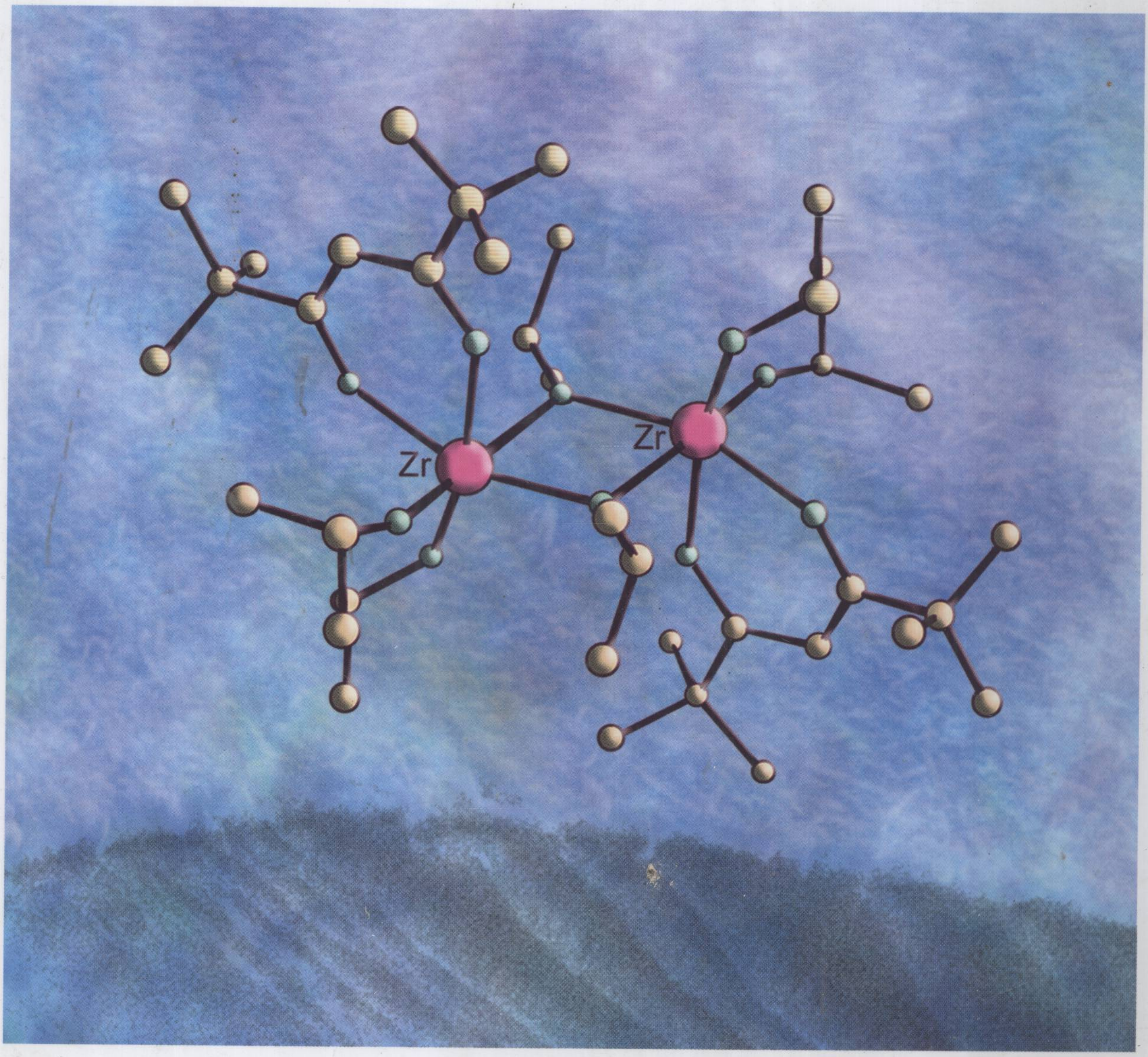
Edited by Anthony C Jones and Michael L Hitchman

