Chapter 1

Introduction to Chemical Vapor Deposition (CVD)

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Introduction

Chemical vapor deposition (CVD) is a widely used materials-processing technology. The majority of its applications involve applying solid thin-film coatings to surfaces, but it is also used to produce high-purity bulk materials and powders, as well as fabricating composite materials via infiltration techniques. It has been used to deposit a very wide range of materials. As indicated by the shaded boxes in Figure 1, the majority of the elements in the periodic table have been deposited by CVD techniques, some in the form of the pure element, but more often combined to form compounds.

CVD has an extensive literature, including a number of other books on the subject. The classic book by Powell, Oxley and Blocher[1] covers much of the earlier work up to the mid 1960s, while a bibliography by Hawkins[2] lists papers in CVD for the 1960-1980 time period.

The handbook by Pierson[3] contains a very useful discussion of specific materials and CVD processes, as does the book by Morosanu.[4] The books by Hitchman and Jensen,[5] and by Sherman,[6] concentrate more on silicon microelectronics applications, while the books by Stringfellow[7] and by Jones and O'Brien[8] concentrate on compound semiconductor applications. The book by Kodas and Hampden-Smith[9] and the series of proceedings volumes, represented by Sandhu et al.[10] focus on CVD of metals. A separate series of books on CVD are the proceedings of the International Conferences on CVD held every two to three years since circa 1967, primarily sponsored by the Electrochemical Society. These provide useful "snapshots" of the field at various times,[11-13] are a few of the more recent volumes in this series. Books by Vossen and Kern[14] and Smith,[15] cover CVD as parts of their larger treatments of thin film deposition.

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PERIODIC TABLE

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IV	VA	VIB	VIIB	O
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.179
11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.948
19 **K** 39.098	20 **Ca** 40.08	21 **Sc** 44.956	22 **Ti** 47.90	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.70	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.22	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (99)	44 **Ru** 101.07	45 **Rh** 102.905	46 **Pd** 106.4	47 **Ag** 107.868	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.30
55 **Cs** 132.905	56 **Ba** 137.33	57 **La** 138.9	72 **Hf** 178.49	73 **Ta** 180.948	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.09	79 **Au** 196.966	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** 227.0															

	57 **La** 138.9	58 **Ce** 140.115	59 **Pr** 140.1	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 174.96
LANTHANIDES	57 **La** 138.9	58 **Ce** 140.115	59 **Pr** 140.1	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 174.96
ACTINIDES	89 **Ac** 227.0	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (256)	102 **No** (259)	103 **Lr** (257)

Fig. 1: Periodic table, where shaded boxes indicate elements that have been deposited using CVD.

In its simplest incarnation, CVD involves flowing a precursor gas or gases into a chamber containing one or more heated objects to be coated. Chemical reactions occur on and near the hot surfaces, resulting in the deposition of a thin film on the surface. This is accompanied by the production of chemical by-products that are exhausted out of the chamber along with unreacted precursor gases. As would be expected with the large variety of materials deposited and the wide range of applications, there are many variants of CVD. It is done in hot-wall reactors and cold-wall reactors, at sub-torr total pressures to above-atmospheric pressures, with and without carrier gases, and at temperatures typically ranging from 200-1600°C. There are also a variety of enhanced CVD processes, which involve the use of plasmas, ions, photons, lasers, hot filaments, or combustion reactions to increase deposition rates and/or lower deposition temperatures. There are also many derivatives of the CVD terminology, such as metal-organic chemical vapor deposition (MOCVD)[16,17] or, less commonly, organo-metallic chemical vapor deposition (OMCVD), which are sometimes used to note the class of molecules used in the deposition process. Some practitioners chose to differentiate epitaxial film deposition from polycrystalline or amorphous film deposition, so they introduced a variety of terms that include "epitaxy" in the acronym. Two of the more common variants are organometallic vapor phase epitaxy (OMVPE)[7] and metalorganic vapor phase epitaxy (MOVPE)[18] which are often used in the compound semiconductor epitaxy literature.

