

# Christophe Vallée

Nanoscale Science & Engineering

## CONTACT

NanoFab East 4327  
[valleec@sunypoly.edu](mailto:valleec@sunypoly.edu)

## EDUCATION

Habilitation à Diriger des Recherches (HDR) – Grenoble Alpes University, France, 2007

Ph.D., Physics of Materials – Specialization plasma-thin film, Nantes University, France, 1999

## ABOUT

### Past Professional Experience

- Professor, Laboratory of Microelectronics Laboratory of Microelectronics Technologies (LTM) - Polytech' Grenoble, Grenoble Alpes University, France, 2010-2020
- Visiting Professor, Graduate school of pure and applied sciences, Tsukuba University, Japan, 2016-2020
- Assistant Professor, Laboratory of Microelectronics Laboratory of Microelectronics Technologies (LTM), Grenoble Alpes University, France, 2001-2010
- Assistant Professor, Laboratory of Electrostatic and Dielectric Materials (LEMD), Grenoble Alpes University, France, 1999-2001

### Areas of Research

- Plasma Processing (RIE, PECVD, PVD)
- Atomic Scale processing (ALD, ALE, ASD)
- High k materials for MIM devices (Capacitors, Resistive memories)
- Semiconductor and nanotechnologies

## Research Description

Plasma and Atomic scale processes are mandatory steps for the fabrication of semiconductor devices (CMOS, DRAM...). Those processes are becoming increasingly complex (pulsing plasma, pulsing precursor...), with many parameters to play with, making them more difficult to understand and optimize. Our research focuses on the development and optimization of Plasma Etching (RIE), Plasma Deposition (PECVD), and Atomic Scale Process (Atomic Layer Deposition – ALD, Atomic Layer Etching – ALE, Area Selective Deposition – ASD) for targeting materials or devices. This activity is carried out on 300 mm industrial tools in CNSE cleanroom, thanks to collaborations with local manufacturers such as TEL, as well as on smaller laboratory equipment. Using in situ and ex situ diagnostics we try to understand plasma/surface or precursor/surface reactions and build innovative strategies for the next generation of plasma/atomic scale processes.

Example of current topics of research: Plasma etching of metal nitride materials, Low temperature plasma etching of low k materials, Impact of by-products in HAR plasma etching, Characterization of Small Molecule Inhibitors for Area Selective Deposition, Area Selective deposition on EUV resists.

## Main management and committees / services

Program Committee of the Thin Film Division (TFD) the AVS conference (2010 - present), member of executive committee since 2019, TFD program chair for the AVS202 conference in 2022 and chair elect of the TFD (2022-2023)

Program Committee of the Int. Conference on Atomic Layer Deposition (2014 - present)

Program Committee of the French Workshop on ALD (RAFALD) (2015 - present)

Head of the joint laboratory between STMicroelectronics and LTM (2014 - 2018)

Head of the material Department of Polytech Grenoble - engineer school - (2010-2015)

## Recent Publications (since 2016)

I. V. Otto IV, C. Vallée, S. Kal, and P. Biolsi, Investigation into the Effect of a PECVD-Deposited SiO<sub>x</sub> Chamber Coating on the Selective, Radical-Based NF<sub>3</sub> Etching of TaN with Respect to BEOL Low-K, J. Vac. Sci. Technol. B 41, 032202 (2023)

C. Badie, H. Tissot, B. Sciacca, M. K. Barr, J. Bachmann, C. Vallée, G. Gautier, T. Defforge, V. Astie, J-M. Decams, M. Bechelany and L. Santinacci, Conductive TiN thin films grown by Plasma-Enhanced Atomic Layer Deposition: Effects of N-sources and thermal treatments, *J. Vac. Sci. Technol. A* 41, (2023) 032401

D. Muñoz-Rojas, M. Weber, C. Valleé, C. Crivello, A. Sekkat, F. Toldra-Reig, and M. Bechelany, Nanometric 3D printing of functional materials by Atomic Layer Deposition, *Advanced Additive Manufacturing*, edited by Igor Shishkovsky, IntechOpen, 2022. 10.5772/intechopen.101859.