Chemical Vapour Deposition

Precursors, Processes and Applications



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PREFACE

Chemical Vapour Deposition: Precursors, Processes and Applications

This book aims to give a comprehensive overview of Chemical Vapour Deposition (CVD). CVD involves the deposition of thin solid films from chemical precursors in the vapour phase, and encompasses various deposition techniques, including metal-organic chemical vapour deposition (MOCVD), plasma-enhanced CVD (PECVD), photo-initiated CVD and atomic layer deposition (ALD). The book has been written with the CVD practitioner in mind, such as the chemist who wishes to learn more about CVD process technology, or CVD technologists who wish to increase their knowledge of precursor chemistry. This book should prove useful to those who have recently entered the field, and certain aspects of the text may also be used in chemistry and materials science lecture courses at undergraduate and postgraduate level.

We have attempted to present a logical and progressive overview of the various aspects of CVD processes. Therefore, basic concepts, such as the various types of CVD processes, the design of CVD reactors, reaction modelling and CVD precursor chemistry, are covered in Chapters 1–5. This is followed in Chapters 6–12 by a detailed description of the use of various CVD techniques to deposit a wide range of materials, including semiconductors, metals, metal oxides and nitrides, protective coatings and functional coatings on glass. Finally, in Chapter 13, some commercial aspects of CVD are discussed. The development of CVD technology owes a great deal to collaboration between different scientific disciplines such as chemistry, physics, materials science, engineering and microelectronics, and it is hoped that this book will promote and stimulate continued dialogue between scientists from these different research areas.

We are greatly indebted to the chapter authors for their enormous effort in summarizing their extensive knowledge of many different aspects of CVD, especially in view of undoubted pressures from many directions. We are also grateful to the many members of our research staff, the unsung heroes of this volume, and it is hoped that the book will be a tribute to them. We must also acknowledge the hard work of the publishing staff at the Royal Society of Chemistry, in particular Mrs Annie Jacob and Mrs Janet Freshwater. Finally, our thanks go to our families and the families of our authors for their unstinting support and understanding.

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CHAPTER 1

Overview of Chemical Vapour Deposition

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1.1 Basic Definitions

In the broadest sense chemical vapour deposition (CVD) involves the formation of a thin solid film on a substrate material by a *chemical reaction* of vapour-phase precursors. It can thus be distinguished from physical vapour deposition (PVD) processes, such as evaporation and reactive sputtering, which involve the adsorption of atomic or molecular species on the substrate. The chemical reactions of precursor species occur both in the gas phase and on the substrate. Reactions can be promoted or initiated by heat (thermal CVD), higher frequency radiation such as UV (photo-assisted CVD) or a plasma (plasma-enhanced CVD). There is a sometimes bewildering array of acronyms covered by the overall cachet of CVD and the interested reader is referred to several reviews.[1–4] Some of the more commonly used acronyms are defined below.

Metal-organic chemical vapour deposition (MOCVD) is a specific type of CVD that utilizes metal-organic precursors. In the strictest sense a metal-organic (or organometallic) compound contains a direct metal–carbon bond (σ or π) (*e.g.* metal alkyls, metal carbonyls). However, the definition of MOCVD has broadened to include precursors containing metal–oxygen bonds (*e.g.* metal-alkoxides, metal-β-diketonates) or metal–nitrogen bonds (*e.g.* metal alkylamides), and even metal hydrides (*e.g.* trimethylamine alane).

Metal-organic vapour phase epitaxy (MOVPE) or organometallic vapour phase epitaxy (OMVPE) is an MOCVD process that produces single crystal (*i.e.* epitaxial) films on single crystal substrates from metal-organic precursors. In MOCVD and MOVPE gas-phase reactions can sometimes play a significant role in the deposition chemistry.

Plasma-assisted or plasma-enhanced CVD (PECVD) is a technique in which electrical energy rather than thermal energy is used to initiate homogeneous reactions for the production of chemically active ions and radicals that can participate in heterogeneous reactions, which, in turn, lead to layer formation on the substrate. A major advantage of PECVD over thermal CVD processes is that

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deposition can occur at very low temperatures, even close to ambient, which allows temperature-sensitive substrates to be used.

