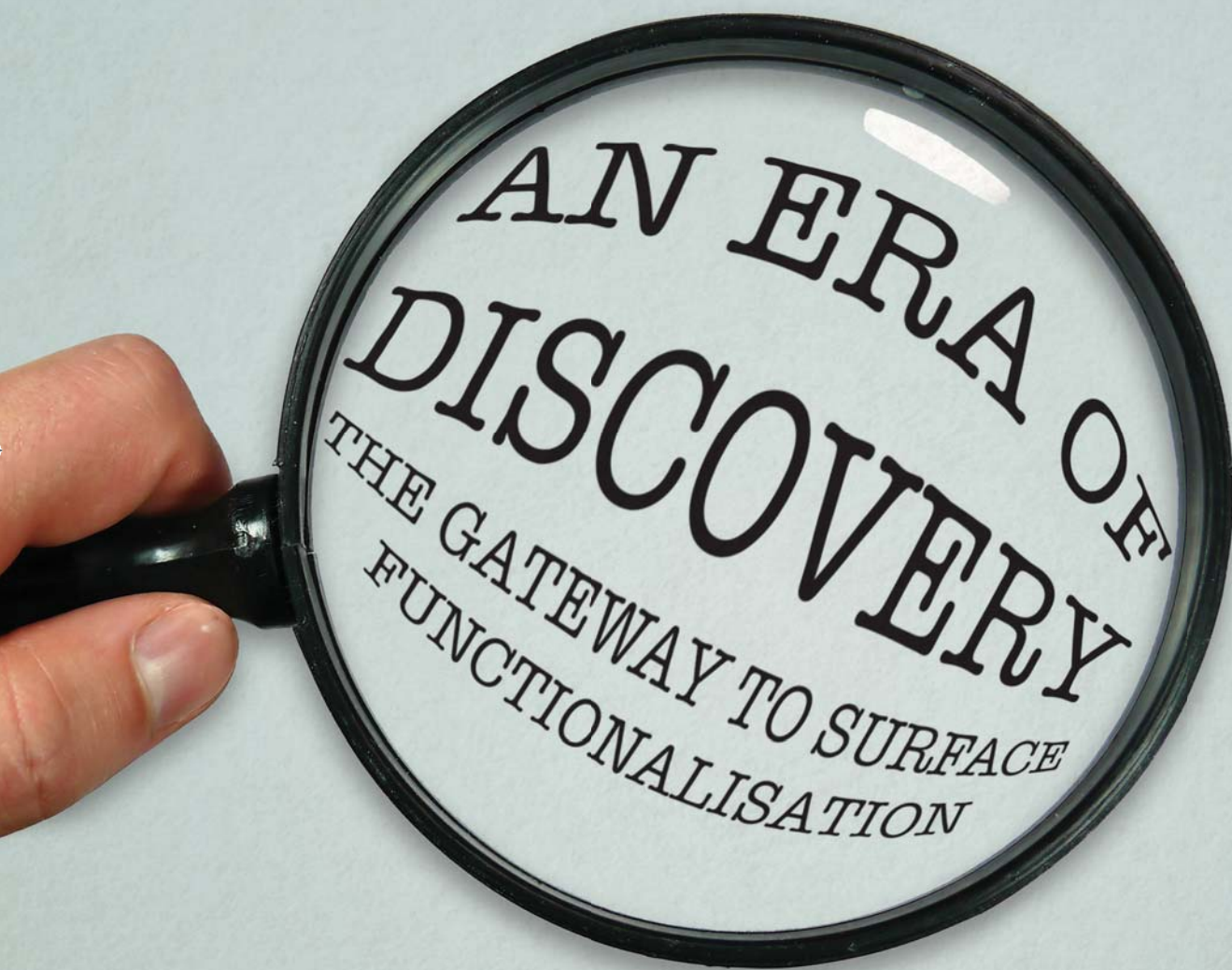


# International Innovation

Disseminating science, research and technology



DR MATHEW HALLS

DR CAROLE ROSSI

PROFESSOR YVES CHABAL

DR ALAIN ESTÈVE



# Beneath the surface

By studying the surface properties of semiconductors at the atomic scale, **Professor Yves Chabal** and his collaborators seek to develop functional nanoelectronic devices for industry



**As an introduction, could you provide a background to your current interests? What has guided your career path?**

Since my undergraduate studies, I have been fascinated by both the simplicity and

complexity of surfaces, and the formation and atomic control of interfaces upon thin film deposition. Their study depends upon precise characterisation, preferably during growth, which is difficult. Aware of this challenge, I have devoted much of my career to developing or implementing *in situ* techniques to characterise surfaces and interfaces, in order to unravel the mechanisms involved in surface chemical modification.