M. Bonvalot, C. Vallée, Cédric Mannequin, Moustapha Jaffal, Rémy Gassilloud, Nicolas Possémé and Thierry Chevolleau, Area Selective Deposition using alternate deposition and etch super-cycle strategies, *Dalton Trans.* 51 (2022) 442-450

L. Goffart, B. Pelissier, G. Lefèvre, Y. Le-Friec, C. Vallée, G. Navarro and J-P. Reynard, Surface Oxidation phenomena in Ge rich GeSbTe alloys and N doping influence for Phase Change Memory applications, *Applied Surface Science* 573 (2022) 151514

D.H. Han, S. Lee, J.H. Hwang, Y. Kim, M. Bonvalot, C. Vallée, P. Gonon and W. Jeon - An Empirical Investigation on the Effect of Oxygen Vacancy in ZrO<sub>2</sub> Thin Film on the Frequency-Dependent Capacitance Degradation in the Metal–Insulator–Metal Capacitor - *IEEE Transactions on Electron Devices* 68 (2021) 5753

T. Vogel, N. Kaiser, S. Petzold, E. Piros, N. Guillaume, G. Lefèvre, C. Charpin-Nicolle, S. David, C. Vallée, E. Nowak, C. Trautmann, and L. Alff - Defect-induced phase transition in hafnium oxide thin films: comparing heavy ion irradiation and oxygen engineering effects - *IEEE Transactions on nuclear science* 68, (2021) 1542

T. Yeghoyan, V. Pesce, M. Jaffal, G. Lefevre, R. Gassilloud, N. Posseme, M. Bonvalot, and C. Vallée - Low Temperature Topographically Selective Deposition by Plasma Enhanced Atomic Layer Deposition with Ion Bombardment Assistance - *J. Vac. Sci. Technol. A* 39 (2021) 032416

M. Jaffal, T. Yeghoyan, G. Lefèvre, R. Gassilloud, N. Possémé, C. Vallée, and M. Bonvalot - Topographical selective deposition: A comparison between

plasma-enhanced atomic layer deposition/sputtering and plasma-enhanced atomic layer deposition/quasi-atomic layer etching approaches - Journal of Vacuum Science & Technology A 39 (2021) 030402

S. Belahcen, C. Vallée, A. Bsiesy, A. Chaker, M. Jaffal, T. Yegohan, and M. Bonvalot - Control of ion energy during Plasma Enhanced Atomic Layer Deposition: a new strategy for the modulation of TiN growth delay on SiO<sub>2</sub> - Journal of Vacuum Science & Technology A 39 (2021) 012410

A. L. Serra Serra, G. Lefevre, G. Bourgeois, C. Sabbione, N. Castellani, O. Cueto, MC. Cyrille, M. Bernard, J. Garrione, N. Bernier, C. Vallée, S. David, C. Charpin-Nicolle, G. Navarro, and E. Nowak - Innovative Low-Power Self-Nanoconfined Phase-Change Memory - IEEE Transactions on Electron Devices 68 (2020) 535-540

O. Khaldi, F. Jomni, P. Gonon, and C. Vallée - AC and DC bias effect on capacitance–voltage nonlinearities in Au/HfO<sub>2</sub>/M (M = Pt, TiN, W, and AlCu) MIM capacitors: effect of the bottom electrode material - J Mater Sci: Mater Electron 31 (2020) 19036-19043

M. Saadi, P. Gonon, C. Vallée, F. Jomni, E. Jalaguier, and A. Bsiesy - Ag/HfO<sub>2</sub>-based conductive bridge memories elaborated by atomic layer deposition: impact of inert electrode and HfO<sub>2</sub> crystallinity on resistive switching mechanisms - J. Mater Sci: Mater Electron 31 (2020) 13487-13495

V. Huong Nguyen, A. Sekkat, C. Arturo Masse de la Huerta, F. Zoubian, C. Crivello, J. Rubio-Zuazo, M. Jaffal, M. Bonvalot, C. Vallee, O. Aubry, H. Rabat, D. Hong, and D. Muñoz-Rojas – Atmospheric Plasma-Enhanced spatial chemical vapor deposition of SiO<sub>2</sub> using trivinylmethoxysilane and oxygen plasma - Chemistry of Materials 32 (2020) 5153-5161

C. Vallée, M. Bonvalot, S. Belahcen, T. Yeghoyan, M. Jaffal, R. Vallat, A. Chaker, G. Lefèvre, S. David, A. Bsiesy, N. Possémé, R. Gassilloud, and A. Granier - Plasma Deposition – Impact of ions in PECVD, PEALD and applications to Area Selective Deposition - Journal of Vacuum Science & Technology A 38 (2020) 033007

C. Mannequin, C. Vallée, K. Akimoto, T. Chevolleau, C. Durand, C. Dussarat, T. Teramoto, E. Gheeraert, and H. Mariette - Comparative study of two Atomic Layer Etching processes for GaN – J. Vac. Sci. Technol. A 38 (2020) 032602

