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In Recognition of Professor Hitchman: Advances in Chemical Vapor Deposition

Francis Maury, Sergey Alexandrov, Davide Barreca, Dimitris Davazoglou, and Martyn Pemble

Chemical vapor deposition (CVD) processes had been around for nearly 100 years before they began to attract interest from materials scientists and electronics engineers in the 60s and 70s, as a result of the rapidly growing microelectronics industry. The successful development of this complicated technology required a deep physicochemical understanding of deposition processes and reaction mechanisms. This resulted in a large number of scientists from different disciplines studying the basics of CVD.

One of the most recognized of these scientists is Professor Michael L. Hitchman, who has been involved in this field since the beginning of the 'new CVD era' and whose contribution to it is difficult to overestimate.

Professor Hitchman was one of the first researchers to develop mathematical models of CVD reactors, which allowed the relative roles of mass transport, heterogeneous and homogeneous kinetics to be de-convoluted from overall process characteristics and for film uniformity to be controlled. His efforts in the implementation of low pressure processes led to a greater understanding of deposition mechanisms and the effect of processing conditions on layer properties. To provide a deeper understanding of process chemistry, his use of spectroscopic methods for in situ diagnostics of reaction gases yielded key insights into reaction schemes for the deposition of many materials. One important innovation was the first really detailed description of the CVD processes for the deposition of organic films.

In addition to fundamental research, Professor Hitchman has devoted much attention to the practical requirements of industry, exploring microelectronic materials, high temperature superconductors, photocatalysts for pollutant degradation, protective anticorrosion layers, and gas sensors. He helped to develop remote plasma enhanced-CVD (RPE-CVD) processes to minimize active defects in deposited layers and to simplify the interrelations between process parameters. The extension to atmospheric pressure RPE-CVD made it relevant to the vacuum-free deposition processes needed for many industrial applications.

Apart from being an eminent scientist, Michael also loves life: he adores gastronomic cuisine, fine wines and languages, being proficient in French and German as well as his native English. He also loves to joke and, having been a leading member of the EuroCVD community for more than 30 years, a meeting is not regarded as successful unless he has presented his latest collection of jokes and anecdotes. He has greatly



Francis Maury



Sergey Alexandrov



Davide Barreca



Dimitris Davazoglou



Martyn Pemble

contributed to the warm, friendly and convivial atmosphere which makes EuroCVD Conferences an unmissable event for the CVD community.

Professor Hitchman is undoubtedly a true champion at promoting CVD science, and is committed to passing on his deep understanding of the field to younger researchers. In 1995, he founded the *CVD Journal* (Wiley). To mark his retirement after 20 years as Editor of this journal, and on the occasion of his 75th birthday, this special issue of *Advanced Materials Interfaces* has been prepared in recognition of Professor Hitchman's outstanding contributions to the development of CVD science and technology.

The 17 papers of this special issue cover topics ranging from microelectronics to photovoltaics, including optical and electro-optical systems, integration issues, flexible devices, photocatalysis, and photoelectron catalysis (water splitting, sensors, etc.).

A remarkable fact of the evolution in CVD is to note that only two of these papers do not use a metalorganic precursor: they report the deposition of polymers and carbon materials (carbon nanotubes (CNTs), graphene), which use organic monomers and hydrocarbons instead. This fact demonstrates the increasing interest in metalorganic compounds as

precursors. A second point to note is the increasing popularity of atomic layer deposition (ALD) over the last decade, as illustrated by the fact that almost half of the contributions are using this technique. For both methods, the development of new processes strongly depends on metalorganic precursors, and some new ones are proposed here.

The ever-present need to reduce the deposition temperature, to avoid damage to fragile substrates, or to control the quality and growth rate of the film leads to processes which are energetically activated or which operate under specific conditions in both families of techniques, e.g., PECVD, HWCVD, AACVD, iCVD, HVCVD as well as PEALD, HWALD, MLD. Examples are given in this special issue for all of these related vapor deposition processes. The deposited materials are also very diverse, which shows the abundant requirement for thin films in many fields. This includes metals (Fe, W, Cu), polymers (poly divinyl benzene), organic-inorganic hybrids (Al-based), CNTs, diamond, nitrides and sulfides (AlN, BN, MoS₂/SiO₂), CaF₂, and many functional oxides (WO₃, BaTiO₃, Fe₂O₃, ZnO) and dielectrics (Al₂O₃, HfO₂).

We would like to thank all of the authors who have helped us to collect this important overview of *Advances in Chemical Vapor Deposition*.

A Quantum Mechanical Life

Michael L. Hitchman

Life often seems to me to be much the same as the many-worlds interpretation of quantum mechanics.

The start of each new life phase is rather like an example of quantum-mechanical branching as seen by an observer: a change of circumstances is equivalent to obtaining a particular outcome from an observation of a quantum system.

My entry into CVD certainly had that characteristic.

I started my scientific research more than 50 years ago by investigating homogeneous kinetics in solution, heterogeneous processes on electrode surfaces, and mass transport using a novel electrochemical system known as a rotating ring-disc electrode. They were exciting years and resulted in a monograph written with my DPhil supervisor which has been described as a 'seminal volume' and has become a classic text.^[1]

Electrochemistry continued to be the dominant feature of my career for a number of years, with studies of environmental problems and gas sensors, and this also produced a best-selling book.^[2]

Then I moved on to a burgeoning field of commercial development with electrochemically based electrochromic displays, but that came to an abrupt halt when I conclusively showed that the materials being used were thermodynamically unstable!

At that point I had talked myself out of a job and I needed quickly to find alternative research to occupy me. Fortunately, I became aware of work in an adjoining lab on CVD, which I saw was a process with features very much akin to those found in electrochemistry; indeed, at that time, CVD was often referred to as 'gas plating' by analogy with electroplating.

My career path was then very much like a quantum mechanical particle hidden under two 'cups': existing under both of them at the same time, with a certain probability of being found in either place. In fact, the many-worlds interpretation means that, when an observer turns over these 'cups', two new 'universes' branch off – one where the particle is under one cup, and one where it is under the other. And that is just what happened with my 'career particles'. I had found a new area of research while at the same time keeping my previous interests: in order to try to begin to understand a CVD growth process—homoepitaxial Si deposition by reduction of SiCl_4 —I built and modelled a rotating disc system with the Si substrate operating at temperatures up to 1300 °C!

In their Editorial, colleagues have kindly and generously outlined subsequent developments in my CVD career. Each new branching-off has produced multiple career paths. In addition,



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the original electrochemical investigations have also branched off, and grown to the extent that many of the doctoral and Masters theses I have supervised have been electrochemically based.

Working on multidisciplinary topics is stimulating and exhilarating, with new ideas that grow out of the fresh insights which different disciplines can offer. What successes I may have had, I believe, can be largely attributed to the influence of contrasting thought patterns migrating from one area of research to another.

I do not forget, though, that any successes have not been mine alone, but have been built on the novel contributions and hard work of all my research students, my post-doc partners, my colleagues in academia and industry, and on the support through good times and difficult times from family and friends.

As I come to the twilight of my research career, I am honoured and humbled to have this Special CVD Issue of *Advanced Materials Interfaces* dedicated to me and I, in my turn, dedicate it to all those with whom I have worked, thanks to the many-worlds branching that has been the basis of my quantum mechanical-type journey through what has been, and continues to be, a fascinating and amazing life.

[1] W. J. Albery, M. L. Hitchman, *Ring-Disc Electrodes*, Clarendon Press, Oxford, UK 1971.

[2] M. L. Hitchman, *Measurement of Dissolved Oxygen*, John Wiley & Sons, New York, USA 1978.