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Initiated and oxidative chemical vapor deposition: a scalable method for conformal and functional polymer films on real substrates
Initiated and oxidative chemical vapor deposition: a scalable method for conformal and functional polymer films on real substrates

Salmaan H. Baxamusa, Sung Gap Im and Karen K. Gleason*

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Chemical vapor deposition (CVD) is a widely-used technology for the preparation of conformal and defect-free inorganic thin films with systematically tunable properties. Polymers are a desirable class of materials for surface modification because of their low cost, wide array of chemical and physical functionality and mechanical flexibility. Initiated and oxidative chemical vapor deposition (iCVD and oCVD) are polymer CVD methods that combine the benefits of CVD processing with the possibilities of polymeric materials. Using these technologies, our laboratory has synthesized a number of functional, biocompatible and electrically conducting polymers as thin films on micro- and nano-structured surfaces. This Perspective will review recent advances in these areas and highlight devices and applications that utilize iCVD and oCVD polymers.

Introduction

Chemical vapor deposition (CVD) is a mature technology for the preparation of inorganic thin films. In its most basic form, CVD describes any process in which vapor phase precursors chemically react at a surface to generate a thin, solid film. It is widely used in the semiconductor industry and is found in virtually every integrated circuit fabrication plant in the world. Because it is a proven industrial manufacturing process, CVD is widely considered to be scalable from the bench to plant and easily integrated into current processing methods for silicon wafers or micro-electromechanical systems.1,2

The principal features of CVD films stem from the semi-continuous, dry nature of the process. By altering the composition of the feed gas, film properties are easily and systematically tunable. The convective flow profiles of the gases can be engineered and the gaseous precursors easily diffuse into small features, resulting in coatings that are uniform over large areas while conformal on the nanoscale. The reduced pressure and continuous flow during CVD prevent impurities or unreacted precursors from entraining into the film.

While CVD is primarily used to deposit inorganic thin films, it is becoming an increasingly relevant technology for the preparation of polymer thin films. Polymer thin films can have a number of properties not afforded by metals and ceramics. Their low cost, mechanical flexibility, wide array of functionalities, and well-understood structure–composition–property relationships make polymers attractive for a number of applications in thin film technology.3,4 Polymer films can also be designed to be responsive so that their physical properties change in response to an external stimulus such as heat, moisture, or pH.5,7 Thus, the recent research in polymer CVD can be understood as a desire to integrate the processing capability and scalability of CVD with the physical, chemical, and economic properties of polymers. Traditional polymer
synthesis and deposition methods occur in the liquid phase but the possibilities of vapor phase deposition of polymers are only now beginning to be realized.

Recent research efforts in our group have focused on initiated chemical vapor deposition (iCVD) and oxidative chemical vapor deposition (oCVD) as enabling technologies for biocompatible, functional, and electrically conducting polymer thin films. This Perspective will review recent advances in polymer thin films and devices achieved using iCVD and oCVD.

The area of greatest potential impact for polymer CVD techniques may be in applications where the elimination of solvent is either advantageous or required. For example, residual entrained solvent in a thin film is a leading cause of failure in biocompatibility testing. In some polymerization systems, such as poly(furfuryl methacrylate), solution phase synthesis can promote undesired side-reactions and yield low-quality polymers. Because of the surface tension inherent in liquid-phase systems, conformal coverage of thin films around micro- and nano-scale features can be difficult to achieve using traditional polymerization systems. As microfabrication techniques continue to shrink the size of achievable features, the need for conformal polymer deposition processes will become increasingly important. Vapor deposition techniques are also advantageous when substrate damage, such as dissolution or swelling, occurs upon exposure to solvent and when the deposited film is not easily soluble, as is the case for many fluoropolymers,9 conducting polymers10 and highly cross-linked polymers.

iCVD and oCVD, developed in our research group, are polymer CVD methods that integrate the physical possibilities of dry processing with the chemical versatility of traditional solution-phase polymerization (Fig. 1). In this Perspective, we will review the polymers that have been deposited using these techniques and their biocompatible, functional and bio-functional, and electrically conducting properties. We will also discuss the physical mechanism governing deposition on geometrically complex surfaces and the variety of substrates used with iCVD and oCVD. At the intersection of film chemistry and deposition physics lies a number of device prototypes and applications investigated by our laboratory. Finally, we will close by highlighting some of the challenges and opportunities in surface modification for which iCVD and oCVD can be enabling technologies.

