

A
Report
On
“Chemical Vapor Deposition (CVD)”



Submitted
In
Micro manufacturing
Of
Master of technology
In
Manufacturing sciences and engineering

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ABSTRACT

Chemical Vapor Deposition (CVD) is a critical method for creating thin films, extensively utilized across industries like semiconductor fabrication, microelectronics, and advanced material science. This report presents an in-depth exploration of CVD, examining its fundamental process, where gaseous precursors undergo chemical reactions on the substrate's surface, leading to the formation of a solid thin film. The technique enables the deposition of uniform, high-quality layers with precise control over thickness, composition, and material properties, making it invaluable in high-tech applications.

The report details various CVD techniques, including Low-Pressure CVD (LPCVD), Plasma-Enhanced CVD (PECVD), and Metal-Organic CVD (MOCVD). Each variant serves specific purposes: LPCVD is favored for high-purity layers of dielectric and polysilicon materials, PECVD is ideal for applications requiring low-temperature processing, and MOCVD is commonly used in fabricating compound semiconductors like gallium arsenide (GaAs), which are essential in optoelectronics and other high-performance devices.

Highlighting CVD's role in semiconductor device production, this study underscores its importance in constructing insulating, conductive, and protective layers crucial for microchips and MEMS components. Additionally, CVD's strengths, including its ability to produce highly uniform films with excellent surface coverage, are discussed, along with its challenges, such as handling hazardous by-products and the need for specialized equipment.

Chapter 1
INTRODUCTION

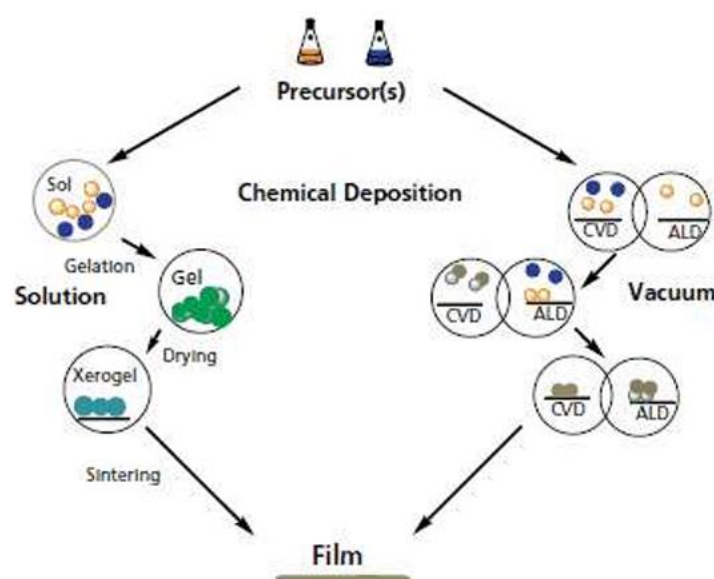
INTRODUCTION

Chemical deposition techniques are essential for designing and fabricating a variety of advanced devices. These methods enable the production of solid materials with high quality and exceptional performance, primarily through the formation of thin films. Compared to physical deposition methods, chemical techniques offer several advantages, such as improved conformal coverage, higher throughput, greater flexibility in material composition, and more versatile deposition directions.

These techniques are broadly categorized into two main types:

1. **Gas-Phase Techniques:** This category includes Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD). Both processes involve the transport of volatile compounds in a gaseous state to a substrate's surface, where they react and form a thin film.
2. **Liquid-Phase Techniques:** This group primarily consists of Chemical Solution Processing, also known as Sol-Gel Processing, where liquid precursors are used to transfer material to the substrate.

In both types, the fundamental approach is similar: precursors, which are specific chemical compounds involved in the reaction, are directed to the substrate surface, where they undergo chemical modifications to create the desired material. The deposition process relies on these precursor compounds, which facilitate the formation of films by reacting on or near the substrate surface.



