Tutorial
Room ETEC Atrium - Session TUT1

Tutorial Session I

Moderators: Kandabara Tapily, TEL TTCA, Albany, **Christophe Vallée**, University of Albany

1:00pm **TUT1-1 Direct Self-Assembly (DSA):From Materials to Integration***, **Patricia Pimenta Barros**,* CEA-LETI, France **INVITED**

The Directed Self-Assembly (DSA) of block-copolymers (BCPs) has been intensively investigated as a cost-effective and complementary solution to conventional i193nm or EUV lithography for CMOS applications [1-3]. This technology has also showed an interest in beyond CMOS applications such as Single Electron Transistor devices [4], in the fabrication of nano-structures for optoelectronic [5] and photovoltaic devices [6], or in various other technology [7], due to its ability to precisely control nanopatterns over large macroscopic length scale.

This tutorial aims to give an overview of the selective processes required in DSA patterning technique. Indeed, the DSA patterning relies on the precise control of the surface modifications in order to orientate and localize the nanopatterns on the wafer surface. For that purpose, chemoepitaxy and graphoepitaxy approaches, which are the two main ways to perform DSA, will be explained and compared. Based on LETI's PS-b-PMMA BCP background, surface modifications solutions such as UV exposure, embedded neutral layers, sequential grafting will be then detailed [8-9]. After the self-assembly process, the nanopatterns created by the BCP is usually transferred into the underlayers. For that purpose, one block (ex: PMMA) has to be selectivity removed over the other one (ex: PS) to create the final nanostructures. Different strategies for a selective etching of PMMA over PS will be exposed depending on the BCP morphology and applications (lines, contact or pillars). For example, cyclic PMMA dry etching steps [10], selective ALD [11] or Sequential Infiltration Synthesis (SIS) [12] methods will be discussed. The basics of the DSA patterning will be addressed through a few DSA application examples.

1. Tiron, R. et al, Proc. SPIE 8680, (2013)
2. Jeong, S-J. et al, Materials today 16 (12), (2013)
3. Lee, K. et al. MRS Commun. 15, 1269–1288 (2025)
4. Gharbi, A. et al, Proc. SPIE 10586, (2018)
5. Feougier, R. et al, Proc. SPIE PC12497, (2023)
6. Garozz C. et al, Phys. Status Solidi A 210, No. 8, (2013)
7. Segalman R. A., Materials Science and Engineering, Vol. 48, Issue 6, (2005)
8. Paquet, A. et al, Proc. SPIE 10958, (2019)
9. Pimenta-Barros, P. et al, Proc. SPIE 10584, (2018)
10. Sarrazin, A. et al, J. Vac Sci. Technol B36, 041803 (2018)
11. Gay, G. et al., Nanotechnology, 21, 435301 (2010)
12. Frascaroli, J. et al., ACS applied materials & interfaces 8 (49), (2016)

2:00pm **TUT1-5 Selectivity in Plasma Processes***, **Eric Liu**,* TEL TTCA **INVITED**

3:30pm **TUT1-11 Selective Epitaxy Growth of Group IV Materials for CMOS Devices***, **Joël Kanyandwkwe**, Justine Lespiaux, Jean-Michel Hartmann,* CEA/LETI-University Grenoble Alpes, France **INVITED**

In advanced logic devices, specific regions of transistors must be highly crystalline, with precise dopant concentration, particularly for junctions and contacts formation. The most effective method to fabricate these high-quality, highly doped regions is epitaxial growth in industrial RP-CVD (Reduced Pressure Chemical Vapor Deposition) reactors.

A critical requirement of this process is localization: epitaxial growth must be precisely confined to areas where crystalline seed layers are exposed, while dielectric regions have to remain free of deposits. Selective Epitaxy Growth (SEG) is a critical technological enabler in advanced Field Effect Transistors.

To achieve high quality selective epitaxy, several approaches have been explored. Historically, straightforward selective epitaxial growth was used to thicken, at relatively high temperatures (e.g. in the 600°C – 750°C range), sources and drains regions with heavily in-situ doped materials such as Si:P or SiGe:B. This was typically done using co-flow processes during which mainstream deposition and etchant gases (such as SiH_2Cl_2, GeH_4, B_2H_6, PH_3 and HCl) were simultaneously fed into the growth chamber. Co-flow processes were up to now well-suited for CMOS mass production as illustrated in *Figures 1-3*.