**The iCVD and oCVD synthetic strategy**

**Free radical iCVD polymerization**

The typical iCVD reactor, shown schematically in Fig. 2a along with typical reaction conditions, is a custom-built, pancake-shaped vacuum chamber with a viewport that enables real-time interferometric measurements of the film thickness. The monomer and initiator are metered into the reactor via mass flow controllers. Resistively heated filaments are suspended several centimeters above a deposition stage which is maintained at a constant temperature by backside contact with a recirculating water bath. In a photoinitiated version, piCVD, ultraviolet light irradiates the substrate through the viewport. In both cases, the hot process gases that enter the reactor adsorb on the cooled substrate to form a polymer. The polymerization takes place almost entirely at the surface, as depicted in Fig. 2b, because the vapor pressure of the growing polymer chain is too low for it to be present in the vapor phase at appreciable concentrations. The reactor pressure is a key parameter and is maintained by a throttling butterfly valve and an exhaust valve controller. It is important to note that the film thickness is controllable; because of the real-time interferometric measurements, the film growth can be terminated at the desired thickness. Typical iCVD growth rates are 10–100 nm min−1 and typical film thicknesses are 100–1000 nm.11,12

iCVD borrows heavily from solution-phase polymerization. In a typical solution-phase polymerization, the monomer-initiator mixture is either heated or exposed to ultraviolet light. The thermal or radiative energy input is high enough to decompose the initiator into radicals, but low enough that the monomer and the resultant polymer are unaffected.4 In iCVD, the filament or the ultraviolet power density is kept similarly low. Initiating radicals react with the vinyl monomers via a
free-radical mechanism to form a growing polymer chain. The chemistry shown in Fig. 2c is representative of a generic free-radical polymerization. An initiator decomposes into radicals (Fig. 2c–i); these radicals can then attack the carbon–carbon double bond of a vinyl monomer (Fig. 2c–ii). These radicals then add additional monomer units to form a growing polymer chain (Fig. 2c–iii). The chain can be terminated by any radical present in the reaction system to form the final polymer chain (Fig. 2c–iv).

The ability to replicate traditional free-radical polymerization chemistry in the vapor phase allows iCVD to produce nearly any free-radical polymer provided that its precursors have sufficient vapor pressures to flow into the reactor. Common iCVD reactions use a peroxide initiator such as tert-butyl peroxide and a methacrylate or acrylate monomer. Combining this robust and well-known chemistry with the benefits afforded by vapor phase processing has led to rapid advances in functional thin films that are conformal on a number of practical substrates. Quantitative models have been developed to predict deposition rate and molecular weight of iCVD homopolymers as a function of reaction conditions.\textsuperscript{13,14} Additionally, quantitative understanding of iCVD copolymers has been developed.\textsuperscript{15} These models are critical to leveraging well-studied structure–property–composition relationships in polymers as well as the scale-up of iCVD reactors.

**Step growth oCVD polymerization**

While iCVD utilizes free-radical chemistry, oCVD relies on step-growth polymerization and is used for the deposition of thin films of conducting polymers from an aromatic heterocyclic monomer. As in iCVD, the reactor pressure, stage temperature and monomer flowrate are key controllable parameters. Unlike iCVD, however, there is no hot filament array; the oxidative polymerization is a spontaneous reaction between appropriate reactants. As depicted schematically in Fig. 3a, a solid-state oxidant is loaded as a powder into a resistively heated crucible with the substrate suspended overhead. The monomer flows into the reactor from a side port and spontaneously reacts with the oxidant, initiating the polymerization on the substrate surface.