Chemical Vapor Deposition (CVD)

In CVD, the substrate—commonly referred to as a wafer—is placed in a reaction chamber and exposed to one or more volatile precursor gases. These gases undergo a chemical reaction, causing the desired material to deposit on the substrate as a thin film. The reaction often generates by-products, which are carried away by a continuous flow of gas through the chamber.

CVD is widely employed in micro-device fabrication due to its ability to deposit materials in various forms, including monocrystalline, polycrystalline, amorphous, and epitaxial layers. Some commonly deposited materials using CVD include sulfides, oxides, nitrides, carbides, and silicide's

Chapter 2

LITERATURE REVIEW

TYPES OF CVD:

CVD is divided into several categories based on different criteria which are as follows:

1. On the basis of OPERATING PRESSURE:

- i. Atmospheric pressure CVD (APCVD)- Deposition is done at atmospheric pressure. This process has advantage of fast deposition at low temperature. But the major disadvantage is low purity.
- ii. Low pressure CVD (LPCVD - Reduced pressure is required for good uniformity of film because it ensures the reduction of unwanted gas-phase reactions). The pressure ranges from 30 to 250 pa
- iii. Ultrahigh Vacuum CVD (UHVCVD - The pressure is significantly reduced upto or less than 10–6 pa ($\sim 10^{-8}$ Torr).

The CVD which is used prominently in modern world is either LPCVD or UHVCVD. The reduced pressure in the reaction chamber during LPCVD and UHCVD processes enhances the gas diffusivity, which reduces the unwanted gas phase reactions and improving coating uniformity.

2. On the basis of Physical Characteristics Of Vapour.

- i) Aerosol assisted CVD (AACVD) – In this the precursors are transported to the substrate by the means of liquid/gas aerosol, which is generated with the aid of ultrasonic treatment. This technique is employed when we have non-volatile precursors.
- ii) ii) Direct liquid injection CVD (DLICVD) – The precursor in this CVD is in liquid form or solid dissolved in suitable solvent. This liquid precursor is injected into the vaporization chamber directed towards the injectors. The precursor vapors in the process are transported to the substrate just as in the case of classical CVD. This technique is being used in the case of solid or liquid precursors. This technique is also an aid in achieving high growth rates due to perfect control of precursor flow (control of the liquid flow). DLICVD also has advantage of Accurate control of doping level

3. On the basis of Plasma Methods.

- i) Plasma Enhanced CVD (PECVD) – This process utilizes plasma to enhance reaction rate of the precursors. This allows the deposition at lower temperature, which is a very critical parameter in the manufacture of semiconductors. Lower temperatures also inhibit the deposition of organic coatings such as plasma polymers, which have been used for nanoparticle surface fictionalization.
- ii) Microwave plasma assisted CVD (MPCVD) - This process utilizes a microwave plasma source.
- iii) Remote plasma-enhanced CVD (RPECVD) – this is similar to PECVD except that in this wafer (substrate) is not directly placed in the plasma discharge region. This has a benefit that we can reduce the processing temperature down to room temperature.