CVD has a number of advantages as a method for depositing thin films. One of the primary advantages is that CVD films are generally quite conformal, i.e., that the film thickness on the sidewalls of features is comparable to the thickness on the top. This means that films can be applied to elaborately shaped pieces, including the insides and undersides of features, and that high-aspect ratio holes and other features can be completely filled. In contrast, physical vapor deposition (PVD) techniques, such as sputtering or evaporation, generally require a line-of-sight between the surface to be coated and the source. Another advantage of CVD is that, in addition to the wide variety of materials that can be deposited, they can be deposited with very high purity. This results from the relative ease with which impurities are removed from gaseous precursors using distillation techniques. Other advantages include relatively high deposition rates, and the fact that CVD often doesn't require as high a vacuum as PVD processes.

CVD also has a number of disadvantages. One of the primary disadvantages lies in the properties of the precursors. Ideally, the precursors need to be volatile at near-room temperatures. This is non-trivial for a number of elements in the periodic table, although the use of metal-organic precursors has eased this situation. CVD precursors can also be highly toxic ($Ni(CO)_4$), explosive (B_2H_6), or corrosive ($SiCl_4$). The byproducts of CVD reactions can also be hazardous (CO, H_2, or HF). Some of these precursors, especially the metal-organic precursors, can also be quite costly. The other major disadvantage is the fact that the films are usually deposited at elevated temperatures. This puts some restrictions on the kind of substrates that can be coated. More importantly, it leads to stresses in films deposited on materials with different thermal expansion coefficients, which can cause mechanical instabilities in the deposited films.

CVD processes can be categorized according to the type of:
1. Application,
2. Process and reactor used, or
3. Precursor and chemical reaction used.

The next three sections of this chapter are arranged around such subdivisions. These sections are followed by a discussion of the fundamental processes underlying CVD, such as mass transport, thermodynamics, and chemical kinetics. Finally, we present a brief analysis of the historical and current status of CVD R & D.

CVD Applications

One of the earliest examples of a large-scale CVD application was a carbonyl process for

refining of nickel, as developed by Mond, Langer, and Quincke in 1890.[19] Many of the early applications involved refining or purification of metals and a limited number of non-metals by carbonyl or halide processes. Other early applications involved deposition of coatings for wear and corrosion resistance, and the fabrication of structural shapes and components. Most of the earliest work, up to the mid 1960s, is reviewed in the book by Powell, Oxley, and Blocher.[1] Many high volume applications, such as refining and the production of powders and pigments, are obviously still important economically, but most of the recent CVD R & D effort is aimed at thin-film deposition.

There is a great deal of ongoing R & D regarding CVD of thin films used primarily for their mechanical or chemical properties. Many of these are discussed in detail in other chapters of this book, so we only briefly mention them here. Chapter 11 discusses the use of CVD films for tribological applications, chapter 13 discusses CVD films used for corrosion protection, and chapter 14 discusses protective CVD coatings for tool steels. Chapter 10 discusses the CVD of diamond, and diamond-like carbon (DLC), which has generated a tremendous interest level in the past decade (see also last section, this chapter), and has significant commercial applications. Diamond films are mainly used for their hardness, but applications utilizing its high thermal conductivity, chemical inertness, or electronic properties are also important.

A great deal of CVD R & D in recent decades, however, is focussed on the semiconductor revolution. We devote somewhat more space here to these applications, as they are not covered elsewhere in this book. CVD has been a critical enabling technology in silicon-based microelectronics; it is even used at the earliest stage during the refining and purification of elemental silicon. Depending on the device, CVD processes are used for depositing thin films of the active semiconductor material (e.g. doped Si), conductive interconnects (e.g. tungsten), and/or insulating dielectrics (e.g. SiO_2), (see Figure 2).

