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Overview of Chemically Vapor Deposited (CVD) Polymers

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1.1

Motivation and Characteristics

Chemical vapor deposition (CVD) is a powerful technology for surface engineering. When combined with the richness of organic chemistry, CVD enables polymeric coatings to be deposited without solvents [1–3]. The implantation of biomedical devices into humans, the stable functioning of printed circuit boards in harsh environments, and long-lasting, highly lubricious surfaces on industrial parts are just a few examples of the applications which employ CVD polymers. Research for CVD polymers has been undertaken in a diverse array of fields that include biotechnology, nanotechnology, optoelectronics, photonics, microfluidics, sensing, composites, and separations.

In CVD polymerization, gas phase monomers are converted directly to thin solid macromolecular films. By eliminating the need to dissolve macromolecules, CVD allows the synthesis of insoluble polymers and highly crosslinked organic networks. CVD also enables the polymerization of monomer units that undergo unwanted side reactions in solution and copolymerization of pairs of monomers that lack a common solvent.

CVD polymer films can be applied to nearly any substrate. Actually, for certain polymers and certain substrates, CVD polymerization can be the sole fabrication option. Low surface temperatures allow CVD polymers to be grown directly on fragile objects such as tissue paper and porous polymeric membranes. CVD is ideal for substrates that swell, dissolve, or otherwise degrade in solvents or for substrates that cannot withstand the high temperatures of “spray and bake” melt processing. This versatility is in contrast to, for example, self-assembled monolayers (SAMs) that are compatible only with specific surfaces, such as gold.

Monitoring during CVD polymerization allows for the *in situ* determination of growth rate and for film growth to be terminated when a precise thickness is reached. High deposition rates ($>1 \mu\text{m min}^{-1}$) and film thickness ($>200 \mu\text{m}$) have been reported, as have ultrathin pinhole-free CVD polymer layers ($<10 \text{ nm}$). Such

ultrathin pinhole-free films are difficult to achieve by solution processing because of de-wetting, liquid thinning, and surface tension effects. Ultrathin layers are also problematic/challenging in melt processing because of the large sizes of the polymer particles which are initially sprayed on.

1.1.1

Quality

For the highest quality polymer films, CVD is the method of choice, even for layers that can be formed by other means. Low impurity levels are possible for vapor deposited films since the low molecular weight reactants utilized can be purified to a high degree. In contrast, when a thin film is cast from a liquid phase solution of polymer dissolved in a solvent, a variety of unintended impurities and intentional additives are typically present, as sodium, excipients, and glidants. When dried, these species remain behind, reducing the purity of the polymer film. Additionally, the removal of the solvent is generally not fully complete and this residual solvent can have significant effects on the film properties, such as lowering the glass transition temperature due to plasticization effects.

1.1.2

Conformality

A uniform thickness of film over every contour of a geometric feature is termed conformal coverage. Conformal coverage is essential for substrates of practical interest, which have micro- and/or nano-scale topography. Conformality results from vapor phase reactants (i) that undergo isotropic diffusion and display a low probability of “sticking” during a single collision with the surface, or (ii) that undergo self-limiting surface reactions. In contrast, achieving conformality is challenging for solution processing. Surface tension can drive the formation of liquid bridges that prevent penetration of the coating into the geometric feature, leaving behind voids. Alternatively, liquid solutions can well up in the bottom of the features, display meniscus formation, and show thinning behavior on the side walls of the features.

Conformal organic functionalization finds utility for micro- and nano-structured surfaces for microelectronics, organic electronics, microelectrical and mechanical systems (MEMS), microfluidic devices, and energy storage and harvesting applications; the encapsulation of micro- and nano-particles; and the chemical modification of the internal surfaces of porous materials, including foams and membranes. The conformal coating of rough fibrous substrates, such as paper and textiles, results in a surface modification completely around each fiber, yet leaves the regions between fibers open, thus maintaining both high surface area and breathability. This capability opens the possibility for device formation on inexpensive and highly utilizable everyday substrates.

1.1.3

Durability

Durability is paramount in the majority of applications for polymeric coatings. The formation of insoluble crosslinked organic networks by CVD is one synthesis strategy for achieving durability. A second strategy is covalent bond formation at the interface, which grafts the CVD film to its underlying substrate. These two strategies have been employed both independently as well as in combination.

Using monomers with multiple propagation sites allows for the direct deposition of crosslinked organic thin film by CVD. For example, CVD biopassive films resulting from the use of a trivinyl monomer have displayed excellent dielectric performance under continuous electrical bias and soaking in saline solution for at over 9 years. Crosslinking can also improve mechanical properties. Moreover, if the level of crosslinking is below the percolation of rigidity limit, the films remain flexible.