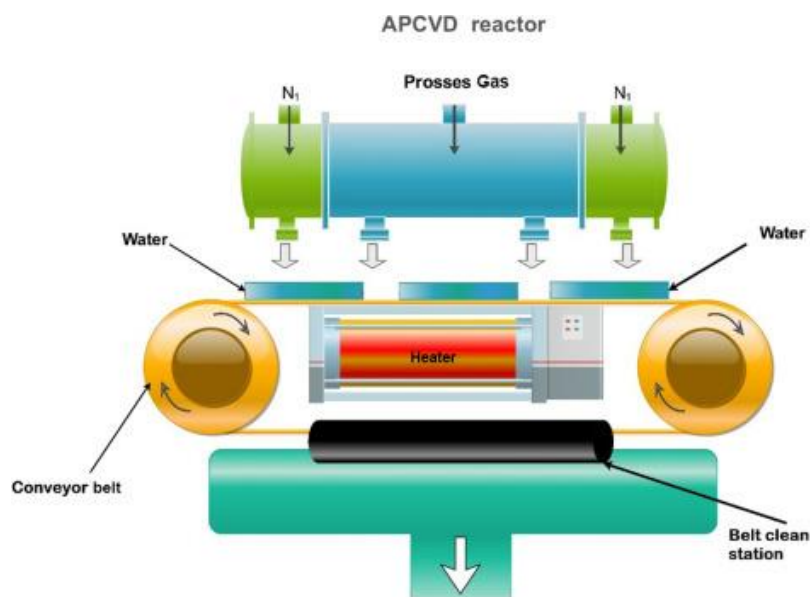
There are several other kinds of CVD processes such as Atomic layer CVD, Combustion CVD, Hot filament CVD, Hybrid Physical-CVD, Metal organic-CVD, rapid thermal-CVD, vapor phase epitaxy and Photo-Initiated CVD. The most frequently used CVD techniques in the modern times are LPCVD and PECVD. So let us learn about them more in the forthcoming sections.

2.1 Low pressure chemical vapor deposition (LPCVD)

It is that chemical vapor deposition technique in which heat is used to initiate the reaction of precursor gas onto the substrate (solid). In this deposition of thin films on semiconductor substrate occurs usually ranging from a few nanometers to many micrometers. The reaction occurring is responsible for the formation of solid phase material. Low pressure ensures that no unwanted gas phase reaction occurs and also the uniformity across the substrate enhances. Hot walls operation has an advantage that it allows batch processing and hence a better throughput. They also increase thermal uniformity and hence as a result, uniform films are obtained.

But it has a disadvantage also. In this process, the deposition also occurs on the hot furnace walls which bound us to frequently clean the chamber and to replace the tube so as to avoid particle contamination in the subsequent deposition. Cold walled reactors have an advantage on this part because they are low maintenance as there is no deposition on the chamber walls. In LPCVD, tube is evacuated to low pressures, in the range of 10 mTorr to 1 Torr.

Now when the tube is under vacuum, it is heated up to the required deposition temperature (which is the temperature at which the precursor gas starts decomposing). Temperatures which are attained in LPCVD generally lie in the range 425-900°C depending upon the process and the reactive gases being used. After attaining the desired temperature, gas is inserted into the tube. This gas then diffuses in the tube and reacts with the surface of the substrate which leads to formation of the solid phase material. Excess gas if any is then pumped out of the tube and goes through the abatement system.

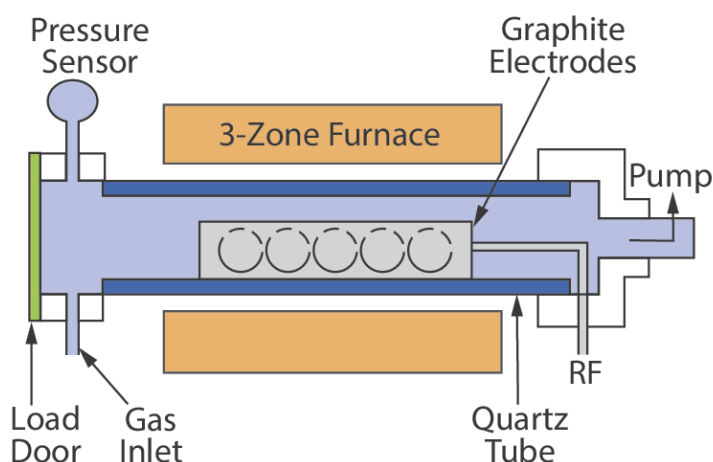


APPLICATIONS – LPCVD is mostly employed to deposit polysilicon (used for gate contacts), silicon nitride and silicon dioxide (used for isolation). Most LPCVD films are with good conformal step coverage and offer good sidewall protection.