The communications revolution also relies on a diverse set of CVD technologies. Some components are similar to those used in silicon microelectronics, but many are unique, involving complex epitaxial heterostructures of SiGe or compound semiconductor (e.g., AlGaAs) alloys that are required to yield high frequency (1-100 GHz) device operation.[20] The communication revolution also relies on optoelectronic components, such as solid state diode lasers (another complex heterostructure device), and these devices are often grown by CVD.[7,21] Even the fiberoptic cables that transmit the optical component of the communications network are manufactured using a CVD technique to achieve the desired refractive index profile.[22]

Optoelectronic material grown by CVD has many applications outside of the communications industry. One example is for solid state lighting using light emitting diodes (LEDs). Recently, Nichia Chemical was the first company to commercialize high brightness blue and green LEDs based on group-III nitride alloys, e.g. InGaN, which are grown on sapphire substrates using CVD technology.[23] This company also introduced the first long-life blue laser diode, based on the same material and technology. In addition to the myriad of lighting and signage applications using colored LEDs, there is a growing interest in generating solid state white light sources to replace incandescent and perhaps even fluorescent sources.[24] A solid-state white light source may be achieved by combining LEDs of different wavelengths, or by pumping a phosphor with an ultraviolet LED.

Another exciting technology utilizing CVD is the production of microelectromechanical structures, or MEMS.[25] Much of the MEMS technology is derived from the silicon microelectronics technology, so it is not surprising that CVD plays a crucial role. Most MEMS devices are fabricated from polycrystalline silicon (polysilicon) films deposited on silicon wafers, with intermediate sacrificial SiO_2 layers that are later removed by chemical etching. Figure 3 shows an example of such a device, in this case a set of interlocking gears that are ~50-200 microns in diameter. Both the polysilicon and oxide are deposited using
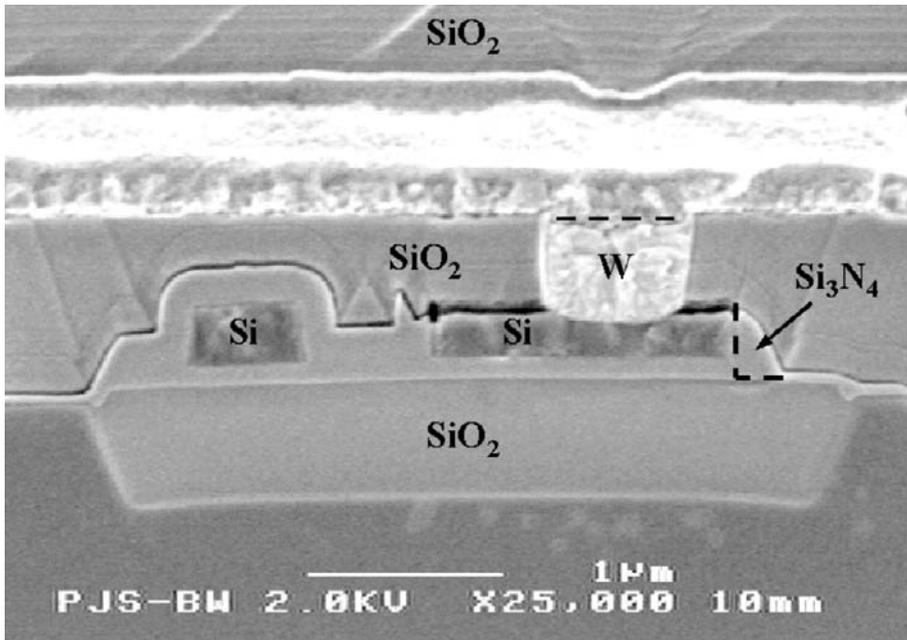
Fig. 2: Cross section of a silicon microelectronic memory circuit showing several materials deposited by CVD; polycrystalline silicon, tungsten (W), SiO_2, and Si_3N_4. Photo courtesy of Pat Shea, Sandia National Laboratories.

