From Bunsen to VLSI

150 Years of Growth in Chemical Vapor Deposition Technology

by Mark Allendorf

With these dramatic words, the German chemist Bunsen began an account in 1852 in which he described his observation that iron oxide condenses as crystals from hot volcanic gases containing hydrogen chloride (HCl). The process is the result of the following chemical reaction

$$2FeCl_3(g) + 3H_2O(g) \leftrightarrow Fe_2O_3(s) + 6HCl(g)$$

and is probably the first documented example of a process closely related to a class of manufacturing techniques generically known as chemical vapor deposition (CVD). At the time, Bunsen was more interested in the phenomenon than in materials synthesis. A few years later, a scientist by the name of St. Claire de Ville became the first person (in modern times) to put CVD to use when he formed "artificial minerals," oxides of magnesium, titanium, and tin, in his laboratory. Since that time, CVD has become an industrial tool used to produce an enormous range of materials, with either the finesse of atomic control used in molecular-beam epitaxy, or the brute force of the Acheson process, in which an electric furnace operating at 2700°C is used to make silicon carbide.

CVD technology is of key interest to many ECS members; papers on this topic appear routinely in the **Journal** and are presented in symposia at nearly every semi-annual meeting. It thus seems appropriate to commemorate
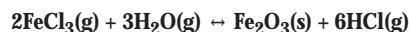
(nearly) 150 years of CVD science and technology in this anniversary issue of **Interface.**

Although the technology is old, the term "CVD" is relatively new. It was introduced by John Blocher, a member of what was then called the Electrothermics and Metallurgy Division of the ECS (now known as the High Temperature Materials Division). Blocher was leading a symposium on "vapor deposition" at the 1960 Houston meeting of the ECS and suggested "chemical vapor deposition" in order to distinguish methods employing chemical reactions from those which did not. The latter, referred to as "physical vapor deposition," included processes such as sputtering. In later articles, Blocher broadened the definition of CVD to include "any process that yields a solid product in a useful form in which the sum of the chemical kinetics and mass transport through the gas or vapor phase is significantly related to the rate of formation and structural morphology of the resulting material." This allowed aerosol processing methods, such as those used to make carbon black and titanium dioxide pigments, to be included under the general heading of CVD, and excluded solid-phase diffusion processes, such as carburizing and nitriding.

Perhaps the earliest commercial use of a CVD-like process was in the production of carbon black. This began in the 1870s when a natural-gas flame was made to impinge on a water-cooled soapstone slab. Although not a brilliant financial success (the plant burned down soon after paying for itself), the development led to modern production processes based on the same method. Today, carbon black is a major commodity and on a volume basis represents the largest use of CVD.

CVD had a high-tech future in store for it, however. Electric light bulbs invented by Edison used fragile carbon filaments whose lifetime was short. To strengthen them, Sawyer and Man in the U.S and Lane-Fox in England invented a process for depositing addi-
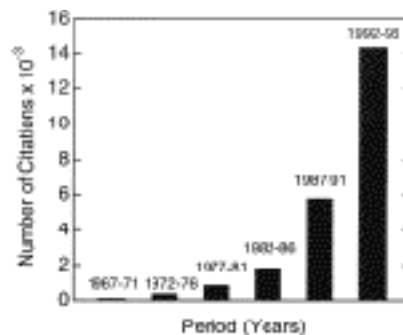

FIG. 1. *Number of references to the term "chemical vapor deposition" for various five-year periods since 1967. The number for the 1967-71 period (obtained by searching Chemical Abstracts) is 105; for the 1992-96 period, the number is 14, 344.*

tional carbon on filament surfaces. Filaments were heated in an atmosphere containing hydrocarbon gases, causing what is now referred to as as pyrolytic carbon to form. The process of St. Claire de Ville thus became much more than a scientific curiosity.

The industrial revolution created a need for other high-purity materials, particularly metals, in the latter half of the nineteenth century. Metals with improved strength, ductility, and corrosion resistance were required for a number of applications. Unfortunately, many materials of interest could not be obtained in high enough purity to achieve their ductile state. In addition, high temperatures, usually above the melting points, were needed to purify many refractory metals. Such temperatures were often difficult to achieve, especially for metals such as niobium and tungsten. However, the industrial revolution also brought an explosion of new chemistry to the world and with it, a host of useful compounds. In 1889, a British chemist by the name of Mond synthesized one of the first organometallic compounds: nickel carbonyl. A volatile liquid, it was used by him to form high-purity nickel pellets at temperatures considerably below the melting point. Motivated again by the need for improved lamp filaments, other workers used CVD processes to deposit Nb, MO, Ta, Ti, Os, W, Si, Cr, and V, as

well as carbides of these elements, in the years leading up to World War I. The recognition that organometallic compounds, such as alkyls and acetylacetonates, could be used to synthesize metals, was also made in 1914 by Weiss.