In the step-growth polymerization, the oxidizing agent first reacts with the monomer to generate cation radicals (Fig. 3b–i). Cation radical pairs dimerize (Fig. 3b–ii) and the anions from the oxidizing agent scavenge two protons to stabilize the dimer (Fig. 3b–iii). The oxidizing agent then reacts again with the dimer to form another radical cation, which subsequently reacts to form the growing polymer chain. Some of the positively charged heterocyclic rings are stabilized by the presence of counter ions, known as dopants, in the polymer (Fig. 3b–iv). The doping process results in charges along the conjugated backbone of the conducting polymer, which enables the flow of current. The dopant concentration is directly related to the conductivity of the polymer.

**Comparison to other polymer CVD methods**

It is worth noting a few distinguishing characteristics of iCVD and oCVD as compared to other polymer CVD methods. Plasma enhanced CVD (PECVD) and pulsed-plasma CVD (PPCVD) are common techniques, but plasma deposited polymer films can have limited functional group retention due to collisions with highly energetic species and lower polymerization rate due to a competition between etching and deposition. Fig. 4 compares the deposition rate, functional group retention, and power input for iCVD, PPCVD, and PECVD of poly(hydroxyethyl methacrylate) (PHEMA).\textsuperscript{16,17} The power input in both plasma methods is non-selective. This results in non-selective chemistry in which unwanted side-reactions, such the destruction of functional groups, occur in parallel with polymerization.\textsuperscript{18,19} The power input in iCVD selectively activates the thermally or photolytically labile...
initiator, so high deposition rates are possible with complete retention of functional groups.

The vapor deposition of poly(para-xylylene) (commonly known by its trade name parylene) was developed over 60 years ago, and there has been much recent work in the CVD of substituted parylenes with functional moieties. The process involves the thermal decomposition of a [2,2]paracyclophane to form reactive intermediates which polymerize at the substrate surface. Unsubstituted parylene (Parylene-N) and chloro-substituted parylenes (Parylene-C and Parylene-D) have found widespread commercial use as inert barriers, electrical insulators, and biocompatible coatings. For most other functionalities, custom monomers representing derivatives of [2,2]paracyclophane must be synthesized. One goal of our research in iCVD and oCVD is to use commercially available monomers in order to demonstrate the large-scale utility of these processes.

**Functional thin films from iCVD and oCVD**

The iCVD chemistry is essentially identical to traditional free-radical chemistry: an initiator is thermally or photolytically decomposed into radicals, and these radicals react with vinyl monomers to form growing polymer chains. This similarity enables a wide variety of commercially available vinyl monomers, especially acrylates and methacrylates, to be synthesized as thin films using iCVD. Many of these monomers are commercially available, which has led to the rapid development of biocompatible, functional, and biofunctional surfaces. Fig. 5a summarizes a number of the polymers that have been deposited by iCVD and oCVD. Fig. 5b shows divinyl monomers that can be homopolymerized to form highly crosslinked, insoluble films or copolymerized with the polymers in Fig. 5a to enhance solvent resistance or thermal stability of the resultant thin films.