2.2 Plasma enhanced chemical vapor deposition (PECVD)

This is the CVD process which uses plasma (cold plasma) to deposit thin films from a gas state to a solid state on a substrate. The reaction involved in this process occurs after the creation of plasma of the reacting gases. This plasma is created by application of RF (AC) frequency or DC discharge between two electrodes. The space between the electrodes is filled with the reacting gases. Through this process, we can deposit films on substrates at lower temperatures than that of standard CVD.

The plasma used for processing is operated at pressures between millitorr to few torr. Since the electrons are very light so they could be maintained at a very high equivalent temperatures (tens of thousands of kelvins) equivalent to several electron volts average energy whereas the neutral atoms remain at the ambient temperature. These highly energetic electrons are efficient to induce many processes that would otherwise be very difficult to process at low temperatures, such as dissociation of precursor molecules and the creation of huge amount of free radicals. Another benefit of deposition within a discharge arises from the fact that electrons are more mobile than ions. Due to this, plasma becomes the most positive among the things it is in contact with. The difference of the voltage between plasma and the objects in its contacts generally occurs across a thin sheath region. Ionized atoms or molecules diffuse to the edge of the sheath region. They feel an electrostatic force and are accelerated towards the neighboring surface.



APPLICATIONS –

It has many important applications in material deposition. It has been used commercially to deposit following films:

- Oxides and Nitrides of Silicon (SiO_x , SiN_x and SiO_xN_y) deposition for a wide range of applications including photonics structures, passivation, hard mask, etc.

- Amorphous silicon (a-Si:H)
- Tetraethyl orthosilicate (TEOS SiO_2) with conformal step coverage, or void-free good step coverage
- Silicon Carbide (SiC) • Diamond-like carbon (DLC)

ADVANTAGES:

- Low operating temperature.
- Uniform coating of different shapes.
- Good step coverage.
- High packing density.
- Film characteristics as a function of depth.
- Less stress.

DISADVANTAGES:

- Precursors are toxic and so are the byproducts.
- Equipment is not economical.
- Capacity is limited.
- Contamination occurs from precursor and carrier molecules.
- Stoichiometry is hard to obtain.

2 ATOMIC LAYER DEPOSITION

ALD is a process in which film is grown by repeated exposure of alternate gaseous species (referred to as precursors) on the substrate. Unlike the case of CVD, all the precursors are not present in the chamber simultaneously, but are inserted in a series of sequential and non-overlapping pulses. In each of these pulses, the precursor reacts with the surface in such a limiting way that the reaction self stops when all the reactive sites present at the surface are occupied.

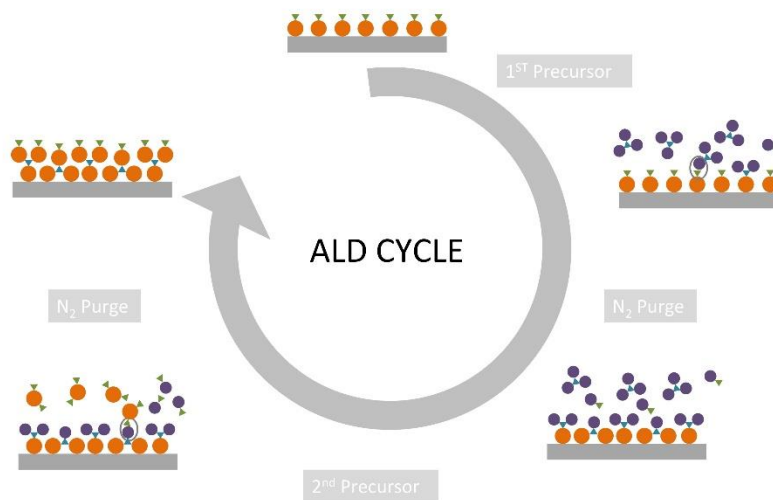
The maximum amount of material deposited on the surface after a single exposure to all of the precursors (known as an ALD cycle) can be only estimated by the nature of precursor-surface interaction. To grow uniform and high precision films on large and complex substrates, one needs to vary the number of cycles.