To achieve grafted interfaces that can resist delamination, surface sites must be activated for reaction with the CVD monomers. Desirable active sites on the surface include unpaired electrons, also known as free radicals or dangling bonds, as well as specific chemical functional groups, particularly vinyl groups. The most desirable strategies for forming active surface sites are carried out in the CVD chamber immediately prior to film growth, allowing the overall process to remain as a single step and also allowing a high-quality interface formation in the controlled environment of the reactor.

1.1.4

Composition

The organic functional groups of CVD polymers provide systematic control over surface properties including, but not limited to, wettability, lubricity, adhesion, and biocompatibility. Through selection of the appropriate monomer(s), CVD films can be optimized for a variety of surface and bulk properties including chemical inertness, corrosion resistance, thermal and UV stability, mechanical stability, coefficient of friction, hydrophobicity, permeability to gases, low dielectric constant, electrical conductivity, and also for biocompatibility, biopassivation, biofouling resistance, and biostability.

The chemical specificity of the functional groups of CVD polymers is valuable for applications in sensing and separations. Additionally, the biological specificity that can be achieved with CVD polymers has broad potential in medicine and biotechnology, and for applications including biosensors, controlled drug release, implantable medical devices, tissue engineering, biometric surfaces, and medical diagnostics. Surfaces with more than one functional group, the so-called multi-functional surfaces, have been fabricated both by CVD copolymerization and via patterning strategies on multilayer CVD polymer stacks.

Functional organic moieties at the surface of CVD polymers can also be utilized for the specific binding of molecules and particles. Fluorescent dyes, biological

growth factors, and antibodies have all been successfully attached to the surfaces of CVD polymers, as have inorganic nanoparticles including metals and quantum dots.

While, inorganic layers typically have fixed thickness, some organic materials display dynamic thickness variations in response to external changes in electrical fields, magnetic fields, temperature, pH, or during exposure to specific chemical or biological molecules. Thus, devices incorporating organic materials can be designed to change dimension for transducing chemical events into electrical or optical responses. To obtain this responsive behavior requires a high concentration of organic functional groups achievable by polymer CVD.

By simply changing the ratio of gases introduced into a CVD reactor over the course of the process, film composition can be graded or layered during growth upward from the substrate. Hence, the concentration of specific organic functional group displayed at the surface of the film can differ from the concentration in the underlying layer. This feature has made it possible to deposit antibiofouling layers where the key zwitterionic moiety is concentrated at the top surface of the film. The ability to independently optimize the properties of the underlying film from the density of the surface functionalization moieties is an important design feature of the CVD polymerization method.

1.2

Fundamentals and Mechanisms

CVD processes are controlled by the introduction rates and the types of the feed gases as well as the conditions inside the reaction chamber, including partial pressures, temperatures, electric fields, and photon fluxes [4–6]. Homopolymer CVD films result from feeding only one monomer, while CVD copolymers result from introducing a mixture of monomers. Additional species may be introduced along with the monomer(s) in order to (i) promote the desired chemical reactions, (ii) inhibit unwanted reactions, or (iii) simply to function as an inert diluent. For reactants, which are not gases, vapors are produced from volatile liquid or solid sources. In the CVD chamber, one or more chemical reactions yield a thin solid polymeric layer as the desired reaction product. Any by-products of a volatile reaction are pumped out of the CVD chamber. For the majority of CVD polymer process, the reactor chamber is operated at modest vacuum levels, but some operate at atmospheric pressure.

1.2.1

Gas Phase and Surface Reactions

Chemical reactions distinguish CVD from physical vapor deposition processes such as evaporation and sputtering. Physical vapor deposition is compatible with small organic molecules but is challenging for macromolecules, as the decomposition of a polymer often precedes its vaporization. Chemical reactions

in CVD processes can occur both in the gas phase and at the surface. For the homogeneous gas phase reactions, the reaction kinetics and equilibria depend on the partial pressures of the reactants and the gas phase temperature. Similarly, the rates and equilibrium concentrations associated with the heterogeneous reactions are determined by surface concentrations and the surface temperature. The surface concentration of a reactant can approach, or even exceed, a monolayer. At these high surface concentrations, the film deposition rates can become quite fast, even though the partial pressure of the reactant in the gas phase may be quite low. In this situation, the surface can be viewed as a means to concentrate the reactant to liquid-like concentrations, albeit only in a very thin surface layer.