**Biocompatibility**

Surface modification to enhance biocompatibility has been studied for several decades. Organosilicones are candidate coatings for electrically insulating, biopassive surfaces. Poly(trivinyltrimethylcyclotrisiloxane) (PV3D3), a cyclic siloxane polymer, has been deposited via iCVD to create such surfaces. The highly crosslinked structure of PV3D3 makes it insoluble in common polar and nonpolar solvents, which makes wet processing of this polymer very difficult. The same highly crosslinked structure also makes it very stable; PV3D3 has been shown to maintain electrical resistance under
Fig. 5  (a) Partial library of iCVD and oCVD polymers. See text for detailed description of polymer function. PPMA = poly(propargyl methacrylate), PGMA = poly(glycidyl methacrylate), PFPM = poly(pentafluorophenyl methacrylate), PFMA = poly(furfuryl methacrylate), P(MA-alt-St) = poly(maleic anhydride-alt-styrene), PHEMA = poly(hydroxyethyl methacrylate), PV₃D₃ = poly(trivinyltrimethylcyclotrisiloxane), PVP = poly(vinyl pyrrolidone), PDMAMS = poly(dimethylaminomethyl styrene), PCHMA = poly(cyclohexyl methacrylate), P(MAA-co-EA) = poly(methacrylic acid-co-ethyl acrylate), PPFA = poly(perfluorodecyl acrylate), PEDOT = poly(3,4-ethylenedioxythiophene), PPY = poly(pyrrole), PTAA = poly(3-thiopheneacetic acid). (b) Partial library of iCVD crosslinkers. EGDA = ethyleneglycol dimethacrylate, DVB = divinylbenzene, DEGDVE = di(ethylene glycol) di(vinyl ether).
simulated bioimplantation for over two years. Fig. 6a shows that neuron growth on PV3D3 is indistinguishable from growth on a glass slide, a preliminary indication that it is biocompatible and non-toxic to neurons.26

Another biocompatibility strategy is to use thin hydrogel films to reduce the degree of non-specific protein adhesion. Two such hydrogels are PHEMA and poly(vinyl pyrrolidone) (PVP); both have been used for biological and biomedical applications27–30 and their biocompatibility, including resistance to non-specific protein adhesion,31–35 has been studied. Both linear and crosslinked versions of these polymers have been deposited via iCVD.17,36 The crosslinking is performed in situ by introducing a divinyl comonomer into the feed gas and the crosslinking density can be systematically controlled. piCVD, the photoinitiated version of iCVD, has also been used to deposit stable, swellable, crosslinked thin films of PHEMA. These films were shown to reduce non-specific protein adhesion as compared to a bare silicon surface.37

Chemical functionality

In addition to coatings whose primary function is to serve as a biocompatible barrier, a variety of chemically functional surfaces have been synthesized using iCVD. Perfectly alternating copolymers of maleic anhydride and styrene (P(MA-alt-St)) can be deposited by iCVD.38 This alternation occurs naturally because the electron-accepting maleic anhydride preferentially adds to the electron-donating styrene, rather than itself, during polymerization.4 The strained-ring anhydride is highly reactive toward amines and hydroxyls and copolymers containing maleic anhydride have been used as a platform for the covalent immobilization of proteins,39 DNA40 and biopolymers.41

Another example is fluorinated phenyl esters, which have been widely used in surface chemistry because their rapid reaction with nucleophiles enables facile modification.42,43 iCVD copolymers based on poly(pentafluorophenyl methacrylate) (PPFM) show retention of this functionality, and Fig. 6b shows a PPFM surface patterned with an amine-terminated dye using soft lithography.44

One of the advantages of a CVD process is the ability to grow a film with a compositional gradient within its depth; this is accomplished simply by changing the feed gas ratios during the deposition. iCVD gradient hydrogel copolymers of P(PFM-co-HEMA) exhibit confinement of the fluorinated phenyl esters to the near-surface region (<20 nm). Combining the principles of CVD processing with functional polymers

Fig. 6  (a) Neuron growth on a PV3D3 surface is indistinguishable from neuron growth on a glass slide. (b) Spatially selective reaction of a PPFM surface with an amine-terminated dye using soft-lithography. The scale bar represents 200 μm. (c) Top left: atomic force micrograph (AFM) of directly e-beam patterned PPMA (scale bar = 20 μm); bottom left: fluorescence micrograph of PPMA film conjugated with quantum dots via click chemistry (scale bar = 20 μm); right: enlarged AFM image of patterned film conjugated with quantum dots (scale bar = 2 μm). (d) PDMAMS effectively kills both E. coli and B. subtilis due to its pendant quaternary amine. (e) A resistance of 123 Ω in a film approximately 100 nm thick corresponds to a conductivity of approximately 1000 S cm⁻¹. Adapted from refs. 26, 44, 55 and 56.
enables this novel vertical architecture. The nanoco confinement of the functional groups to the near-surface region makes all of them accessible, even to large functionalizing agents. Grading therefore avoids having unreacted groups present in the bulk of the film after functionalization.45