ALD is considered to be one of very good deposition methods which have the potential to grow very thin, conformal films with controlled thickness and composition at the atomic level.

UNDERLYING PROCESS:

In a typical ALD process, a substrate is exposed to two reactants A and B in a sequential way such that no overlapping is there. Unlike other techniques such as chemical vapor deposition (CVD), where thin film grows in a steady-state process, in ALD each reactant reacts with the surface in a self-limited way. The reactant molecules can react only with a limited number of reactive sites on the surface. As soon as all such sites are consumed in the reactor, the growth stops.

The remaining reactant molecules are ejected out and only then reactant B is inserted into the reactor. By this kind of alternating exposures of A and B, a thin film is deposited. This process is shown in the figure below. Therefore, when describing an ALD process, one defines both dose times (the time a surface is being exposed to a precursor) and purge times (the time in between doses for the precursor to empty the chamber) for each precursor. The dose-purge-dose-purge sequence of a binary ALD process constitutes an ALD cycle. ALD processes are described in terms of their growth per cycle.



APPLICATIONS:

ALD can be used in various applications including,

- High-k gate oxides
- Storage capacitor dielectrics
- Pinhole-free passivation layers for OLEDs and polymers
- Passivation of crystal silicon solar cells
- High aspect ratio diffusion barriers for Cu interconnects
- Adhesion layers
- Organic semiconductors
- Highly conformal coatings for microfluidic and MEMS applications
- Other nanotechnology and nano-electronic applications
- Coating of nanoporous structures
- Fuel cells, e.g. single metal coating for catalyst layers
- Bio MEMS

ADVANTAGES:

ALD produces film of atomically controlled thickness. Also, the growth of different multilayer structures is forthright. Due to the sensitivity and precision of the equipment, it is an asset to those in the field of microelectronics and nanotechnology in producing small, but efficient semiconductors. ALD is usually run at lower temperatures. The lower temperature is beneficial when working with fragile substrates, such as biological samples. Some precursors that are thermally unstable can also be used as long as their decomposition rate is relatively slow.

DISADVANTAGES:

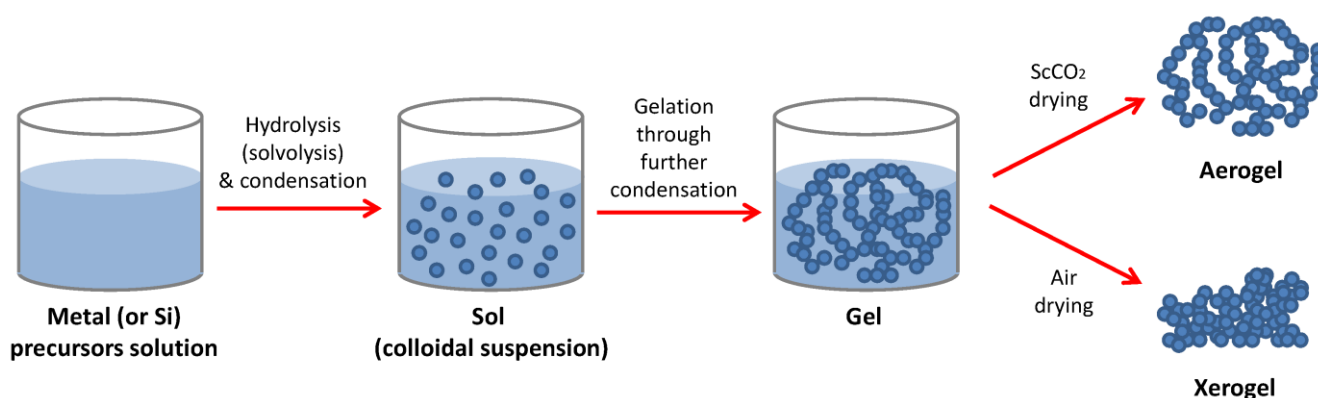
High purity of the substrates is very important, and so high costs will follow. Though this cost is not much relative to the cost of the equipment needed but one needs to perform several trial runs before finding out the apt conditions that favored their desired result. So it is not much economically viable. Also ALD is a very slow process and can be effectively used for substrates used in microelectronics and nanotechnology because their thick atomic layers are not needed. There are some chemical limitations as well. Precursors which are used should be volatile but not subject to decomposition. So this imposes a limitation on the substrates that can be used.