Following World War I, CVD research was renewed, producing several major developments. Perhaps most noteworthy was the invention of the iodide process (sometimes referred to as the van Arkel process), in which impure metal, containing small amounts of dissolved nitrogen or oxygen, is purified by reaction with iodine to form one or more volatile iodides. The iodides are then transported through the gas-phase to a heated tungsten filament where they decompose, forming the pure metal. Since the impurities do not form volatile iodine compounds, they are left behind. In this way, A. E. van Arkel and his colleagues, de Boer and J. D. Fast, prepared metals such as titanium, hafnium, and zirconium, free of the impurities that made them brittle. The concept laid the foundation for the purification of many other metals and is used commercially today. The method has also been extended to a number of other metals, including silicon and chromium.

The postwar period also saw patents for the production of titania and zirconia pigments via an aerosol-based CVD process, for epitaxial deposition of tungsten, and for purification of platinum-group metals using metal-carbonyls and halide gases. Again, technological developments in other fields drove much of the research. For example, the communications industry was growing rapidly at this time and needed electron tubes fabricated from high-purity refractory metals. Other researchers proposed using CVD methods to form seamless tubes and other structural forms of metals. Much of this work continued through World War II, which created a demand for improved materials for aircraft, electronics (such as radar), and other military applications.

FIG. 3. A modern single-wafer processing system for producing epitaxial silicon films. This equipment can process wafers as large as 300 mrn in diameter. (Photograph courtesy of Applied Materials)

In the 1960s, several major technological developments led to an expansion of research and the development of numerous new and sophisticated CVD methods. First and foremost, the invention of the transistor in 1947 and the development of integrated circuits made modern computers possible. This nascent technology required high-purity materials but in very thin layers, and CVD methods soon proved to be capable of producing both. In particular, epitaxial films of silicon were essential for the construction of bipolar devices, which were the first ones to be used in integrated circuits. Work by H. C. Theuerer, Harold Basseches, and others at Bell Telephone Laboratories laid the foundation for the formation of doped epitaxial silicon layers via "hydrogen reduction" of silicon tetrachloride. Later, in the 1970s, the increasing popularity of CMOS technology created even more demand for epi-Si. Today, the electronics industry is by the far the largest user of CVD technology; deposition of epi-Si alone accounts for more than $1 billion/year in revenues.
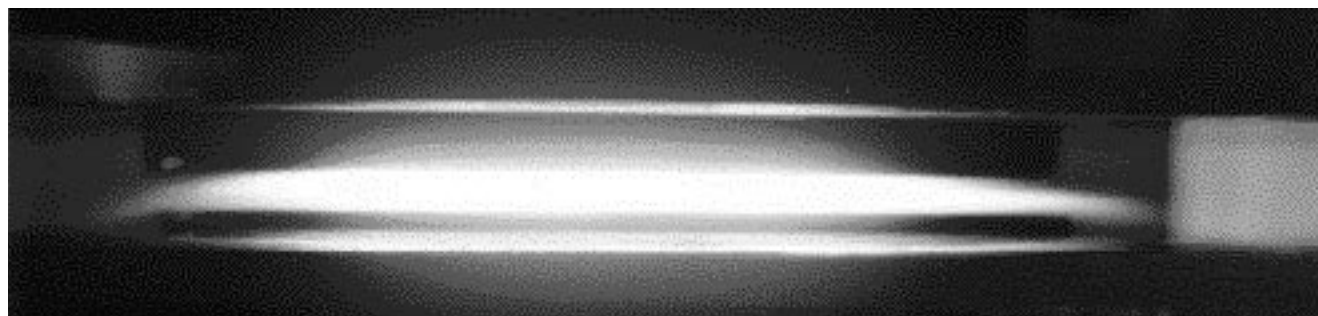
FIG. 2. High-velocity oxygen-acetylene-hydrogen flame used to deposit diamond. The inlet gas velocity is 72 m/s and the peak flame temperature is approximately 3200°K. Uniform diamond films can be deposited over areas as large as 20 cm^2. (Photograph courtesy of David Hahn, Sandia National Laboratories)