Functional surfaces, particularly those designed for biological and physiological contact, must have well-defined surface chemistries. Deposited surfaces that undergo subsequent functionalization must do so rapidly and selectively, and preferably with either no or only harmless reaction byproducts. Click chemistry is a class of organic reactions that generally satisfy these requirements.46 “Clickable” surfaces can thus undergo facile functionalization with high yield and no side reactions. By choosing commercially available vinyl monomers with click-active moieties, iCVD has been successfully used to deposit clickable surfaces. Clickable thin film polymers enabled by iCVD can potentially serve as a platform for the modification of many types of surfaces. Other researchers have shown that click-active surfaces can easily be conjugated with biofunctional ligands such as peptides or proteins.5,47

One common click reaction is the nucleophilic substitution to a small, strained ring. Poly(glycidyl methacrylate) (PGMA), which contains a three-membered epoxy ring, has been successfully deposited by iCVD with little or no detectable degradation of the highly-reactive epoxy pendant group.48 This is remarkable considering that the liquid monomer is vaporized and then contacts either hot filaments48 or ultraviolet light.49 The successful deposition of this monomer is an object lesson in the mild nature of iCVD. Plasma polymerization of PGMA, even at low power input, does not fully retain the delicate pendant epoxy ring.49 The highly energetic species present in plasmas make several reaction pathways available and many of these side reactions result in destruction of monomer functionality. The ability to retain chemically fragile pendant groups is a general feature of iCVD and one of its advantages over plasma polymerization. The reaction of the epoxy group of iCVD PGMA with primary amines has been successfully demonstrated in a number of applications.50,51

Another common click reaction is the famous Diels–Alder cycloaddition, in which a substituted alkene and a conjugated diene react to form a cyclohexene. The furan ring of poly(furfuryl methacrylate) (PFMA) is such a diene. The iCVD synthesis of thin PFMA films has been demonstrated and the retention of the furan ring allowed the film to be functionalized by 4-phenyl-1,2,3-triazolin-3,5-dione (N-PTD).52 The azide-alkyne Huisgen cycloaddition, sometimes described as the “cream of the crop” of click reactions, forms a 1,2,3-triazole from an alkyn and an azide. Poly(propargyl methacrylate) (PPMA), which contains a terminal alkyn, has been deposited by iCVD and patterned by both capillary force lithography54 and direct e-beam writing, shown in Fig. 6c.55 The PPMA regions in both cases were successfully functionalized by azide-conjugated dyes.

Biological functionality

A directly biofunctional surface can be created by the iCVD of poly(dimethylaminomethyl styrene) (PDMAMS). The pendant group for this polymer contains a quaternary amine, which has antimicrobial properties. Fig. 6d shows that fabric coated with PDMAMS was effective at killing both E. coli and B. subtilis.56 Because iCVD is capable of coating a wide variety of substrates, the deposition of PDMAMS suggests a general method for creating microbicidal surfaces. By using a grafting photoinitiator, the film was robust enough to withstand repeated washing steps.57

Electrically conductive thin films

While iCVD is used to deposit chemically and biologically functional thin films, electrically conductive thin films of poly(3,4-ethylenedioxythiophene) (PEDOT),58 poly(pyrrrole) (PPY), and poly(3-thiopheneacetic acid) (PTAA) can be deposited via oCVD.59 See Fig. 5a. Several alternative methods exist for the deposition of PEDOT, but they are limited by low conductivity (less than 10 S cm−1) commercially60 or substrate limitations (for example, electropolymerization requires a conductive substrate).61,62 oCVD can deposit PEDOT on practically any substrate and conductivities as high as 1000 S cm−1 have been observed (see Fig. 6e and 7a).