In the late 1990s, my interest evolved from studying surfaces in ultra-high vacuum environments to examining wet-chemical cleaning and modification of semiconductor surfaces because of their importance for industrial processes. Currently, our work spans all types of surfaces and processing conditions, making use of techniques such as infrared

spectroscopy, X-ray photoelectron spectroscopy, ion scattering and atomic force microscopy, to fully characterise complex surfaces and interfaces. These systems are the basis for micro- and nanoelectronics, energy harvesting and biosensing devices and for advanced displays and smart windows.

**What are the highlights of your research to date?**

The most interesting findings so far have been associated with hydrogen-terminated silicon surfaces. Over the past 20 years, it has been shown that oxide-free silicon surfaces, initially obtained under ultra-high vacuum conditions, could also be generated by wet chemical treatments and maintained in a stable state in air. The discovery in 1990 that atomically flat, hydrogen-terminated Si(111) surfaces could be prepared opened the door for investigations of fundamental surface properties as well as the chemical functionalisation of these model surfaces.

In 2010 we discovered that immersion of hydrogen-terminated Si(111) surfaces in methanol resulted in a nanopattern of methoxy that could be transformed into F or OH groups, providing an ordered template for further reactions on an otherwise atomically flat, oxide-free silicon surface.

We are currently in the process of developing a comprehensive mechanism for nanopattern formation in solution, which could be transformative for the field. Such a task is both highly challenging and stimulating, and will require close collaboration with our theoretical and experimental colleagues.

**Does collaboration complement the research programme of your group? How does it facilitate more meaningful results?**

In our research, collaboration is critical at all levels, particularly with theorists. Since little is known about vibrations of surfaces at the submonolayer level, there is scarce reference work in the literature to unambiguously assign the measured vibrational bands. Fortunately, the current level of first principles modelling

is good enough to test model structures and their associated vibrational signatures. We therefore rely heavily on our theoretical colleagues, in particular Dr Mathew Halls, Director of Materials Science at Schrödinger Inc. and Dr Alain Estève from the National Centre for Scientific Research, France, who can not only provide assignments but also chemical pathways for the formation of the proposed surface and interface structures. The theoretical input is absolutely essential to deriving mechanistic information.

In addition, imaging techniques such as scanning tunnelling microscopy (STM) are important to our work because we often study atomically flat or precisely patterned surfaces. In this respect, the STM research of Professor Melissa A Hines at Cornell University, USA, nicely complements our research.

**Have you encountered any substantial challenges in your work?**

The main challenge in surface science is to determine the role of impurities and the degree of perfection of surfaces. This is even more significant when using wet-chemical processes performed in ambient conditions with impure chemicals. However, the importance of understanding these complexities for industry is such that it is critical to rise to the challenge by bringing together a host of characterisation techniques, theoretical modelling and deep chemical insight, developed over the past century, by many colleagues.

**In the past few years, what have been the advancements in your field? What might the future hold?**

The most significant discovery is the work of Hines at Cornell who demonstrated, in 2011, that quasi-atomically flat Si(100) surfaces could be obtained by ammonium fluoride etching, following a procedure very similar to the one conducted on Si(111) surfaces. Since the (100) plane of silicon is the only one used in microelectronics, this work is groundbreaking with significant impact for industry. Importantly, it not only proves that surfaces can be made flat within a double atomic plane, but provides exquisite detail relating to their structure and individual surface silicon atom reactivity. These findings open the door for the development of practical devices for a variety of applications.