A. Chaker, C. Vallee, V. Pesce, S. Belahcen, R. Vallat, R. Gassilloud, N. Posseme, M. Bonvalot and A. Bsiesy - Topographically selective deposition – Applied Physics Letters 114 (2019) 043101

R. Vallat, R. Gassilloud, O. Salicio, K.E. Hajjam, G. Molas, B. Pelissier and C. Vallée - Area Selective Deposition of TiO<sub>2</sub> by intercalation of plasma etching cycles in PEALD process: a bottom up approach for the simplification of 3D integration scheme – Journal of Vacuum Science & Technology A 37 (2019) 020918

G. Sassine, C. Nail, P. Blaise, B. Sklenard, M. bernard, R. Gassilloud, A. Marty, M. Veillerot, C. Vallée, E. Nowak, and G. Molas – Hybrid-RRAM toward next generation of nonvolatile memory: coupling oxygen vacancies and metal ions – Adv. Electron. Mater. (2019) 1800658

W. Jeon, O. Salicio, A. Chaker, P. Gonon, and C. Vallée - Controlling the Current Conduction Asymmetry of HfO<sub>2</sub> Metal–Insulator–Metal Diodes by Interposing Al<sub>2</sub>O<sub>3</sub> Layer - IEEE Transactions on Electron Devices 66 (2018) 402-406

L. Tian, S. Ponton, M. Benz, A. Crisci, R. Reboud, G. Giusti, F. Volpi, L. Rapenne, C. Vallée, M. Pons, A. Mantoux, C. Jimenez, and E. Blanquet - Aluminum nitride thin films deposited by hydrogen plasma enhanced and thermal atomic layer deposition – Surface and Coatings Technology 347 (2018) 181-190

W. Jeon, Y. Kim, C. Hyun An, C.S. Hwang, P. Gonon and C. Vallée – Demonstrating the ultrathin metal-insulator-metal diode using TiN/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> stack by employing RuO<sub>2</sub> top electrode – IEEE transactions on Electron Devices 65 (2018) 660-666

P. Noé, C. Vallée, F. Hippert, JY Raty, F. Fillot - Phase Change Materials for Non-Volatile Memory devices: From Technological Challenges to Materials Science Issues – Semicond. Sci. Technol. 33 (2018) 013002

E. Oudot, M. Gros-jean, K. Courouble, F. Bertin, R. Duru, N. Rochat, and C. Vallée - Hydrogen passivation of silicium/silicium oxide interface by atomic layer deposited Hafnium Oxide and impact of silicon oxide underlayer – J. Vac. Sci. technol. A 36 (2018) 01A116

C. Nail, G. Molas, P. Blaise, B. Sklenard, R. Berthier, M. Bernard, L. Perniola, G. Ghibaudo, and C. Vallée - A link between CBRAM performances and material microscopic properties based on electrical characterization and atomistic simulations - IEEE Transactions on Electron Devices 64 (2017) 4479-4485

C. Nail, P. Blaise, G. Molas, M. Bernard, A. Roule, A. Toffoli, L. Perniola, and C. Vallée - Atomistic mechanisms of copper filament formation and composition in Al<sub>2</sub>O<sub>3</sub>-Based Conductive Bridge Random Access Memory – Journal of Applied Physics 122 (2017) 024503

A Chaker, P Gonon, C Vallée, A Bsiesy - High capacitance density of 185 nF/mm<sup>2</sup> achieved in three-dimensional MIM structures using TiO<sub>2</sub> as a dielectric - Applied Physics Letters 110 (2017) 243501

PD Szkutnik, M Aoukar, V Todorova, L Angélidès, B Pelissier, D Jourde, P Michallon, C Vallée, P Noé - Impact of In doping on GeTe phase-change materials thin films obtained by means of an innovative plasma enhanced metalorganic chemical vapor deposition process - Journal of Applied Physics 121 (2017) 105301

R. Vallat, R. Gassilloud, B. Eychenne and C. Vallée – Selective deposition of Ta<sub>2</sub>O<sub>5</sub> by adding plasma etching super-cycles in plasma enhanced ALD steps - J. Vac. Sci. technol. A 35 (2017) 01B104

A. Chaker, C. Bermond, P. Artillan, P. Gonon, C. Vallée, A. Bsiesy - Wide Band Frequency Characterization of Al-Doped and Undoped Rutile TiO<sub>2</sub> Thin Films for MIM Capacitors IEEE Electron Device Letters 38 (3) (2017) 375-378

F. Piallat, R. Gassilloud, P. Caubet, and C. Vallée - Evolution of TiN oxidation depending on the film's temperature at vacuum break – J. Vac. Sci. Technol. A 34 (2016) 051508