Atomic layer deposition (ALD), sometimes called atomic layer epitaxy (ALE), alternatively-pulsed CVD, or atomic layer chemical vapour deposition (ALCVD), is a modification of the CVD process in which gaseous precursors are introduced sequentially to the substrate surface and the reactor is purged with an inert gas, or evacuated, between the precursor pulses. The chemical reactions leading to film deposition in ALD occur exclusively on the substrate at temperatures below the thermal decomposition temperature of the metal-containing precursor and gas-phase reactions are unimportant.

Chemical beam epitaxy (CBE) is high vacuum CVD technique that uses volatile metal-organic precursors and gaseous co-precursors. The closely related technique of metal-organic molecular beam epitaxy (MOMBE) uses volatile metal-organic precursors and co-precursor vapour derived from the solid element. In CBE and MOMBE the chemical reactions occur only on the substrate, leading to single crystal films and so gas-phase reactions play no significant role in film growth. Section 1.3 gives a more detailed description of these processes.

1.2 Historical Perspective

In common with many technologies, developments in CVD have largely arisen out of the requirements of society. These developments have been most rapid when other thin film deposition technologies have proved problematic or inadequate, for instance in the production of multiple thin films, as in modern semiconductor devices, or when the coating of large surface areas is required, as in large-scale functional coatings on glass. Several excellent reviews describe the historical development of CVD processes,[2,5,6] and the published literature from the earliest days to the mid-1960s is covered by a comprehensive review by Powell *et al.*[7] Therefore, this section gives only a brief description, highlighting some key advances.

Probably the earliest patent describing a CVD process was taken out by a certain John Howarth, for the production of "carbon black" for use as a pigment. Unfortunately, due to rather lax health and safety standards, the process only succeeded in burning down the wooden plant.[8] The early electric lamp industry provided another early impetus for CVD, and a patent issued in 1880 to Sawyer and Mann describes a process for the improvement of carbon fibre filaments.[9] However, these proved too fragile and later patents describe CVD processes for the deposition of various metals to produce more robust lamp filaments.[10,11]

One of the earliest examples of the CVD of metals is the deposition of tungsten, reported as early as 1855. Wöhler used WCl_6 with hydrogen carrier gas to deposit tungsten metal.[12] Later in the century (1890), the famous Mond Process was developed. This describes the deposition of pure nickel from nickel tetracarbonyl, $Ni(CO)_4$,[13,14] and was used for the refinement of nickel ore.[15]

The first reports of the deposition of silicon by CVD by the hydrogen reduction of $SiCl_4$ appear as early as 1909[16] and 1927,[17] and the widespread use of thin silicon films in the electronics industry is anticipated by the CVD of Si-based photo cells[18] and rectifiers[19] just after World War II.

During the late 1950s, triisobutylaluminium, $[Bu^t_3Al]$ began to be used extensively to catalyze the polymerization of olefins by the Ziegler–Natta process. At around the same time, it was found that the pyrolysis of $[Bu^t_3Al]$ gave high purity Al metal (>99 at.%). This led to its use in the early 1980s as a CVD precursor to Al metal for very large scale integration (VLSI) applications.[20,21] In patent literature of the late 1960s, aluminium trihydride (AlH_3, alane) was found to be useful for plating Al films from the vapour phase and by electroless deposition,[22–24] which led to the much later use of alane adducts such as $[AlH_3(NMe_3)]$ as CVD precursors for high purity Al thin films.[25] The reader is referred to Chapter 7 (Section 7.3) for recent developments in Al CVD.

