Atomic Layer Etching
Room Baekeland - Session ALE-TuM2
Atomic Layer Cleaning (ALC), ALE Integrated with ALD, and Alternative ALE Approaches

Moderators: Jessica Murdzek, University of Colorado Boulder, Fred Roozeboom, University of Twente & LionVolt B.V., Netherlands

10:45am **ALE-TuM2-1 ALE from Selective Etching to Selective Deposition***, **Christophe Vallee**,* SUNY POLY, Albany*; M. Bonvalot, M. Jaffal,* LTM-CNRS, University Grenoble Alpes, France*; C. Mannequin,* Tsukuba University, Japan*; R. Gassilloud, N. Posseme, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France **INVITED**

Atomic layer etching (ALE) is a powerful process to perform either isotropic or anisotropic etching at the atomic scale with a quasi-infinite selectivity. In this presentation, we will address an emerging technological concept based on the selective etch characteristics of ALE to selectively deposit a material on a patterned substrate on a given surface or space direction. This concept relies on a standard atomic scale deposition process (ALD) sequentially combined with ALE to advantageously lead to a selective deposition process [1-2]. We will show, by discussing examples from the literature, that combining atomic-scale deposition and etching processes offers new perspectives in materials thin film elaboration with accurate control of their physical properties, such as roughness, density and microstructure. We will also discuss various strategies for the optimization of this sequential selective deposition process to overcome its inherent weaknesses in terms of contamination and throughput, in view of its potential implementation in high volume manufacturing lines.

[1] M. Bonvalot C. Vallée, M. Jaffal, C. Mannequin, R. Gassilloud, N. Possémé and T. Chevolleau, *Dalton Trans.***51** (2022) 442-450

[2] M. F. J. Vos, S. N. Chopra, J. G. Ekerdt, S. Agarwal, W. M. M. Kessels and A. J. M. Mackus, *J. Vac. Sci. Technol. A***39 (**2021) 032412.f

11:15am **ALE-TuM2-3 Surface Modification for Atomic Layer Etching of TiAlC Using Floating Wire-Assisted Liquid Vapor Plasma at Medium Pressure***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; K. Shinoda, H. Hamamura,* Hitachi, Japan*; K. Maeda, K. Yokogawa, M. Izawa,* Hitachi High-Tech, Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Isotropic and selective etching of metal gate materials such as TiC, TiAlC, and TiN is required in the fabrication of fin-type or nanosheet field effect transistor (FET) of logic semiconductor devices. Ternary material TiAlC belongs to high-melting point, high-hardness, and high-wear resistance materials, and there are only few reports for wet etching this material by H_2O_2 mixtures with poor etching performance and device damages. No dry etching of TiAlC has been reported yet. Therefore, development of a high-performance etching method with highly selective and isotropic removal of TiAlC over TiN at an atomic layer level is strongly demanded.

In this study, an atomic layer etching of the ternary material TiAlC has been first developed by a transferring approach from wet etching to dry etching using a floating wire (FW)-assisted liquid vapor plasma of Ar gas mixed with NH_4OH-based liquid vapors. The FW-assisted non-halogen liquid vapor plasma generated at medium pressure can produce a large amount of etchant or co-reactant species to enhance the reaction rate with sample surface. This radical-rich environment (electron density of 10^{14} cm^{-3}) plays a key role in controlling isotropic etching of 3D multilayer semiconductor devices. Surface modifications, such as oxygenation, hydroxylation, hydrogenation, and nitridation of the TiAlC film were obtained by controlling the active radicals, such as O, OH, H, and NH. This leads to form volatile products having chemical bonds including methyl ($Al–CH_3$), methylamine ($Ti–(NH_n(CH_3)_{2-n})$), and alkoxy ($Ti–(OC_nH_{2n+1})$) groups. Thus, the treated TiAlC surface can be removed via the formation of modified layers. A mechanism for selective etching of TiAlC over TiN is proposed here. This FW-assisted plasma technique is expected to be available for highly selective and isotropic atomic layer etching of metal and metal compounds in semiconductor device fabrication.

11:30am **ALE-TuM2-4 Atomic Layer Processing Approach for Achieving Abrupt Epitaxial Interfaces on AlN***, **Virginia Wheeler**, D. Boris, A. Lang, G. Jernigan, N. Nepal, S. Walton,* Naval Research Laboratory

Next generation devices will require novel heterojunctions with abrupt, pristine, defect-free interfaces. Naturally occurring surface oxides on semiconductor materials represent a significant impediment to achieving such interfaces. AlN is one of several ultra-wide bandgap semiconductor of interest for future high power, high frequency devices. Since Al has a high affinity for oxygen, it is hard to completely remove oxygen from AlN surfaces by traditional wet or dry etching methods. Even if successful, AlN immediately reoxidizes during transfer to deposition chambers. This amorphous native oxide layer (typically 3-10nm thick) consists of species with high bond energies requiring temperatures in excess of 900°C to remove, which can alter the characteristics and prevent the formation of an intimate, crystalline optical or electrical interface. Thus, for promoting atomic layer epitaxy at ≤ 500°C a new approach is necessary to attain pristine AlN surfaces.

Here, we merge a low temperature fluorine-based plasma etch process [1] with a etch/passivation technique previously applied to Al mirrors [2], to simultaneously remove the AlN native oxide and passivate the surface with a stable oxi-fluorine film. The process employs a pulsed, electron beam driven plasma produced in an Ar/SF_6 background with an RF substrate bias of -40V. XPS and TEM results show this produced a 1nm $Al_xO_yF_z$ layer that was stable even after 3 days in atmospheric conditions. Temperature dependent XPS revealed that the majority of this layer was removed at 500°C in ultra-high vacuum conditions. AFM and TEM measurements also revealed that the plasma-processed surfaces were slightly smoother than as-received AlN substrates.

To demonstrate the feasibility of this approach as an ex situ process, plasma treated AlN substrates were transferred to a Veeco Fiji G2 ALD system. Samples were exposed to an in-situ anneal at 400°C in 10^{-7} Torr, after which they were cooled under vacuum to 295°C and a 20nm optimum TiN film was deposited. TEM analysis shows a defective, abrupt, interface between the polycrystalline TiN and AlN substrate. EELS was used to show that the majority of the interface has a N-K edge that shifts from AlN to TiN in only 1-2 pixels without any evidence of residual fluorine or oxygen. Occasionally, pyramidal defects containing fluorine and oxygen were observed and resulted in localized crystallinity loss within the TiN film. This demonstrates the importance of clean, abrupt interfaces for promoting epitaxial films by ALD.

[1] S.G. Walton, et al. *J.Vac. Sci. Technol. A***39**, 033002 (2021)

[2] L.V. Rodriguez de Marcos, et al. *Opt. Mat. Expr.***11(3)**, 740-756 (2021).

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