CVD processes comprise a series of chemical and physical steps. For a surface reaction, the reactants must diffuse through the gas phase to arrive at the surface, adsorb on the surface, and then undergo chemical reaction. Any volatile products must desorb from the surface and diffuse away. The overall rate of the CVD process can be controlled by any one of these individual steps. Understanding which step is rate limiting is essential for optimizing the CVD process. For example, if the surface reaction is rate limiting, raising the surface temperature while holding all the other conditions constant will increase the film deposition rate. However, CVD polymerization rates are often observed to decrease as the surface temperature rises. This behavior is consistent with the rate limiting step being the adsorption of the reactant to the surface.

Solid films formed by surface reactions are typically desired over films formed by the agglomeration of particles formed by gas phase reactions. The latter are powdery deposits that are often quite rough and lack cohesion. Solid particles impinging on the surface are also a potential source of pinhole defects.

1.2.2

The Monomer Saturation Ratio

Two important parameters for CVD polymerization are the partial pressure of the monomer, P_m , and the saturation pressure of the monomer at the temperature of interest, P_{sat} . The saturation ratio, S , is equal to P_m/P_{sat} , and determines (i) the concentration of monomer absorbed on the surface, (ii) the film growth rate, (iii) the number-average molecular weight of the polymer film formed, and (iv) the degree of conformality achieved. For example, monolayer coverage for an adsorbed vinyl monomer has been observed at $S = 0.35$.

For $S = 1$, a liquid will be in equilibrium with the monomer vapor. Formation of a liquid in the CVD system is typically undesirable as it may necessitate physical cleaning of the reactor or pumping the reactor out for a long time so that the residual condensate does not introduce subsequent run to run process variability. Condensation occurs at cold spots, including regions cooled by the expansion of a gas. Condensation can also result from temporary increases in P_m , which can occur when system valves open and close. To avoid condensation, CVD polymerization often operates with S significantly below unity. However, with care,

CVD polymer synthesis can be carried out at high values of S , resulting in both extremely high deposition rates and high molecular weight films.

1.2.3

Process Simplification and Substrate Independence

For polymers applied to a surface by any number of well-known solution-based methods including spin-coating, dip-coating, and ink-jet printing, a post-deposition curing step is often used for removing residual solvent and/or crosslinking the films. In this case, the overall process can be considered to have three steps: (i) synthesis of the bulk polymer from its monomer(s), (ii) thin film formation, and (iii) curing. In contrast, the synthesis of polymer chains from their monomers and the thin film formation occur in a single step in the CVD reactor. Since there is no residual solvent, no curing step is required after the deposition. Also, CVD can allow for *in situ* grafting of the film to its substrate and the formation of patterns in the same single step.

Solution-based techniques require that a substrate is wetted by the solution. Hence, different surface preparation protocols typically need to be developed and optimized for each type of substrate. This need for customization is absent in CVD because de-wetting effects are eliminated. Combining the dry processing conditions with low surface temperatures make CVD a substrate independent method. For instance, antibiofouling polymeric layers grow equivalently on silicon wafers and polymeric membranes that are placed side by side in a CVD chamber. Also, directly patterned vapor printed electrodes are formed using the identical process on a wide variety of textiles, plastics, and papers.

Another consideration is avoiding the dissolution of previously applied layers during the fabrication of multilayer stacks by solution processing. This requires identification of mutual exclusive solvents, a requirement which is obviated by the use of CVD.

1.3

Scale-Up and Commercialization

Much of the knowledge for scaling up the reactors for organic CVD processes is built upon the much larger and more mature field of CVD processes for inorganic materials [2, 4]. For the inorganic materials, CVD is well known for the repeatable synthesis of high-purity, defect-free films; for the capability to systematically tune film properties through variations in process parameters; and for the ability to be scaled-up and automated for the manufacture of uniform films on silicon wafers of ever larger diameter in the semiconductor industry. Understanding the chemical kinetics and fluid dynamics of CVD polymer reactors has allowed successful scale-up to batch reactors >1 m in width. Larger reactors offer the process throughput required for commercial applications.

The flexibility of iCVD (initiated chemical vapor deposition) polymers makes them compatible with substrates like plastics, papers, textiles, and membranes. Such flexible substrates are required for use with economical roll-to-roll processing. For commercialization, the all-dry nature of CVD has the potential to reduce environmental, health, and safety impacts associated with solvents as well as the economic costs associated with their use, recycling, or disposal.