The dopant concentration and work function of oCVD PEDOT films can be directly controlled by varying the substrate temperature, which is of potential advantage for organic electronic devices.63 Increasing the substrate temperature also leads to longer conjugation lengths in the polymer and, consequently, higher conductivities. The conductivity is tunable over five orders of magnitude by changing the substrate temperature over the range 15–100 °C.64 The electrical conductivity is also dependent upon the oxidizing agent used because the first oxidation reaction in Fig. 3b is the rate determining step in the stepwise polymerization; typically, FeCl3 or CuCl2 are used. The oxidant species also controls the surface morphology. FeCl3 is a much stronger oxidant than CuCl2, and this is reflected in the final film morphology; using FeCl3 results in a smooth film with an RMS roughness of 4 nm whereas using CuCl2 results in a film with a basalt-like nanoporous morphology.65

Deposition on practical substrates

In most thin-film studies, rigid, flat substrates such as glass slides and silicon wafers are the substrates of choice because...
they are compatible with most analytical and characterization techniques. For many practical devices and applications, deposition on flexible or non-planar substrates is required. Substrate compatibility is a key feature of iCVD and oCVD. The deposition process occurs near room temperature without the use of potentially corrosive solvents, and the resultant film is conformal around various geometries. The library of functional iCVD and oCVD materials enables wide latitude in materials choice and the vapor-phase process makes CVD a good choice for deposition on practical substrates.

**Deposition and grafting on flexible substrates by oCVD**

oCVD PEDOT has been deposited on commodity polymers such as poly(styrene) (PS), poly(ethylene terephthalate) (PET) and poly(carbonate) (PC). The ability to deposit a conducting polymer on a plastic substrate could potentially be of great benefit for the production of flexible electronics. A transparent PEDOT film deposited on a flexible PET substrate is shown in Fig. 7a.

The oxidant can activate both the aromatic group in the substrate and in the monomer simultaneously. Consequently, the PEDOT polymer can be grafted onto any aromatic-containing substrate without a separate surface treatment. This includes plastics such as PS, PET and PC. Inorganic substrates without aromatic groups can be treated with a phenylated silane in order to graft a PEDOT film to the surface. The grafting is a result of the oCVD oxidant acting as a Friedel–Crafts catalyst to create aromatic radical cations on the substrate. These radical cations react with the radical cations of the heterocyclic monomer to create covalently grafted chains of conducting polymer in a single processing step. The grafted films have increased adhesion to their substrates, which allows for micron-scale patterning using conventional photolithography. As seen in Fig. 7b, surfaces that do not contain aromatic groups do not graft the PEDOT, and conventional photolithography destroys the polymer film during the liftoff step.

**Physicochemical factors affecting film conformality**

There has been great interest in the use of nanofibers, micro-particles, membranes and other high surface area materials that can act as sensors, actuators and filters for applications ranging from biological sensing to microfluidics. While the substrates themselves may have novel properties, their use in real-world environments often requires surface modification. A well-known example is the surface modification of biological devices in order to enhance resistance to non-specific protein adhesion. Other examples are the presentation of ligands for specific cell–substrate interactions and insulators for flexible electronics. Polymers are candidate materials for each of these thin-film applications.

Surface modification techniques for use on non-planar and high surface area substrates must be conformal. Conformal polymer films from a solvent-based system can be difficult to achieve because of solvent-induced surface tension. Such surface tension can lead to agglomeration in the case of particles or fibers, which can also negatively impact the properties of the native substrate. In membranes or trenches, surface tension tends to lead to preferential coating at either the top or bottom surface of the trench. For this reason, vapor-phase polymerization processes are preferred.

