]. In this contribution, we investigate a thermal ALD process of NiO, with the motivation of expanding the ALD process capabilities on sensitive (e.g. to O_2 plasma) hybrid organic-inorganic chemistry substrates and offering opportunity for NiO process upscaling by spatial ALD, which is generally based on thermal processes.

For the present study, we selected (N,N'-di-tert-butylacetamidinato)Nickel(II) ($Ni(^tBu\text{-}MeAMD)_2$) based on the relatively low melting point (87°C) with reasonable vapor pressure, and the availability of the precursor. Although literature addresses several thermal ALD processes of NiO based on $Ni(^tBu\text{-}MeAMD)_2$ with reasonable growth rates [4,5], to our best knowledge, no saturation curves have been reported and only hot wall reactors were used so far. The decomposition temperature of the precursor (237°C), can limit the processing temperature, thereby suggesting the application of cold wall reactors. Hence, in this study, we use a cold wall reactor (FlexAL™ MK1 Oxford Instruments).

We report saturation curves using $Ni(^tBu\text{-}MeAMD)_2$ as the precursor and H_2O as the co-reactant resulting in a growth per cycle of 0.40-0.80 Å within a temperature window of 50-200°C. The process at ALD saturated condition also yields excellent uniformity (≥92% homogeneity over an 8 inch silicon wafer), with low impurity level in the film (3% C and 1% N), as observed by X-ray photoelectron spectroscopy (XPS). Rutherford backscattering spectroscopy analysis confirms a nearly stoichiometric film of O:Ni = 1.1 (deposition at 150°C). XPS also reveals the presence of oxide and (oxy)hydroxide terminal groups indicating the presence of both Ni^{2+} and Ni^{3+} oxidation states, imparting the p-type character to the film, key for selective hole transport behavior. Moreover, X-Ray diffraction data show a preferred orientation in the (111) direction for the film as opposed to (200) earlier observed in plasma-assisted ALD NiO, and beneficial for the O_2 evolution reaction in water-splitting [1].

1. Chen, *et al.* (2019) *Chem. Eur. J. 25*, 703 – 713
2. Phung, *et al.* (2022) *ACS Appl. Mater. Interfaces 14*, 1, 2166–2176
3. Koushik, *et al.* (2019) *J. Mater. Chem. C7*, 12532–12543
4. Thimsen, *et al.* (2012) *J. Phys. Chem. 116,* 16830−16840
5. Hsu, *et al.* (2015) *Nanotechnology26*(38), 385201

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