CVD or PECVD. The CVD steps define the structure of the device perpendicular to the silicon substrate, while numerous lithographic and etching steps define the structure in the other two dimensions. CVD is sometimes used to apply coatings to reduce friction after the 3-D structure is created. Work is also being done to integrate MEMS devices with silicon microelectronic devices on the same chip.

The field of nanotechnology has generated a lot of recent interest, and focused research programs have been initiated in almost all industrialized countries in the last five years. In 2000 the U.S. launched the National Nanotechnology Initiative, with plans to nearly double the nanoscale R & D effort.[26] Nano-technology is an extremely diverse topic, but some of the best examples of existing nanoscale R & D are in the area of epitaxial heterostructures for laser diodes and LEDs grown by CVD.[7,23,27] Many of

these devices contain two dimensional (2-D) quantum wells or superlattices composed of strained epitaxial layers that are 1-10 nm thick. An example of a strained layer superlattice is shown in Figure 4. In addition to quantum wells, laser structures such as the vertical cavity surface emitting laser (VCSEL) contain mirror stacks composed of a large number of alternating layers of semiconductor material that are typically 50-100 nm thick. The thickness of each layer often must be controlled with a precision better than 1 nm. Despite this requirement these devices can be grown routinely with relatively high yield in finely tuned and calibrated OMVPE reactors.[28] A related CVD technique that automatically yields subnanometer control is known as atomic layer epitaxy (ALE).[29]

An extension of 2-D quantum well R & D involves the generation of quantum wires (1-D) and quantum dots (0-D).[27,30] Quantum dots are
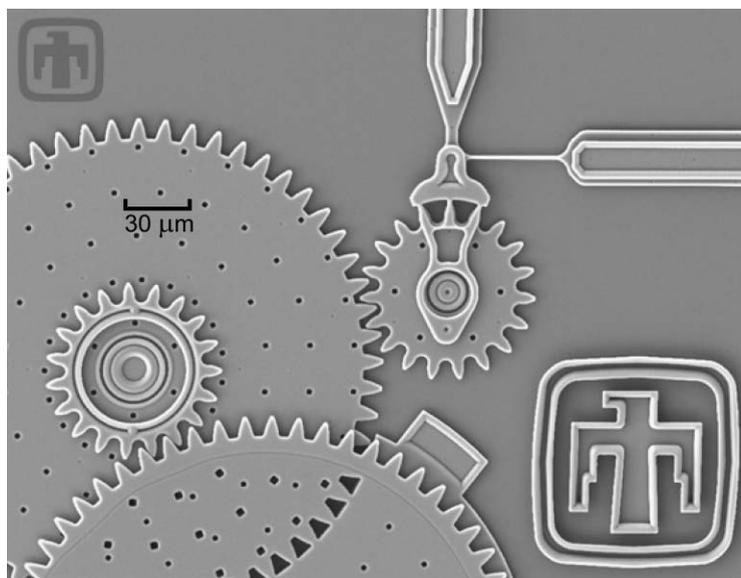
Fig. 3: Example of a silicon surface micromachined gear train. Courtesy of the Intelligent Micromachine Initiative, Sandia National Laboratories.
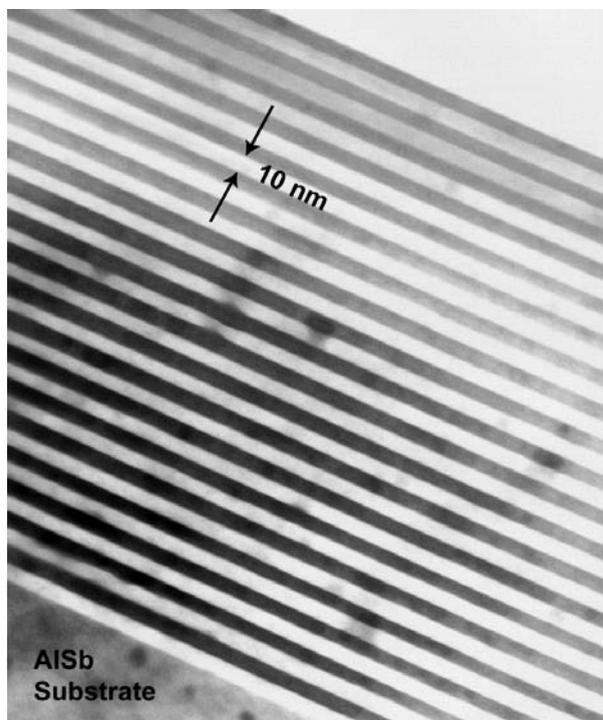
Fig. 4: Strained layer superlattice of InAsSb on InSb with 10 nm layer thickness. Photo courtesy of R. M. Biefeld, Sandia National Laboratories.
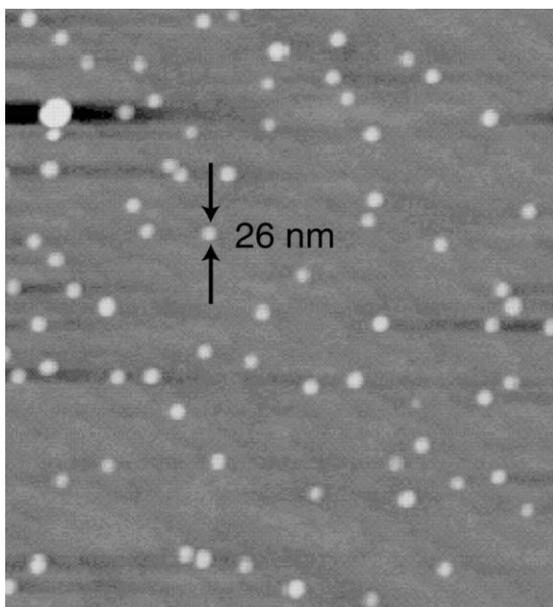
Fig. 5:   Indium arsenide quantum dots deposited on gallium arsenide by OMVPE. Photo courtesy of Jeff Cederberg and R. M. Biefeld, Sandia National Laboratories.