In CVD, the probability that a reactive vapor-phase molecule irreversibly adsorbs to the substrates is known as the sticking probability. For conformal deposition on non-planar substrates, the sticking probability should be low. Previous iCVD studies have shown that surface-adsorbed monomer is in equilibrium with its vapor. Thus, it is believed that the reactive species of interest for iCVD is the radical formed by the pyrolysis of the peroxide initiator.

Micron-scale trenches are an ideal geometry for quantifying the sticking probability of the initiating radical. If the sticking probability of the initiating radical is high, then it will be consumed by collisions with the wall along the trench depth. This leads to spatial variations in the concentration of the initiator and therefore non-uniform deposition rate within the trench. By defining step coverage $S$ as the ratio of thickness at the bottom of the trench to the thickness at the top of the trench, a perfectly conformal film is described by $S = 1$. The step coverage is a function of the trench aspect ratio, defined as the ratio of the trench depth $L$ to its width $W$. Fig. 8a illustrates these quantities in a schematic cross-section of the trench. The relationship between the step coverage and the aspect ratio (AR) is:

$$\ln(S) = -0.48 \times (\Gamma) \times (AR)^2$$  \hspace{1cm} (1)

where $\Gamma$ is the sticking probability. Eqn (1) is valid when vapor phase molecular collisions are rare compared to substrate–molecule collisions. This is true of iCVD inside of micro-trenches, which occurs at low enough pressures that the mean free path of a vapor molecule is greater than the width of the trenches. Using eqn (1), sticking probabilities have been mapped to deposition conditions. In particular, it has been found that, as the monomer partial pressure approaches its saturation vapor pressure, the sticking probability increases.
Measured sticking probabilities range from 0.011 to 0.050, which are low enough to result in conformal coverage. This can be understood by considering the chemical mechanism governing whether an initiating radical will adsorb reversibly or irreversibly to the surface. A radical that impinges on and adsorbs to the surface (Fig. 8b–i) will desorb within tens of microseconds. If it does not directly strike and react irreversibly with an adsorbed monomer (Fig. 8b–ii–a), then it will go back into the vapor phase (Fig. 8b–ii–b). Increasing the monomer partial pressure increases the density of surface sites occupied by an adsorbed monomer molecule, which in turn increases the frequency with which an impinging radical reacts with an adsorbed monomer. Therefore, as observed, increasing the fractional saturation of the monomer vapor during iCVD increases the sticking probability. Consequently, the conformality of films deposited by iCVD can be tuned by altering the monomer partial pressure. Fig. 9a shows that films can be designed to conform to the trench geometry or completely bridge the mouth of the trench.

As with any dry process, iCVD obviates the need for solvents and the resultant surface tension induced non-uniformities. The presence of electric fields in PECD, PECVD and PPCVD can also lead to non-conformal deposition. This is a consequence of the competition between etching and deposition in plasma polymerization; in areas where the electric field is locally strong, one of these processes will dominate the other. Electric fields are non-uniform near the surfaces of non-planar substrates, resulting in non-uniform deposition rates and therefore non-conformal coverage. The self-limited nature of atomic layer deposition (ALD) yields inherently conformal films of condensation polymers, but the deposition rate is typically less than 1 nm min⁻¹. In contrast, iCVD deposits free-radical polymers at growth rates typically between 10–100 nm min⁻¹.

Examples of solvent- and plasma-induced non-uniformities can be seen in Fig. 9b. All three images show a cross-sectional view of a microtrench approximately two microns wide and seven microns deep. The middle image shows spin-casted PMMA and the right image shows poly(cyclohexyl methacrylate) (PCHMA) deposited using PPCVD. The spin-casted film has little or no polymer coating the sidewalls but a thick deposition layer at the bottom of the trench. The meniscus-like shape of the film at the bottom of the trench is a clear artifact of solvent surface tension. The plasma film is better in terms of overall conformality, but there are regions of high and low coverage at the interior and exterior corners of the trench, respectively. At these corners, the electric field is locally non-uniform, resulting in non-conformal coverage. In contrast, iCVD eliminates these sources of non-conformality because it is a dry process that relies on neutral chemistry. The iCVD deposition of PCHMA in a trench, seen in the leftmost image of Fig. 9b, is smooth and continuous around the top, sidewalls and bottom of the trench.