Several challenges must nowadays be overcome for advanced technological nodes. First, top transistors have to be fabricated with a drastically reduced thermal budget (e.g. lower than 500°C, ideally close to 400°C) above already existing transistors in monolithic 3D [1] and Complementary FET architectures (CFET) [2]). Second, the demand for aggressive device performance requires ultra-low electrical resistance materials (for sources/drains and contacts). This comes with stringent requirements in terms of morphology, the presence of new materials and aggressive doping levels, all being challenging in terms of growth selectivity control.

However, low-temperature SEG processes present major technical challenges, fueling intense research and innovation in the CVD epitaxy community [3][4][5]].

In this presentation, we will describe some specific features and challenges of advanced SEG processes. We will notably present the innovative solutions implemented to have low temperature SEG, such as the use of new gaseous or liquid precursors, cyclic processes with the alternance of non-selective growth steps and selective etch steps for different process and so on.

[1] D. Bosch *at al., 2025, IEDM.*

[2] S. Liao *et al., 2023, IEDM*, pp. 1-4.

[3] E. Rosseel *et al.,* 2024, *Meet. Abstr.* MA2024-02 2298.

[4] R. Khazaka *et al*.,2022, *Meet. Abstr.* MA2022-02 1187.

[5] J. Kanyandekwe *et al,* 2022, *ECS Trans.* 109, 121.

4:30pm **TUT1-15 Selective Thermal Atomic Layer Etching or Spontaneous Etching***, **Marcel Junige**, Steven M. George,* University of Colorado Boulder **INVITED**

Microelectronic devices have advanced from historic planar to complex 3D architectures.Corresponding nanomanufacturing needs selective atomic layer deposition (ALD) and etching (ALE).Vertical pattern transfer relies on unidirectional, anisotropic plasma ALE.Conversely, lateral pattern release without line of sight requires the omnidirectional, isotropic material removal that is provided by thermal ALE or spontaneous etching.

This tutorial will overview selectivity studies, describe materials that have been etched selectively by thermal chemistries, and provide explanations of this selectivity.Strategies to achieve selective thermal dry etching are based on different combinations of thin film materials and reactants, thermodynamic favorability of reactions, stability or volatility of reaction products, as well as reactant pressures and process temperature.

Selectivity has been observed during thermal ALE.Al_2O_3 thermal ALE is a model system defined by sequential fluorination using hydrogen fluoride (HF) and ligand exchange using $Al(CH_3)_3$.This Al_2O_3 etch mechanism exhibited high selectivity versus ZrO_2 non-etch because ZrF_4 did not ligand exchange with $Al(CH_3)_3$.Consequently, ZrF_4 provided an excellent etch stop after Al_2O_3 thermal ALE using HF and $Al(CH_3)_3$.

In contrast, ZrO_2 or HfO_2 thermal ALE using sequential HF and $SiCl_4$ exposures was selective versus Al_2O_3 non-etch. After fluorination, ZrF_4 or HfF_4 can ligand exchange with $SiCl_4$, whereas the reaction of AlF_3 with $SiCl_4$ is thermodynamically unfavorable at 250°C.

Selective TiN thermal ALE has been demonstrated via sequential oxidation using O_3, followed by halogenation to a volatile halide using HF.TiF_4 readily sublimed at 250°C.In contrast, AlF_3, ZrF_4, and HfF_4 are thermally stable even above 300°C.This resulted in Al_2O_3, ZrO_2, and HfO_2 non-etch using O_3 and HF.

Selectivity has also been observed during spontaneous etching.Selective Si spontaneous etching has been demonstrated using consecutive HF exposures that released volatile SiF_4 and H_2 products above 150°C.In contrast, HfF_4 is a thermally stable solid, resulting in HfO_2 non-etch using HF at 275°C.

Selective SiN_x versus SiO_2 spontaneous etching has also been discovered and depends on the presence of polar co-adsorbates during consecutive HF exposures.Anhydrous HF alone formed F^- surface species that selectively etched SiN_x.In contrast, co-dosing NH_3 with HF formed HF_2^- surface species that selectively etched SiO_2.

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