often considered to be artificial atoms, where the effect of quantum confinement significantly perturbs the normal bulk electronic properties of the material. One method of growing quantum dots involves depositing one material on another with a large lattice mismatch. The example in Figure 5 is InAs on GaAs(100) by CVD. Due to the interfacial properties of this highly strained layer, InAs spontaneously forms islands on the 10-nm scale with a relatively narrow size distribution. The electronic and optical properties of the InAs quantum dots are dramatically different from bulk InAs, allowing for novel device fabrication.

In addition to the numerous electronic and optoelectronic applications mentioned above, novel applications of CVD are also being used to generate macroscopic components (10 cm as opposed to 1 nm). One interesting example is the production of Ir/Re thrust chambers for liquid rocket motors (see Figure 6).[31] For this structure a thick Rhenium CVD coating is applied to a sacrificial molybdenum mandrel, which is later removed by etching. Another example is the production of large-scale infrared optical materials (ZnSe and/or ZnS up to several feet across).[32]

CVD Reactor Types

As mentioned in the introduction, CVD encompasses a wide range of reactor and process types. The choice of process/reactor is determined by the application via the requirements for substrate material, coating material and morphology, film thickness and uniformity, availability of precursors, and cost. Here, we discuss the general types of reactors used for CVD, and refer the reader to the other chapters in this and other books for detailed information on specific systems.