3. CHEMICAL SOLUTION PROCESSING OR SOL GEL PROCESSING:

SOL-GEL is a chemical solution process used to produce ceramic or glass material in the form of thin films, fibers or powders. This method is generally used for deposition of oxides specially oxides of silicon and titanium. The term sol-gel refers to a process in which solid nanoparticles dispersed in a liquid (a sol) gather together to form a continuous three-dimensional network extending throughout the liquid (a gel). A sol is a colloidal (the dispersed phase is so small that gravitational forces do not exist; only Van der Waals forces and surface charges are present) or molecular suspension of solid particles or ions in a solvent. A gel is a semi-rigid mass which is formed when the solvent from the sol begins to evaporate and the particles or ions which are left behind start to join together in a continuous network.

UNDERLYING PROCESS

The precursors that are used in sol-gel process are typically metal alkoxides and metal chlorides, which undergo hydrolysis (this is a process where a chemical compound is broken down by reacting with water). The sol then proceeds towards the formation of an inorganic network which contains a liquid phase called gel. Then formation of metal-oxo (M-O-M) and metal hydroxo (M-OH-O) polymers starts in the solution. These form because formation of metal oxides involves connecting the metal centre with these groups. Then the drying process starts which remove the liquid phase from the gel thus forming a porous material. Then thermal treatment may be given to enhance polycondensation and the mechanical properties.



APPLICATIONS:

- It is used in ceramics manufacturing processes, as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes.
- Sol-gel derived materials have various applications in optics, electronics, energy, space, (bio) sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology. One of the more important applications of sol-gel process is to carry out Zeolite synthesis.
- Other elements (metals, metal oxides) can be easily incorporated into the final product and the silica sol formed by this method is very stable.
- Other products manufactured with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration, pervaporation and reverse osmosis.

ADVANTAGES:

- It produces thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
- It produces thick coating to provide corrosion protection performance.
- It can easily shape materials into complex geometries in a gel state.
- It can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed and dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition is highly controllable.
- It can have low temperature sintering capability, usually 200-600°C.
- It can provide a simple, economic and effective method to produce high quality coatings.

DISADVANTAGES:

- Despite its advantages, sol-gel technique possesses some industrial limitations which are, weak bonding, low wear-resistance, high permeability, and difficult controlling of porosity.
- Generally, the limit of the maximum coating thickness is 0.5 μm when the crack-free property is a critical requirement.
- The trapped organics with the thick coating quite often result in failure during thermal process.
- The present sol-gel technique is substrate-dependent, and the thermal expansion mismatch limits the wide application of sol-gel technique.

Chapter 3

Directions for Future Research and Development

Directions for Future Research and Development in Chemical Vapor Deposition (CVD)

1. Enhanced Process Control and Monitoring:

- Real-Time Diagnostics: Develop advanced sensors and real-time monitoring systems to measure parameters such as temperature, gas flow, and deposition rate with high accuracy. This can improve process reliability and enable dynamic adjustments during deposition.
- In-Situ Characterization: Explore in-situ characterization techniques like spectroscopic ellipsometry and Raman spectroscopy for real-time analysis of film composition and thickness, which can enhance control over deposition uniformity and quality.

2. CVD for Complex and Multilayer Structures:

- Gradient and Multilayer Deposition: Advance CVD processes to achieve gradient coatings or multi-layered films with precisely controlled interfaces, which are essential in semiconductor and energy applications.
- Integration with 3D Nanostructures: Develop CVD techniques capable of uniformly coating 3D nanostructures and high-aspect-ratio features, which are increasingly required in fields like microelectronics and catalysis.