In semiconductor manufacturing, multiple vacuum processing tools are integrated into clusters. These cluster tools are essential for producing high-quality interfaces because they allow wafers to be transferred between steps without(?) exposure to ambient contaminants. Similarly, the reactor designs for organic CVD are also amenable with integration with cluster tools, and hence offer the promise of hybrid organic–inorganic optoelectronic devices having high-quality interfaces.

At the scale of the laboratory bench, less investment in equipment is required to apply and cure polymer solutions to form thin films. However, at commercial scales, vacuum deposition is a proven and cost-effective technology. For example, large-scale roll-to-roll vacuum deposition processing is commonly utilized for applying barrier materials in the food packaging industry. In the semiconductor industry, spin track systems with automated wafer handling systems and a controlled humidity environment are of comparable cost to a CVD tool. However, for spin-on materials, additional capital investment is required for the highly controlled furnaces for curing the spin-on materials. Such curing equipment is not required for a single-step CVD process. While for many years, spin-on low dielectric constant materials were expected to be adopted by the semiconductor industry, current low dielectric constant materials are predominately manufactured by CVD. This choice was driven both by the superior performance of the CVD films and the higher than anticipated costs for spin-tracks, furnaces, and the high-purity specialty spin-on resins.

1.4

Process and Materials Chemistry

In many cases, CVD polymerization methods represent the direct translation of solution phase organic synthesis methods into heterogeneous processes for surface modification [4, 7]. The vast knowledge of traditional chain growth and step growth polymer synthesis provides insight into the chemical mechanisms responsible for the assembly of monomers into macromolecular units for achieving the properties desired in the resulting thin solid films. The use of each type of CVD process used, as discussed in following text, is determined by the polymerization mechanisms for the monomer(s) of interest and the resultant film properties desired.

1.4.1

Initiated CVD (iCVD) and Its Variants

The iCVD is a versatile method for synthesizing chain growth polymers. While iCVD has been predominately used for free radical polymerization, ionic polymerization has also been demonstrated [1, 8]. For the iCVD process, a thermal initiator is simultaneously introduced into the growth chamber along with the monomer(s). Heated filament wires suspended a few centimeters above the growth surface result in the selective thermal decomposition of the initiator. The resulting fragments react with the monomers adsorbed on the cooled substrate surface and polymerization ensues. Without the use of an initiator, film growth rates are quite low. Two variations of iCVD are *photo initiated chemical vapor deposition* (piCVD) and *initiated plasma enhanced chemical vapor deposition* (iPECVD). For piCVD, a photosensitive initiator is decomposed to free radicals using a UV light. For iPECVD, low-power plasma excitation induces the decomposition of the initiator.

The iCVD method is compatible with vinyl monomers, including, but not limited to, acrylates, methacrylates, and styrenes. The highly desirable pendant functional groups of the monomers, such as epoxy, amine, or carboxylic acid moieties, can be fully retained in the iCVD films, even at high deposition rates. Full retention of the functional groups is essential for fabricating films that are responsive to changes in humidity, temperature, or pH. Most iCVD vinyl polymers are electrical insulators but using monomers with acetylenic bonds extends iCVD to conjugated semiconducting polymers. Monomers already available in commercial quantities at low cost are highly favored for commercial applications.

1.4.2

Plasma Enhanced CVD (PECVD)

The longstanding method of PECVD (plasma enhanced chemical vapor deposition) makes use of the partially ionized gas, known as plasma [4, 9, 10]. Electric fields necessary for ionization can be excited by a direct current, radio frequency, or a microwave frequency generator. The plasma is capable of monomer fragmentation that can self-initiate deposition. Thus, the introduction of an intentional initiator species is not required. Monomers for PECVD include those employed for iCVD as well as those that extend to other gases that react upon fragmentation. However, monomer fragmentation reduces the incorporation of desired functional groups into the PECVD films, and can also result in branching, undesirably high degrees of crosslinking, and “dangling bond” defects (e.g., an unsatisfied bond with an unpaired electron). For this reason, PECVD films often lack the regular repeat units found in conventional polymers. Lowering the plasma power and/or using process variations such as pulsed, atmospheric, or downstream PECVD, can reduce monomer fragmentation but often reduces the film growth rates as well. Dangling bond defects inside the film can lead to reactions with oxygen and water from the air to produce undesirable aging effects. The use of

plasma excitation at the start of a deposition can be highly advantageous because subsequent reactions of the free radical sites with the film forming species can greatly improve adhesion.