Hot wall reactors represent one of the major categories of CVD reactors. In such systems,

Fig. 6:   Rhenium rocket thrust chamber fabricated using CVD. Photo courtesy of B. H. Tuffias, Ultramet.[31]

shown schematically in Figure 7, the chamber containing the parts is surrounded by a furnace that heats the system. The parts are loaded into the system, it is heated to the desired temperature, then the reactive gases are introduced. The reactor may be equipped with shelves for coating many parts at once, or be sized for specific large parts. These systems are often run at very high temperatures, limited only by the materials used in constructing the furnace, and at reduced pressures, on the order of Torr to tens of Torr. Figure 8 shows a schematic for a hot-wall reactor that has been tailored to low-pressure CVD (LPCVD) batch processing in the microelectronics industry. In this case, a specialized support holds a large number (over a hundred) of closely-spaced silicon wafers for simultaneous processing. In general, hot wall reactors have the advantages of being able to process large batches of substrates, and having relatively uniform substrate temperatures and thus coating thicknesses. The primary disadvantages are that the walls get heavily coated, requiring frequent cleaning and causing particle problems, and that it involves higher thermal loads and energy usage.

Cold wall reactors are the other major category of CVD reactors. In such systems, the substrates are heated but the walls are cooled. Figure 9 shows an example of a cold wall rotating disk CVD reactor.[28,33] This system has water-cooled quartz walls, with a rotating holder for (silicon or compound semiconductor) wafers that is resistively heated from below. Other commercial cold-wall reactors include lamp heated single-wafer reactors that are widely used in microelectronics fabrication, and inductively heated horizontal flow reactors. Cold-wall reactors are often run at relatively high pressures, several hundred torr to atmospheric total

Gas Inlet

Heating
Elements

Parts
Being
Coated

Shelves

Exhaust
to Pump
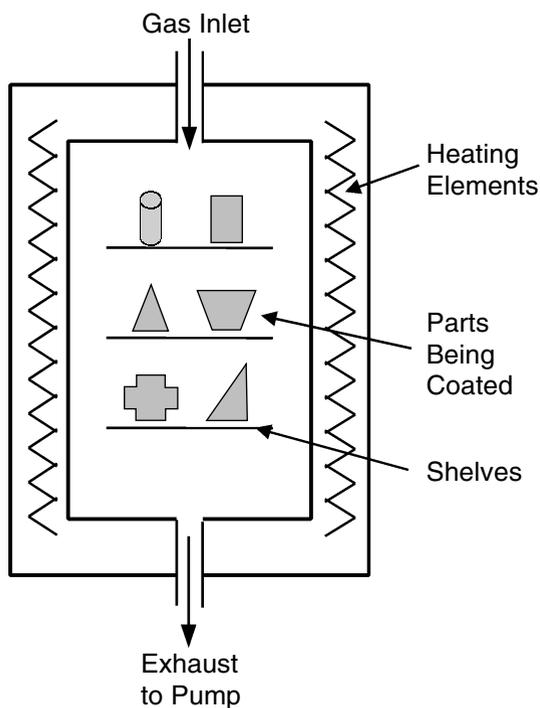
Fig. 7:   Schematic drawing of hot-wall CVD reactor used to coat multiple parts.

