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CVD, ALD and Nanoparticles

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With contributions by
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M. A. Malik · A. M. B. van Mol · J. Müller · L. Niinistö · P. O’Brien
M. Putkonen · R. Schmid · S. Schulz · P. Serp · M. Veith

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The series *Topics in Organometallic Chemistry* presents critical reviews of the present and future trends in polymer and biopolymer science including chemistry, physical chemistry, physics and material science. It is addressed to all scientists at universities and in industry who wish to keep abreast of advances in the topics covered.

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Since the rise of organometallic chemistry, marked by the discovery of the molecular structure and unusual reactivity of ferrocene about five decades ago, one of the principal driving forces behind it has been the application of newly gained fundamental knowledge about metal–carbon bonds to improve and extend the “tool box” for selective organic synthesis in a very general and broad sense. Homogeneous catalysis is a true success story of organometallic chemistry, a discipline that has structured and combined inorganic and organic chemistry to an unprecedented extent. In parallel, the chemistry of metallo-organic coordination compounds (MOCs) – molecular compounds without direct M–C bonds but containing hydrocarbon moieties or substituents at the ligator atoms – has developed along the lines of Werner-type classical coordination chemistry and even developed beyond its relevance to biochemistry and molecular biology. Across the borders of molecular chemistry, materials research is bridging the molecular sciences with condensed matter and solid state chemistry as well as physics and engineering disciplines. The advent of the microelectronic industry and information technology, together with the intrinsic demand for the miniaturisation of devices down to the ultimate limits given by fundamental laws of quantum mechanics, has undoubtedly greatly stimulated the merger of physics and chemistry in nanospace, which we are all currently witnessing. One option that chemistry offers this self-accelerating enterprise is certainly organometallic and metallo-organic molecular precursors, compounds that are themselves particularly useful or even specifically engineered for the fabrication and processing of materials and functional architectures made therefrom, no matter if we are talking about micro- and nanosized devices or about macrosystems. The sub-discipline of inorganic molecular chemistry dealing with that option is called precursor chemistry.

Precursors are defined as molecular compounds containing one or more atoms or groups of atoms that are constituents of the particular target material and are selectively released upon decomposition of the precursors during materials synthesis and processing. Precursors are thus not building blocks or “molecular bricks” like monomers in polymer chemistry or subunits for the assembly of supramolecular architectures. Typically, the molecular structures of the precursors are completely destroyed rather than integrated to some extent into the final material. In that sense, precursor chemistry has a long
tradition within classical inorganic solid-state chemistry. Precursors are thus a sort of molecular container for the delivery of the smallest possible unit for chemical construction: the atom. It follows that the key problem in precursor chemistry is the detailed understanding and control of the decomposition of the precursor under the conditions defined by the requirements and limitations of the particular engineering process of the target material or device. Thus, organometallic and metallo-organic precursors are particularly interesting because modification of composition, structure and the ligand shell, e.g. the organic hydrocarbon-type wrapping of the atoms of interest, changes the chemical reactivity and the physical properties of the precursor. Control of these parameters is essential for rational precursor engineering. Simple inorganic molecular precursors, such as the molecular elements, binary hydrides or halides clearly do not offer similar degrees of freedom but are advantageous because of their chemical simplicity. The introduction of complexity at the precursor level is likely to complicate rather than simplify the overall chemical complexity of materials synthesis. The goal of precursor engineering is finding an optimum compromise between the demands of materials synthesis and processing on one hand and the possibilities and limitations of precursor chemistry on the other hand.

The study and development of organometallic precursor chemistry has been intimately connected with thin film processes over the last few decades, in particular with the development of chemical vapour deposition (CVD). This began with the early work of H.M. Manasevit in the late 1960s on organometallic CVD (OMCVD) of III/V and II/VI compound semiconductors using metal alkyl compounds as precursors. Similarly, sol-gel chemistry related to the processing of metal oxide-based advanced ceramics has been and continues to be a field of application for metallo-organic precursors. Metal alkoxide compounds have also been extensively studied as precursors. In the course of the discovery of ceramic high-temperature superconductors of the type YBa$_2$Cu$_3$O$_{7-x}$ in the 1980s, metallo-organic precursors for metal oxides suitable for sol-gel processing and thin film deposition by CVD increasingly became the focus of interest and the related need for improved precursors linked CVD and preceramic research closer together. The research on molecular precursors for pure elementary metals, mixed metal alloys and non-oxide ceramic materials (e.g. SiC) and protective, hard coatings (e.g. TiC and TiN) has lagged behind compound semiconductors and metal oxide ceramic materials. However, this is quite likely to change in the future and we wish to draw the attention of the reader to a selection of review articles listed in the bibliography below, covering the diverse fields of organometallic and metallo-organic chemistry as well as inorganic molecular precursor chemistry in relation to thin film research around CVD and applications in materials science.