# The gateway to surface functionalisation

Work led by researchers at the **University of Texas at Dallas**, is taking an interdisciplinary and collaborative approach to understanding the surface properties and functionalisation chemistries of silicon surfaces

**SILICON IS A VERY** common chemical element that was mainly used commercially, until the advent of electronic technology, as a constituent of building materials such as clay, sand and stone. Now, because silicon is at the heart of almost every modern electronic device, research into its physical and chemical properties is of significant importance. Despite being a nonmetal, pure silicon can be designed to conduct electricity by 'doping' it with small quantities of impurities to modify the non-conducting lattice, allowing electrons to flow. Because its conductivity is not as high as that of metals, a silicon lattice is known as a semiconductor. The use of semiconductors in electronic circuits, as the basis of all components, enables the intricate control of nanoscale circuits.

Supported by the Divisions of Chemistry and Materials Research of the National Science Foundation, researchers in the Department of Materials Science and Engineering at the University of Texas at Dallas, USA, led by Professor Yves Chabal, along with collaborators Dr Mathew Halls, Director of Materials Science at Schrödinger Inc. and Dr Alain Estève from the National Centre for Scientific Research, France, are investigating further uses of semiconducting materials by developing a fundamental understanding of their surface properties.

## **SURFACE STABILISATION AND FUNCTIONALISATION**

To realise the full potential of these surfaces and carry out chemical processing, they first need to be cleaned to remove foreign atoms such as oxides that reduce reactivity, and then immediately stabilised or temporarily passivated to prevent foreign atoms from re-adsorbing. The surface can finally be functionalised to enable a specific application to be carried out.

The challenge of surface stabilisation is something that Chabal has been working on over the last 30 years. He has made significant progress towards investigating factors that determine the details of the atomic-scale interactions. Previously it was thought that the stronger the bond between the silicon and the outermost surface atom, the more stable the surface would be. But his group showed, by studying fluorine-terminated silicon surfaces, that this is not the case. While the fluorine-silicon covalent bond is the strongest known, the surface has poor stability because the strong polarity of the fluorine atom increases the reactivity of the underlying silicon atoms. Consequently, when silicon surfaces are etched with hydrofluoric acid to remove a thin layer of silicon oxide, they become terminated with hydrogen instead of fluorine, with

all outer electrons fully coordinated. Because the hydrogen-silicon bond is less-polar, the surfaces remain stable even in ambient conditions, producing a passive homogeneous surface. The simplicity of hydrogen-terminated silicon surface synthesis and the chemical stability and electrical properties of the resulting surfaces make them invaluable, not only in microelectronics, but for a wide range of applications based on general functional chemistry.

Hydrogen-terminated silicon surfaces act as an excellent 'blank canvas' for reactions with many kinds of inorganic or organic compounds, all made possible because of their critical ability to be chemically modified without the silicon substrate becoming oxidised during intermediate reaction steps. For instance, many molecules with terminal unsaturated bonds can react with the surfaces to confer a particular function. Chabal and other researchers have so far developed two types of hybrid organic/inorganic systems that could reap the rewards of this novel behaviour. The first is composed of terminal amine groups, attached to clean silicon surfaces via an organic linker molecule. This enables interaction with biological molecules and could thus be important for the integration of biosensors into electronic circuits

and technological devices. The second system also makes use of organic linker molecules but the molecules are modified to enable their attachment to non-organic substances such as nanoparticles or semiconducting quantum dots. Functionalizations such as these show great potential for use in the electronics and energy industry. Chabal exemplifies this by explaining: "The attachment of optically active quantum dots are being used to develop efficient, silicon-based photovoltaic cells or light emitters. These approaches are far from being mature technologies, but encouraging results have been obtained for all these applications".

### VISUALISING ATOMS IN PRACTICE AND THEORY

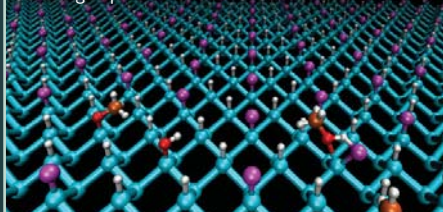
Because of the sensitive, microscopic and fragile nature of the surfaces being investigated, it has been necessary for the researchers to employ a wide variety of spectroscopic techniques, often carried out under vacuum conditions, to avoid re-contamination of surfaces after cleaning. These include, but are not limited to, Auger spectroscopy, mass spectrometry, electron energy loss spectroscopy and X-ray photoelectron spectroscopy. The facilities afforded by the University of Texas at Dallas enable the work of the research group, providing access to world-class equipment for implementing traditional and novel surface science techniques. These include a diffraction suite, scanning electron microscope, scanning tunnelling microscope and an aberration-corrected transmission electron microscope. In addition, the use of infrared spectroscopy has been critical for Chabal's work as it represents the most discriminating and versatile tool from which to derive chemical and structural information of material surfaces.