A. Chaker, P. Szkutnik, J. Pointet, P. Gonon, C. Vallée, and A. Bsiesy - Understanding the mechanisms of interfacial reactions during TiO<sub>2</sub> layer growth on RuO<sub>2</sub> by ALD with O<sub>2</sub> plasma or H<sub>2</sub>O as oxygen source - Journal of Applied Physics 120 (2016) 085315

M. Kassmi, J. Pointet, P. Gonon, A. Bsiesy, C. Vallée, and F. Jomni - Low-frequency dielectric properties of intrinsic and Al-doped rutile TiO<sub>2</sub> thin films

grown by the atomic layer deposition technique – Journal of Applied Physics 119 (2016) 244101

C. Mannequin, A. Delamoreanu, L. Latu-Romain, V. Jousseau, H. Grampeix, S. David, C. Rabot, A. Zenasni, C. Vallée, and P. Gonon - Graphene HfO<sub>2</sub>-based resistive RAM memories – Micro. Eng. 161 (2016) 82-86

A. Rouahi, F. Challali, I. Dakhlaoui, C. Vallée, S. Salimy, F. Jomni, B. Yangu, M.P. Besland, A. Goulet and A. Sylvestre – Structural and dielectric characterization of sputtered tantalum titanium oxide thin films for high temperature capacitor applications – Thin Solid Films 606 (2016) 127-132

T. Wakrim, C. Vallée, P. Gonon, C. Mannequin, and A. Sylvestre – From MEMRISTOR to MEMImpedance device – Applied Physics Letters 108 (2016) 053502

M. Saadi, P. Gonon, C. Vallée, C. Mannequin, H. Grampeix, E. Jalaguier, F. Jomni, and A. Bsiesy – On the mechanisms of cation injection in conducting bridge memories: the case of HfO<sub>2</sub> in contact with noble metal anodes (Au, Cu, Ag) – Journal of Applied Physics 119 (2016) 114501

### Invited presentations in International Conferences

49<sup>th</sup> International Conference on Metallurgical Coatings and Thin Films (ICMCTF), San Diego (USA), 2023: “An Imperfect high k dielectric (O vacancies, contamination) can give a perfect MIM device”

MS&T22 Pittsburgh (USA), 2022: “Ions in PEALD processes: from material modification to selective deposition”

AVS 68th International Symposium, Pittsburgh (USA), 2022: “Imperfectly perfect materials and/or processes as a route for ASD”

SPIE 2021 (virtual conference due to COVID) (USA): “Selective patterning using deposition and etch: case of area selective deposition”

73rd GEC (Gaseous Electronics Conference) (virtual conference due to COVID) (USA), 2020: “Plasma ALD strategies for area selective deposition”

ECS Fall Meeting, Atlanta (USA), 2019: “PEALD and ALE for Area Selective Deposition”

International workshop on nanoparticles and nanostructures synthesized by plasmas for energy applications, Sapporo (Japan), 2019: “Cold plasma for Atomic Layer Processing: from ALD and ALE to Area Selective Deposition”

EMRS Fall meeting – SYMPOSIUM N: New ALD approaches towards functional materials and devices - Warsaw University of Technology (Poland) 2018: “Using plasma etching (RIE-ALE) and ions in Plasma ALD tool for Area Selective Deposition”

3rd area selective deposition workshop (ASD), Raleigh (USA), 2018: “ASD process using ALD, etching (plasma or ALE) and surface passivation”

17th International Conference on Atomic layer Deposition (ALD2017), Denver (USA), 2017: “Selective deposition process combining PEALD and ALE”

AVS 63rd International Symposium, Nashville (USA), 2016: “Plasma Enhanced CVD processes: Dual Frequency with pulsing of liquid precursors and PEALD for Selective Deposition”

20th International Colloquium on Plasma Processes (CIP2015) – Saint-Etienne (France), 2015: “Plasma deposition processes (PECVD and PEALD) for next generation of microelectronic devices”

Tutorial workshop of the 14th International Conference on Atomic layer Deposition (ALD 2014) Kyoto (Japan), 2014: “ALD in semiconductor applications”

IEEE Bipolar/BiCMOS Circuits and Technology Meeting (BCTM2013) – BORDEAUX (France), 2013: “Resistive switching in metal-oxide-metal devices: fundamental understanding in relation to material characterization”

MAM2012 conference, Grenoble (France), 2012: “Materials and processes for non-volatile resistive memories”

10th international conference on Atomic Layer Deposition (ALD2010) – Seoul (Korea), 2010: “Atomic Layer Deposition of high k materials for MIM devices: MIM capacitors and non-volatile memories (RRAM)”