The purpose of this volume of Topics in Organometallic Chemistry, however, is to highlight recent and emerging directions and aspects of molecular precursor chemistry for advanced inorganic materials rather than give a sys-
tematic and comprehensive overview of the whole field, which would be an impossible task anyway. We will present a few examples of precursor chemistry connected with thermally activated CVD and related techniques of materials synthesis and processing. CVD employing organometallic or metallo-organic precursors represents a non-equilibrium process highly dependent on the details of chemical kinetics and fluid dynamics exhibiting a complex coupling of gas-phase and surface processes. This complexity goes far beyond the issues of coordination chemistry, such as synthesis, structure and reactivity in the homogeneous phase, e.g. in organic solution, as is typical in organometallic chemistry, e.g. motivated by applications in homogeneous catalysis. In CVD, precursors delivered in the gas-phase produce a variety of reactive intermediates in the course of both homogeneous and as well heterogeneous gas/solid reactions (see Fig. 1, p. 3). A certain fraction of the species distributed in the boundary layer over the substrate will adsorb at the surface where subsequent surface reactions take place to yield the solid deposit and side products that are desorbed and transported away.

The nature of the layer grown by CVD clearly relates to the selectivity of the decomposition process, including the selectivity of the surface chemistry. In the case of crystalline films or even epitaxial film growth, the quality of the deposited material also depends on nucleation and crystal growth kinetics, which again depend on the coupling of gas-phase and surface effects. CVD is closely connected with both heterogeneous catalysis and combustion chemistry. In heterogeneous catalysis, gaseous starting compounds are catalytically transformed into gaseous products by adsorption, surface reaction and desorption processes, but without deposition of a solid residue and without a heavy coupling of homogeneous gas-phase pre-reactions. In combustion, there is ideally no solid deposit and the walls of the combustion chamber do not interfere with the homogeneous gas-phase reactions.

Our first example that attempts to unravel this complexity is entitled “Gas-Phase Thermochemistry and Mechanism of Organometallic Tin Oxide CVD Precursors”. The authors, M. Allendorf and A.M.B. van Mol, describe the development of quantum chemistry methods that can predict heats of formation for a broad range of tin compounds in the gas phase, which need to be considered when Sn(CH$_\text{3}$)$_{4}$ or (CH$_\text{3}$)$_{2}$SnCl$_{2}$ and other tin alkyls are used as precursors together with oxygen and water for tin oxide deposition.

The second contribution by A. Devi, R. Schmid, J. Müller and R. A. Fischer entitled “Materials Chemistry of Group 13 Nitrides” reviews the organometallic precursor chemistry of group-III nitride OMCVD. The authors discuss the various efforts undertaken in the past decade to come up with alternative precursors to compete with the classical system of Ga(CH$_\text{3}$)$_{3}$ and NH$_{3}$ to grow GaN, which is commercially employed in industry. The potential of the rather exotic organometallic azide compounds as precursors for the nitride materials is critically discussed, showing the limitations and prospects of that approach as well as representing one of the few examples of comprehensive studies on
single molecule precursors using combinations of different techniques, i.e. matrix isolation IR spectroscopy and quantum chemical modelling, in order to shed light onto the complex situation.

The third contribution is particularly devoted to the concept of so-called single source precursors (SSPs). SSPs contain all the atoms of the different elements necessary for the deposition of the desired material in one single molecule. One motivation for using this concept is to simplify the accompanying gas-phase reactions and thus reduce the process parameters to be controlled and optimised. However, SSPs may offer a unique chance of depositing metastable materials that cannot be derived by other methods. M. Veith and S. Mathur provide such an example in their paper entitled “Single-Source-Precursor CVD: Alkoxy and Siloxy Aluminum Hydrides”.