In order to deepen understanding of semiconductor surfaces, Chabal emphasises the importance of perfecting surfaces and collaborating with theorists. "Theorists make transformative contributions to the field by using chemically and atomically controlled model surfaces to develop the fundamental surface chemistry to understand how the surface chemical structure affects the interface electronic properties," he explains. For this reason, his team works closely alongside Estève (see page 104), and Halls (see page 105).

### NANOPATTERNING

The generation of stable H-terminated silicon surfaces has been pivotal for the growth of the microelectronic industry as the material acts as a gateway for further surface chemistry. Starting from flat, H-terminated Si (111) surfaces, Chabal and colleagues have recently devised a method for producing a nanopattern of functional

An illustration of the nanopattern. In 2010, Chabal and colleagues discovered that immersion of hydrogen-terminated Si(111) surfaces in methanol resulted in a nanopattern of methoxy that could be transformed into F or OH groups.



groups (F, OH, OCH<sub>3</sub>). This work, published in *Nature Materials* in 2010, further extends the possibilities for functionalisation. Chabal adds: "Functional groups such as -F and -OH can be uniquely stabilised on an unoxidised silicon surface when using a partially alkoxyated surface as a nanopatterning template". Once these stable surfaces have been established, 'snap' surface chemistry can be achieved, involving the interchange of functional groups without any apparent degradation of the underlying silicon surface.

More recent work from the Department (published in the *Journal of the American Chemical Society*, 2012) has been investigating how to functionalise silicon surfaces with phosphonates, which are particularly useful in coatings, sensors, electronics and adhesive promoters. For applications other than electronics, they have been successfully grafted onto metal oxides, but silicon surfaces have, in the past, presented a challenge. Now, it has been revealed that functionalisation of a silicon surface is possible by starting from an oxide-free, OH-terminated nanopatterned silicon surface and, importantly, can be achieved at room-temperature in an aqueous environment. Furthermore, it has been shown experimentally, and confirmed theoretically, that the resulting surface is stabilised by a 2D network of hydrogen-bonded water molecules within the phosphonic acid groups, right at the interface of the material – a new paradigm for surface stabilisation.

### BROADER IMPACT

This fundamental, interdisciplinary and ongoing research project by Chabal and colleagues has made, and will continue to make, a significant contribution to the development of applications using silicon-based materials. In the not too distant future, this technology could be realised for the efficient function of technologies such as chemical and biological sensors, fuel and photovoltaic cells, catalysts and single electron devices. Thus, results of the research will have a wide ranging impact, not just with respect to semiconductors but throughout the chemical, biomedical, energy and defence industries.

## INTELLIGENCE

### SURFACE CHEMICAL FUNCTIONALIZATION OF SEMICONDUCTORS AND NANOSTRUCTURES

#### OBJECTIVES

- To explore elementary processes at surfaces and interfaces of technologically important electronic, photonic, organic and biological heterostructures by using developing optical spectroscopic and imaging techniques
- To develop a detailed mechanistic understanding of semiconductor surface cleaning, passivation and chemical functionalisation using infrared absorption spectroscopy and other surface sensitive techniques
- To probe the interaction of chemical species with surfaces and formation of thin dielectric films using a variety of methods based on wet chemistry, ultra-high vacuum and vapour deposition with sensitive, *in situ* methods
- To investigate the interaction of hydrogen in a variety of environments, including storage nanoporous materials for carbon capture and the hydrogen fuel economy (funded by DOE - BES Award DE-FG02-08ER46491)

#### KEY COLLABORATORS

Mathew Halls, Alain Estève, Carole Rossi

#### FUNDING

National Science Foundation – award nos. CHE-0911197 (now CHE-1300180) and DMR-1312525

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**YVES CHABAL** is Professor and Head in the Department of Materials Science and Engineering at UTD. He received his MSc and PhD from Cornell University (1997, 1980), worked 22 years at Bell Labs, five years at Rutgers University, before joining UT Dallas in 2008 and holds a Texas Instrument Distinguished University Chair in Nanoelectronics.