3. Low-Temperature CVD Processes:

- Plasma-Enhanced and Catalytic CVD: Continue research on Plasma-Enhanced CVD (PECVD) and catalytic processes to enable deposition at lower temperatures, making CVD compatible with heat-sensitive substrates such as polymers and flexible electronics.
- Hybrid Approaches: Investigate hybrid techniques that combine CVD with physical vapor deposition (PVD) or atomic layer deposition (ALD) to lower thermal requirements while maintaining high film quality.

4. Green and Sustainable CVD Processes:

- Development of Eco-Friendly Precursors: Research eco-friendly and non-toxic precursors to reduce environmental impact, especially as stringent environmental regulations become more common.
- Minimizing Hazardous By-Products: Develop methods for capturing or recycling hazardous by-products, reducing waste, and lowering the environmental footprint of CVD processes.

5. CVD for Emerging Materials:

- 2D Materials: Advance CVD processes to deposit 2D materials like graphene, hexagonal boron nitride, and transition metal dichalcogenides with precise control over thickness and crystalline quality.

- Oxide and Perovskite Films: Explore CVD methods for oxide and perovskite films to enhance applications in photovoltaics, batteries, and sensors, where these materials offer high functionality and efficiency.

6. Scalability and Cost Reduction:

- Scaling for Large-Area Applications: Develop scalable CVD methods suitable for large-area applications, such as display technologies and solar panels, where uniformity and efficiency across large substrates are critical.
- Cost-Effective Systems and Equipment: Innovate to design CVD systems with reduced energy consumption, lower material costs, and minimal maintenance requirements to make the technology more economically viable at industrial scales.

7. Integration with Emerging Technologies:

- 3D Printing and Additive Manufacturing: Integrate CVD processes with additive manufacturing techniques to enable coatings and material modifications directly onto printed components, opening possibilities in aerospace and biomedical applications.
- Quantum and Photonic Devices: Tailor CVD processes for applications in quantum computing and photonics, where material purity, defect control, and precise layer thickness are crucial for performance.

By addressing these research directions, CVD technology can expand its applications, improve sustainability, and meet the demands of emerging fields and next-generation devices.

Chapter 4

SUMMARY

Summary of Chemical Deposition Techniques

1. Overview of Chemical Deposition Techniques:

- A detailed overview of various chemical deposition techniques has been provided, outlining the processes used to deposit thin films and coatings via chemical reactions.

2. Advantages of Chemical Techniques over Physical Techniques:

- The benefits of chemical deposition techniques in comparison to physical deposition techniques have been highlighted, focusing on aspects such as lower energy requirements, ability to coat complex geometries, and superior film uniformity at the atomic level.

3. Modern Chemical Deposition Techniques:

- Advanced chemical techniques, such as Low-Pressure Chemical Vapor Deposition (LPCVD) and Plasma-Enhanced Chemical Vapor Deposition (PECVD), have been explained. Their advantages over traditional CVD processes include:
 - LPCVD: Lower operating pressures that lead to enhanced film uniformity and higher step coverage.
 - PECVD: Utilizes plasma to reduce the deposition temperature, making it suitable for sensitive substrates and resulting in improved adhesion and film density.

4. Atomic Layer Deposition (ALD) for Precision Thin Films:

- The Atomic Layer Deposition (ALD) technique has been explored in depth, emphasizing its significance in achieving precise control over film thickness at the atomic scale.
- ALD's stepwise deposition process ensures uniformity and conformity, even on complex 3D surfaces, making it essential for applications requiring nanometer-level thickness control.

5. Sol-Gel Technique:

- The Sol-Gel method has been broken down into a step-by-step description, detailing the process of transforming a liquid precursor into a solid thin film through gelation and drying stages.
- Economic advantages of the Sol-Gel technique have been discussed, including its cost-effectiveness for large-scale production and compatibility with diverse materials.

Each technique is thoroughly described, along with its unique applications, advantages, and role in modern thin film and coating technology.