Gas Inlet

Heating
Elements

Wafers

Exhaust to Pump
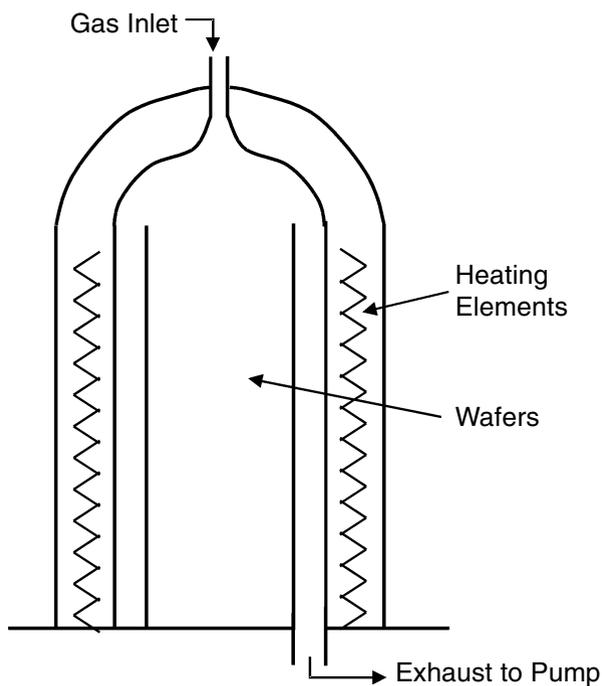
Fig. 8:   Schematic drawing of LPCVD furnace for batch processing of multiple silicon wafers.
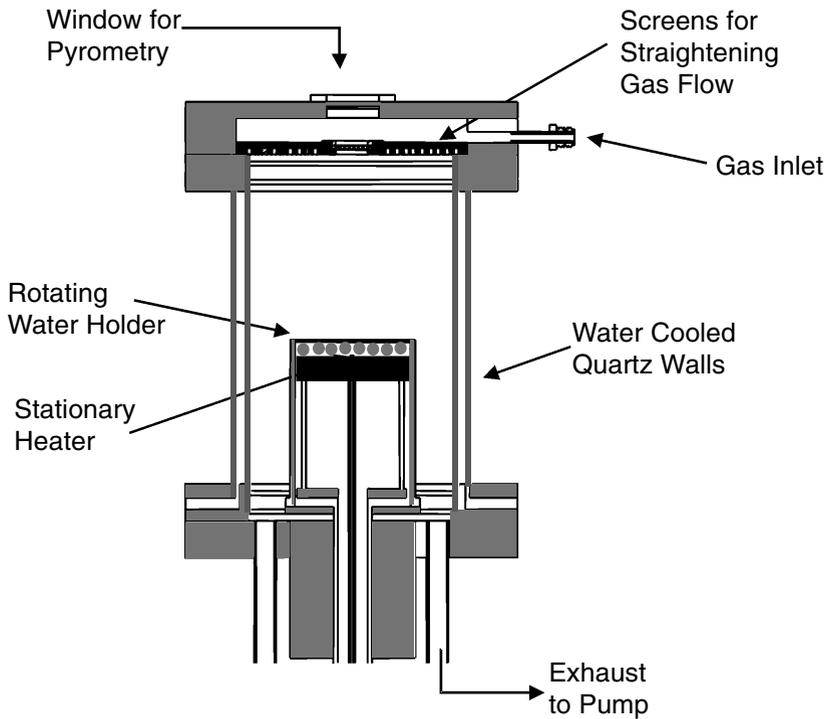
Fig. 9:   Schematic diagram of a cold-wall rotating disk CVD reactor used for depositing thin films on semiconductor wafers.

pressure, and usually have the reactive precursors diluted in a carrier gas. Most compound semiconductor CVD processes use reactors of this type. Cold wall reactors have the advantages of reduced deposition of material on the walls, which means less cleaning, lower thermal loads on the substrates because of faster heat-up and cool-down times, lower energy consumption, and the avoidance of vacuum equipment. The primary disadvantages are larger temperature non-uniformities on the substrate, which may lead to film thickness non-uniformities, the smaller batch sizes, and possible thermal stresses on the substrates if the heating/cooling is too rapid.

A specialized variation of a cold wall reactor is the continuous reactor shown schematically in Figure 10. In this system, the surface to be coated moves underneath a set of gas injectors and is heated from below. In some cases, the substrates (wafers) are placed on a belt moving over a set of rollers. In other cases, such as the large-scale application of optical coatings (i.e. low-E coatings) to glass, the moving belt could be the float-glass sheet itself. These systems are essentially open to atmosphere – the reactive gases are contained by "curtains" of inert gas on either side of the deposition zone. Such systems have the advantage that they can do very large scale production, and avoid vacuum equipment. The disadvantages are a relatively high rate of gas consumption, potential non-uniformities in film thickness, relatively low operating temperatures because of the high volumes of gas involved, and relatively low efficiency for precursor use.

Plasma-enhanced (PECVD) or plasma-assisted (PACVD) CVD, (see chapters in Refs. 5, 14, and 15), constitute a smaller category of CVD processes that also involves a variety of reactor designs. In these systems, a plasma is

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