**MATHEW HALLS** is Director of Materials Science for Schrödinger Inc. and an Adjunct Associate Professor in the Materials Science and Engineering Department at UTD.

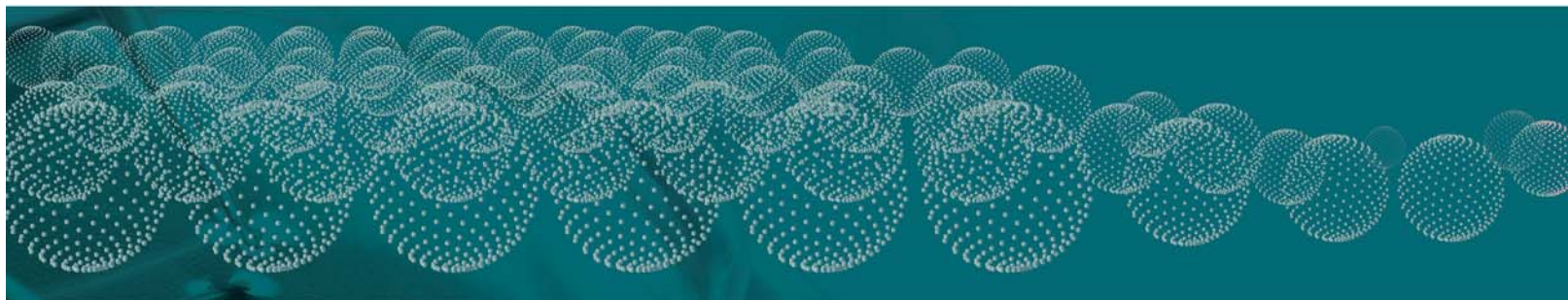
**ALAIN ESTÈVE** received his PhD in Condensed Matter Physics in 2000. He joined LAAS-CNRS in 2001 after a postdoctoral position in Bell Labs, Murray Hill. His activity focuses on nanoenergetic materials and on the modelling of biological/non-biological interactions.

**CAROLE ROSSI** joined LAAS-CNRS in Toulouse in 1998 where she is a researcher in the MicroNanoSystems department. Her main interests are nanoenergetics for MEMS micropyrotechnical systems and power MEMS for electrical generation.



## A French-US Initiative for nanoengineering surfaces

Drs Alain Estève and Carole Rossi of ATLAB – a multidisciplinary CNRS French-American initiative that bring fundamental understanding to reactive materials interfaces and DNA/inorganic surface interactions – along with Professor Yves Chabal, overcome the processing complexity of nanomaterials by combining advanced characterisation, molecular modelling and technology



**OVER THE LAST** two decades there has been a move to downscaling of devices to enable the production of smaller, more compact and functional technology. To facilitate their design and development, it is essential to develop a fundamental understanding of the mechanisms that govern interface formation between materials. This is only feasible through the synergy of multi-scale modelling (from atomic- to mesoscale), *in situ* characterisation techniques and appropriate synthesis capability.

As such, a highly collaborative project between French and US researchers aims to bring together surface and materials chemists with members of the nanoenergetic materials and nanostructure community.

Under the umbrella of an associated laboratory, launched by the Centre national de la recherche scientifique (CNRS) to allow for a collaborative framework between the Laboratory for the Analysis of System's Architecture (LAAS)-CNRS (Toulouse, France) and the LSNM at the University of Texas at Dallas, researchers are able to combine a theoretical and technological perspective to develop and characterise novel micro-electro-mechanical systems (MEMS). The National Science Foundation's (NSF) Materials Research Division, and the French National Research Agency (ANR) are both funding this joint project on MEMS (Control of Interfacial Chemistry in Reactive Nanolaminates) to open new perspectives in developing tuneable materials through 'smart' interfaces.

The increasing use of nanotechnology to modify complex surfaces and manipulate them has created many opportunities for the use of biological molecules now capable of producing biomaterials or bio-inspired technologies with novel functions and applications. However, the complexity of these materials creates the need to combine advanced characterisation with atomic-scale modelling to predict how these biomolecules will assemble, function and behave when brought into contact with other nano-patterned, abiotic surfaces.