The forth chapter by S. Schulz also deals with single-source precursors and provides a study case on “CVD Deposition of Binary AlSb and GaSb Material Films – a Single-Source Approach”. The article summarises recent studies on the synthesis of M–Sb compounds and their potential application as precursors in OMCVD processes. General reaction pathways for the synthesis of Lewis-acid-base adducts $\text{R}_3\text{M-ER}_3'$ and heterocycles of the type $[\text{R}_2\text{MSbR}_2']_x$ ($\text{M} = \text{Al, Ga}$) are described. The results of deposition studies are discussed.

The fifth contribution by M. Putkonen and L. Niinistö presents an overview of “Organometallic Precursors for Atomic Layer Deposition” (ALD). The key principle of ALD in contrast to CVD is the exclusion of any gas-phase pre-reaction allowing the thin film growth to be fully controlled by surface reactions and adsorption/desorption kinetics. ALD is thus ideally suited for the growth of ultra-thin layers and atomically abrupt interfaces needed in future nanoelectronic devices. While CVD and ALD have many aspects in common, precursors suitable for ALD generally need to be much more reactive than those used for CVD. Another challenge is to combine low steric demand with very high selectivity of the surface reactions.

The sixth chapter emphasises the role of surface defects, surface reactive groups and autocatalytic phenomena at the very early steps of thin film growth. The authors P. Serp, J.-C. Hierso and P. Kalck discuss the “Surface Reactivity of Transition Metal CVD Precursors: Towards the Control of the Nucleation Step”. Organometallic precursors have been used for the CVD preparation of heterogeneous catalysts, i.e. the deposition of metal particles on the internal surfaces of porous support materials. As a general conclusion, maintaining a high supersaturation level of precursor in the gas phase is a required condition to achieve better control of the nucleation step regarding the controlled growth of nanostructures on surfaces.

With the seventh chapter, we move away from CVD. M. A. Malik and P. O’Brien present a review of “Organometallic and Metallo-Organic Precursors for Nanoparticles”. Nanoparticles have been recognized as suitable systems for studying the transition from the molecular to the macrocrystalline level and exhibiting unusual chemical and physical properties. They have thus been
extensively studied in recent years. Precursor chemistry comes into play, for example, if these particles are synthesized in the condensed phase by wet chemical methods and are stabilized as colloids by the addition of suitable surfactants or surface capping ligands to prevent Ostwald ripening. Again, heterogeneous nucleation and growth phenomena are involved. Nanoparticles dispersed in a fluid medium (gas-phase or organic solvent) exhibit a high surface to volume ratio. Particle growth by adsorption and decomposition of precursors at the surface parallels thin film growth by CVD or ALD discussed above. Many precursors, in fact, designed for CVD are also well suited for nanoparticle synthesis.

These seven contributions span the diverse field of molecular precursor chemistry for CVD and related techniques presenting a collection of different perspectives for the use and prospects of organometallic and metallo-organic compounds in materials science. Little research has been published in these areas although there is a wealth of ongoing development. Particularly hot topics relate to ALD, nanoparticles, nanostructures and composites. The current trend in materials research is moving away from precursor synthesis and development to the application of known and established precursors. The understanding of the growth mechanisms on a molecular level, especially at surfaces, will play a key role in the future. The bibliography given below summarises a selection of review articles that we found suitable and instructive to get a broad overview of the field of inorganic molecular precursor chemistry related to CVD and nanomaterials research beyond the case studies discussed in this volume.

Bochum, August 2005

Roland A. Fischer

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Contents

Gas-Phase Thermochemistry and Mechanism of Organometallic Tin Oxide CVD Precursors
M. D. Allendorf · A. M. B. van Mol .......................... 1

Materials Chemistry of Group 13 Nitrides
A. Devi · R. Schmid · J. Müller · R. A. Fischer ............... 49

Single-Source-Precursor CVD: Alkoxy and Siloxy Aluminum Hydrides
M. Veith ................................... 81

CVD Deposition of Binary AlSb and GaSb Material Films – a Single-Source Approach
S. Schulz ................................... 101

Organometallic Precursors for Atomic Layer Deposition
M. Putkonen · L. Niinistö .......................... 125

Surface Reactivity of Transition Metal CVD Precursors: Towards the Control of the Nucleation Step
P. Serp · J.-C. Hierso · P. Kalck .......................... 147

Organometallic and Metallo-Organic Precursors for Nanoparticles
M. A. Malik · P. O’Brien .......................... 173

Author Index Volumes 1–14 ................................ 205

Subject Index ................................ 211