Another important development in the history of CVD was the introduction of "on-line" CVD architectural coatings by Pilkington (now NSG Group). These coatings are deposited on a very large scale by atmospheric pressure CVD on a float glass production line.[26] By applying the coating directly to the float glass manufacturing line, economies of scale and production are achievable that are not possible with "off-line" deposition processes such as sputtering. Perhaps the most notable of these is fluorine-doped tin oxide, [SnO_2:F] developed by Pilkington in the mid-1980s ("Pilkington K-Glass"). This is a low thermal-emissivity (low–E) coating on windows, which prevents heat loss from the home and is essential to modern ecological energy saving efforts (Chapter 10, Section 10.1.1). It can be deposited using precursors such as [Me_4Sn], [$SnCl_4$] with halo-fluorocarbons or HF (Chapter 10, Section 10.2.2). A much more recent commercial product of Pilkington is "self-cleaning" glass. This has been coated on-line with a thin transparent film of TiO_2, and this chemically breaks down dirt by photocatalysis in sunlight (Chapter 10, Section 10.6).

Despite the various developments in CVD described above, the major impetus to the technology has undoubtedly been provided by the rapid development of the microelectronics industry since the mid-1970s. This has led to a requirement for very thin high purity films with precise control of uniformity, composition and doping.

Thin epitaxial films of n- or p-doped Si are the basic requirement for all Si integrated circuit technology. One of the earliest reports of silicon epitaxy was the closed tube transport of SiI_4 produced by heating solid Si in the presence of iodine.[27] Epitaxial Si films were later produced in the 1970s on a large commercial scale by the pyrolysis of monosilane (SiH_4) in H_2.[28]

Interest in the use of metal-organic compounds for CVD applications began in the early 1960s. The first reported preparation of a III-V material from a Group III metal-organic and a Group V hydride was by Didchenko *et al.* in 1960, who prepared InP in a closed tube by the thermal decomposition at 275–300 °C of a mixture of [Me_3In] and liquid [PH_3].[29] Next, in 1962, Harrison and Tomkins produced InSb in a closed tube by heating a mixture of [Me_3In] and [SbH_3] at 160 °C, and they also produced GaAs by heating a mixture of [Me_3Ga] and [AsH_3] at 200 °C.[30] In 1961 and 1965 patent applications by the Monsanto Co. claimed methods of depositing III-V compounds "suitable for use in semiconductor devices".[31,32] The processes involved the pyrolysis of volatile Group III and Group V compounds in an open tube system on a cubic crystal substrate to produce epitaxial films.

However, the Monsanto applications were of a rather general nature, listing a large range of volatile Group III compounds, and the few specific process examples given mainly involved Group III trihalides. In 1968, Manasevit and co-workers at the Rockwell Corporation gave the first clear description of the use of metal-organic compounds for the chemical vapour deposition of III-V materials. The first publication describes the deposition of GaAs by pyrolysis of a gas phase mixture of [Et_3Ga] and [AsH_3] in an open tube system using H_2 as the carrier gas.[33] Manasevit named the technique metal-organic chemical vapour deposition (MOCVD) and a patent was later filed for the MOCVD of a range of III-V materials and wide band-gap compound semiconductors.[34]

The emphasis in Manasevit's early work was on growth of non-epitaxial films on insulating substrates such as sapphire and spinel. However, in 1969 the growth of epitaxial GaAs on a GaAs substrate by metal-organic vapour phase epitaxy (MOVPE) was demonstrated.[35] Subsequently, a wide range of III-V compounds were deposited by MOCVD (or MOVPE), including AlGaAs,[36] InP, InAs, InGaAs,InAsP,[37,38] GaN and AlN,[39] although semiconductor device quality III-V materials still had not been produced. This was due largely to low purity precursors (often obtained from commercial suppliers of metal-organics for catalysis applications) and non-optimized MOCVD reactors and processes. In 1975, however, high-purity device quality GaAs films were grown[40] that had a low residual carrier concentration of $n = 7 \times 10^{13}\,\mathrm{cm}^{-3}$ and high electron mobility ($\mu_{77K} = 120\,000\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$) (Section 1.7.2.4). Conventional techniques for the deposition of III-V materials such as liquid phase epitaxy (a combined melt of the components) proved incapable of producing the very thin multilayer structures required for efficient III-V devices and so MOVPE technology developed with ever increasing pace, and state-of-the-art GaAs photocathodes and field effect