### ATLAB

The nanoengineering work carried out at Accelerated Technology Laboratories (ATLAB) has four main scientific goals toward which research projects are focused:

- To provide a quantitative assessment of the interface parameters (structure, thickness and chemical nature) that control the reactive Al-CuO's material kinetics and stability at low temperatures
- To provide computational tools that enable understanding and prediction of interface formation under diverse experimental conditions
- To explore atomically precise technologies, such as atomic layer deposition, to tune the thermal properties of reactive nanolaminate coatings as a function of the layer chemical composition
- To explore alternative technological approaches such as DNA-directed assembly of nanoenergetic materials

Together, achieving these goals will represent a giant leap forward in the understanding of energetic and reactive nanostructured materials and significantly elevate the reputation of ATLAB within the reactive materials community.

### COMPLEMENTATION

CNRS's LAAS is carrying out research under the banner of Atomic Scale Modeling and Simulation for Micro, Nano and BioNano Technologies, focusing on ultra-thin oxides, energetic materials, DNA-based technologies and biological and biological-hybrid molecules. Two members of this group, Drs Carole Rossi and Alain Estève, work in close collaboration with Professor Yves Chabal, Department of Materials Science and Engineering, University of Texas at Dallas, to consider predictive modelling at the atomic scale of micro- and nano-devices, thus complementing the experimental results from the

US, and filling the knowledge gaps that are intrinsic to lab-based research strategies.

Rossi's expertise lies in the preparation of advanced sputtered Al/CuO reactive nanolaminates, used for a number of nanoenergetic applications, while Estève has significant expertise in the field of multiscale modelling. He is able to implement his skills in density functional theory-based calculations to unravel elementary physicochemical mechanisms and take advantage of his experience with kinetic Monte Carlo models to facilitate large-scale simulations of technological processes with atomic-scale precision. Both methodologies are critical for the development of a fundamental understanding of interface processes formation during material synthesis. This simulation work, combined with the experimental approach implemented by Chabal, is vital for improving the fundamental understanding of surface physicochemical processes.

### DEVELOPING NETWORKS

To ensure the success of this field of research into the future, and facilitate the effective training of potential researchers, ATLAB are in the process of developing an educational programme to instill interested postdoctoral researchers with the necessary skills and expertise for this area of work and initiate new, fruitful and culturally diverse collaborations. This programme was initially established with an NSF Travel Grant, awarded in 2003, to Chabal and Estève. Recently, renewal of funding from the Partner University Fund program, MOdelling integrated nano-structured energetic MATerials (MOMA) has enabled this important work to continue and has produced many collaborative publications, the quality of which has been greatly enhanced by work carried out by visiting US and French students and researchers, made possible by the grant.