1.4.3

Poly(*p*-xylylene) (PPX) and Its Derivatives (“Parylenes”)

Interestingly, some CVD polymers, such as poly(*p*-xylylene) (PPX) and its various functional variants, commonly termed “parylenes” have no direct analog in solution chemistry [11–14]. Volatizing and pyrolyzing the solid [2,2]paracyclophane dimer produces a monomer that absorbs and polymerizes on a cooled surface. The dimer and several of its substituted forms are commercially available. The corresponding dielectric films, particularly parylene C, which contains one chlorine per monomer unit, have a long history of commercial use for the encapsulation of biomedical devices and for the protection of electronics. Several transition metals, metal salts, and organometallic complexes inhibit PPX deposition, and this inhibition effect has been exploited to achieve additive patterning. Deposition has also been demonstrated using custom synthesized dimers possessing a variety of functional groups including, amino, hydroxyl, anhydride, triflate, and trifluoroacetyl moieties. Using the same type of reactor as for PPX, the electroluminescent material, poly(phenyl vinylene), can be synthesized for integration into light emitted diodes.

1.4.4

Oxidative CVD (oCVD)

The oCVD (oxidative chemical vapor deposition) method enables the step growth of conjugated polymers that are typically either semiconductors or electrical conductors [15]. For oCVD, both the oxidant and monomer impinge on the substrate through the vapor phase. Adsorption and spontaneous surface reaction proceeds directly on the substrate without the need for heated filaments, plasma excitation, or UV exposure. oCVD poly(ethylenedioxythiophene) (PEDOT) displays both high conductivity and transparency as desired for the integration of an electrode material into flexible electronic devices. The conductivity, transparency, and work function of oCVD PEDOT can be systematically tuned. Additionally, oCVD PEDOT can be grafted to its substrate for producing novel organic/inorganic hybrid interfaces as well as for ensuring resistance to delamination. Sufficient adhesion is essential for high-resolution lithographic patterning.

1.4.5

Vapor Deposition Polymerization (VDP) and Molecular Layer Deposition (MLD)

Both VDP (vapor deposition polymerization) and MLD (molecular layer deposition) are useful for step growth polymers synthesized through condensation reactions [13, 16, 17]. For VDP, reactive bifunctional monomers are simultaneously

coevaporated and then spontaneously polymerize on the substrate, releasing a condensation by-product. For example, the VDP of diamines with dianhydrides yields poly(amic acid) films by the elimination of water. Also, the condensation reaction of carbonyl chloride and amine groups, which releases HCl, has also proved useful for forming nylons and for Kevlar® by VDP.

Alternating the introduction of the difunctional precursors under conditions that lead to self-limited surface reactions, differentiates MLD from VDP. In analogy to the related method of atomic layer deposition (ALD) for inorganic materials, MLD excels at producing uniform, defect-free, conformal coatings with thicknesses as low as 5 nm. MLD is also useful for hybrid organic–inorganic alucone and zincone polymers. The growth rates of MLD films are limited by the number of reactive surface sites and the experimental time required to switch between the different precursors.

1.4.6

Additional Methods

Other CVD polymerization techniques which have been less commonly used to date include ring-open polymerization by free radical, anionic, and cationic mechanisms; ring-opening metathesis polymerization (ROMP); and polyaddition to from polypeptides [4, 15, 18].

Additional methods have been developed, which are closely allied to CVD. Here, not all of the reactants are introduced through the vapor phase. Examples include the pre-application of low volatility initiators or oxidants to a surface, typically from a solution, before exposure to volatile monomer(s). A broad range of synthesis strategies are opened up by the pre-application of less volatile reactants. For chain growth polymers, the pre-application of initiators is used for *vapor-phase assisted surface polymerization (VASP)* for living free-radical polymerization, *surface-initiated vapor deposition polymerization (SI-VDP)* for nitroxide-mediated synthesis, and *gas-phase assisted surface polymerization (GASP)* for atom transfer radical polymerization (ATRP). *Vapor phase polymerization (VPP)* uses the pre-application of oxidant for step growth polymerization of conjugated polymers. In each of these methods, the available supply of the pre-applied reactant is fixed. Additionally, the pre-application is a second processing step, which introduces additional cost and integration challenges.

1.5

Summary

CVD polymerization represents the intersection of all-dry and scalable micro-fabrication technology with the chemistry of functional and responsive organic materials. Unique applications enabled by CVD polymers derive from the ability to avoid high substrate temperatures and solvents. In a single step, vapor-phase monomers undergo selective reactions to produce high-purity, conformal, and

durable polymeric layers. CVD polymer processes for functionalizing solid surfaces have only begun to be exploited for novel surface modification and device applications.

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1) Only review articles and books have been cited. The reader is advised to consult these or the subsequent chapters in this volume for more detail and for citations to original research papers.