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A second important development was the invention of CVD processes using gas-phase nucleation to produce metal-oxide powders such as titania, which is used as a pigment. In the 1980s, this technology was extended to the manufacture of ultrapure silica for use in fiber-optic transmission lines. Methods for depositing refractory nitrides and carbides on machine tools and die inserts constitute the third significant CVD technology of the 1960s. High-speed cutting tools, typically constructed of cemented carbides, can reach temperatures as high as 1000°C during operation. CVD coatings used in this application are relatively thick compared with those used in IC manufacturing (~10-20 μm vs. ≤ 1 μm in integrated circuits). Titanium nitride, titanium carbide, and aluminum oxide are the most common coating materials; their use dramatically extends the life of machine tools by reducing friction and increasing oxidation resistance.

Finally, growth of the nuclear power industry during the 1960s drove the development of fluidized-bed CVD techniques. Nuclear reactors, in particular the so-called high-temperature gas-cooled reactors, required fuel pellets encapsulated in materials that allowed fission to occur without the release of radioactive byproducts. To accomplish this, fluidized-bed CVD reactors were designed to coat large volumes of powder with materials such as silicon carbide, graphite, and boron nitride.

Although the application of this technology appears to have been short-lived, due to loss of interest in the development of nuclear power, it was the initial motivation for the enduring series of CVD conferences that are sponsored by the ECS. As mentioned above, the first of these was held in 1960 in Houston. However, the current series, known as the International Conference on Chemical Vapor Deposition, began in 1967 and was cosponsored by the American Nuclear Society (ANS) and the Metallurgical Society. The first meeting was held in Gatlinburg, Tennessee and was lead by J. E. Cunningham and W. E. Dunn of Oak Ridge National Laboratories. The interest within the ECS in electronic materials made it a natural for the Society to sponsor the Second International Conference, with John Blocher and James Withers as co-chairmen. ANS involvement with the conference ended with the Third International Conference in 1972, after which it became a regular feature of ECS meetings on an approximately biennial basis. Blocher remained involved in conference organization through the Tenth International Meeting in 1987. In 1990, he was honored by the ECS at the Seattle meeting for his "leading role in maintaining the strength and continuity of the International Chemical Vapor Deposition Symposium series."

Although many ECS members may think that the recent meeting in Paris was the Society's first venture onto the European continent, two CVD conferences had already been held there: CVD-V in 1975 at Fulmer Grange, England, and CVD-VIII, in Gouvieux, France. Although these did not constitute full meetings of the Society, they served the valuable purpose of establishing a relationship between the European and American CVD communities. In 1977, European researchers, under the initial leadership of Georg Wahl, established their own regular series of CVD conferences, known as EUROCVD. At the 1997 Paris meeting, the two conferences were held simultaneously. CVD-XIV/EUROCVD-11 was the largest conference of its kind in the history of either series, with a total of 243 papers submitted, nine sessions of oral presentations, an enormous poster session (160 papers), and a 1600-plus page proceedings volume. The two organizations have pledged to work together to advertise each other's meetings and to avoid overlap and duplication by coordinating conference schedules.

The success of the CVD conferences is just one indication of the increasing interest and importance of this technology to manufacturing world-wide. Another indication is the exponential growth in the publication of papers related to CVD. A search of Chemical Abstracts reveals (FIG. 1) that only 105 papers used the term CVD between 1967-71. By the 1992-96 period, the number had grown to over 14,300!

The scope of CVD continues to expand, as evidenced by an almost incredible variety of work appearing in the literature. For example, a recent issue of **Journal** (Vol. 144 (6), 1997) contained articles on the following subjects: diamond CVD using fullerenes as the precursors (an intersection of two of the hottest fields in materials science in the last decade); control of silicon-oxide film hardness and reduction of impurities by tuning precursor reactivity (in this case, varying the number of methoxy groups) and by irradiating the substrate during deposition with ultraviolet (UV) light; development of a surface-modification resist process using polysiloxane films deposited by CVD; and a first-time report of the deposition of low-K-dielectric Teflon films, again using UV light to control film morphology.

Nearly 150 years of science and engineering have combined to make CVD one of the most versatile and important synthetic methods ever developed. It is clear that this technology will continue to play a major role in our increasingly high tech society. Beyond helping to reach the ambitious goals of the Semiconductor Industry Association (SIA) Roadmap, it will undoubtedly be used to form an expanding array of new materials with ever improving molecular and microstructural control. There should thus be no shortage of new material for presentation at future International CVD meetings. ∎

Acknowledgments

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