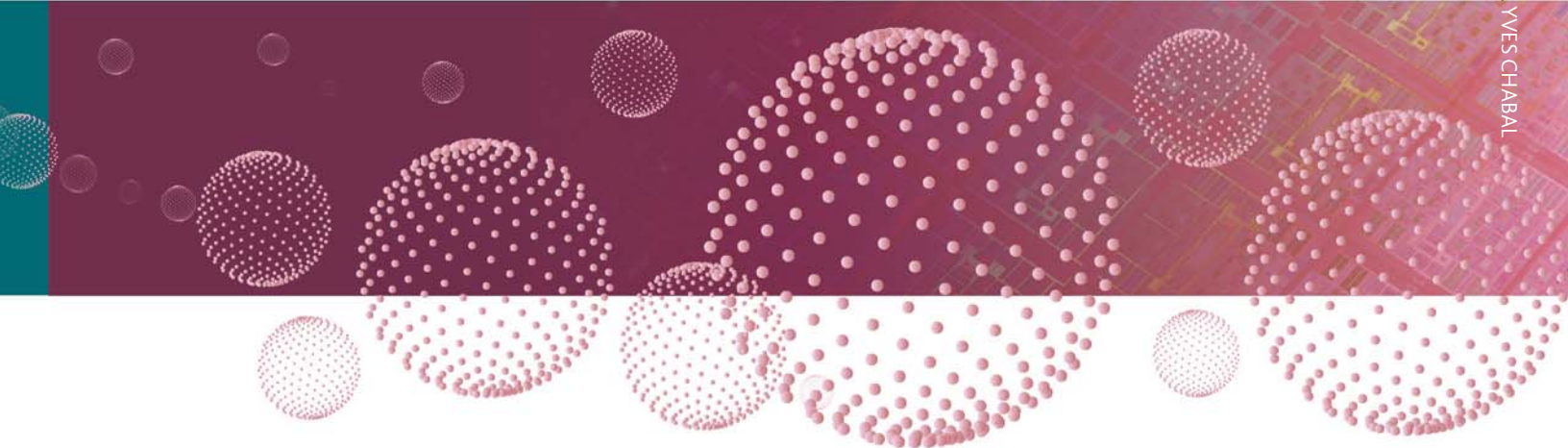


# From theory to practice

In the study of thin film growth and interfaces at the atomic-scale, **Dr Mathew Halls**, from Schrödinger Inc., takes a theoretical approach to understanding chemical interactions of surface structures complementing the work of experimental physicists



PROFESSOR YVES CHABAL



**THE DEVELOPMENT OF** tomorrow's electronic devices with improved speed and enhanced capabilities is made possible by taking an interdisciplinary approach involving a combined effort from both theoretical and experimental scientists.

Over the past two decades, the tremendous increase in the power of computers and advances in quantum mechanics simulation techniques have made atomic-scale simulation a powerful tool for exploring the chemical details at the heart of advanced technologies. The improved processing power has greatly extended the size of chemical models that can be accurately simulated, while experimental feature sizes are shrinking. This coalescence of length scales sets the stage for unprecedented progress in surface modification and interface engineering.

The role of atomic-scale simulation in the development of processes and materials for new technologies is expanding. Software tools that are accessible, efficient and accurate are being developed and supported by private companies, such as Schrödinger Inc. Dr Mathew Halls is Director of the Materials Science Program at Schrödinger where he leverages his knowledge and experience in atomic-scale materials modelling to lead a team developing an industry-leading chemical simulation package. For the last 10 years he has been working with Professor Yves Chabal, to support his experimental studies on the surface properties and functionalisation chemistry of semiconductors. The focus of their collaboration has been the reactivity and modification of surfaces at the atomic level.

## THE THEORETICAL APPROACH

In pursuit of extending knowledge and capabilities for novel surface applications, the contribution of computer simulation is two-fold. Firstly, theoretical modelling can help develop a clearer understanding of the atomic structure of the surface and reacting molecules by predicting properties for varying atomistic models and looking for agreement with experimental measurements. This is particularly important for surface applications, where experiments often provide partial information needed to fully determine the chemical composition and structure at the surface. Additionally, simulation can provide details about charge distributions, electronic orbitals and chemical interactions that determine the specificity and reactivity of the surface structures.

The second way in which theoretical analysis can help in this area of research is by modelling and predicting the reactivity between the prepared surfaces and reagents. If the atomic structures and electronic properties of the surfaces and molecular co-reactants are known, the reaction pathways can be analysed to determine the energetically favourable reactions and the timescale over which the reactions occur. Predictive capability is a key function of atomic-scale simulation as it is able to calculate the energy changes as a surface and molecule interact and bonds rearrange leading to a change in surface structure and therefore surface properties. In this way, it is feasible to explore the chemical design space of the molecular reactant to identify promising systems that will react with prepared surfaces

in a desired way. These theories can then be tested by carrying out the reactions experimentally and monitoring the outcome using spectroscopy.

## THIN FILMS AND FUNCTIONAL SURFACES

Halls' current research is focused on using theory to understand and tune the chemical design parameters of semiconductor surfaces and co-reactants to help inform experimental efforts toward achieving improved thin films and functional surfaces. Thin films are commonly used in the manufacture of optics, for reflective or anti-reflective coatings, for electronic applications such as in semiconductor devices and, more recently, in energy-related devices such as photovoltaic (PV) cells. For these applications, the quality of the thin films is critical as any atomic-scale defect degrades the physical and chemical properties of the films. Work performed by Halls is looking to understand how and why these defects occur, utilising computer simulations to consider the reactive system as a whole. From this perspective, it is possible to design better deposition schemes that will produce desired surface products. The use of modelling can predict how effective different practical methods will be, help identify potential defect-causing problems and consider a range of different factors that must be understood in order to produce 'perfect' surfaces.



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