**Deposition on non-planar substrates**

The conformal nature of iCVD has enabled our group to apply polymers to a variety of micro and nanostructured substrates. For example, internal modification of high aspect ratio microstructures is an important challenge in filtration and membrane systems. Poly(perfluorodecyl acrylate) (PPFA) is a low surface energy fluoropolymer that has been used to coat micron-scale pores with an aspect ratio of over 80:1. The presence of fluorine along the depth of the pores, as measured by an electron microprobe, confirmed that the reactants diffused through the pores and reacted to form a coating on the pore walls.

The oCVD conducting polymer films also demonstrate a high degree of conformality over nonplanar microstructured substrates when CuCl₂ is used as an oxidant. While the mechanism governing the conformality of oCVD films has not yet been systematically investigated, Fig. 9c compares an oCVD PEDOT film to a film synthesized by spin-casting and polymerizing a liquid solution containing EDOT monomer and FeCl₃. Similar to the iCVD films, the oCVD PEDOT is conformal around the trench geometry. In the spin-casted film, surface tension appears to have confined much of the polymer to the bottom of the trench, but there is little coverage at the side wall and upper mouth. The resultant step coverage is highly irregular compared to the original shape of the trench.

In addition to straight pores, iCVD and oCVD coatings can also be applied to randomly-structured fibrous substrates across several length scales. Deposition of iCVD polymers has been visualized by electron microscopy on wires (Fig. 10a), commercial papers and fibers (Fig. 10b), electrospun fiber mats (Fig. 10c) and even carbon nanotubes (Fig. 10d). The ability to conformally coat fibers with polymer films is important for hierarchical materials design. Design across multiple length scales can expand the range of available materials properties, such as surface wettability. Superhydrophobic surfaces, on which the water contact angle is greater than 150°, can be achieved by iCVD by coating mats of submicron electrospun fiber with the hydrophobic polymer poly(perfluoroalkyl ethyl methacrylate) (PFPEMA). The naturally low surface energy of PFPEMA coupled with the surface roughness inherent in the electrospun mat resulted in water contact angles as high as 175°.

![Fig. 9](image-url)

**Fig. 9** Cross-sectional scanning electron micrographs (SEM) of trenches with polymer coating. Each scale bar represents 2 μ. (a) iCVD films can be designed to be conformal (left) or nonconformal (right) to the substrate geometry. (b) Conformality of an iCVD film (left) is better than both spin-casting (middle) and plasma deposition (right). (c) oCVD PEDOT (left) shows conformality not seen in its solution-synthesized counterpart (right). Adapted from refs. 37 and 65.
Fig. 10 iCVD deposition on substrates across several length scales visualized by scanning electron microscopy (a–e) and transmission electron microscopy (f). (a) A 1 μ insulating film of PVDD on a wire. The arrow indicates an area of intentional ablation. (b) A commercial nylon fiber coated with 195 nm PDMAMS. The arrows indicate the polymer layer; a layer of carbon deposited for focused ion beam milling is visible on top of the iCVD coating. (c) Electrospun fiber mat as-spun (left) and coated with PFEMA (right). (d) A cleaved ~ 50 μ particle coated with 1 μ of PHEMA. The arrows indicate the polymer layer and the inset shows the entire cleaved microparticle. (e) Nanobowls of polybutyl acrylate) created by using microspheres as a colloidal template. (f) Uncoated (left) and iCVD coated (right) multiwalled carbon nanotube. Adapted from refs. 26, 56, 73, 76, 77 and 52.

PEDOT synthesized with CuCl2 as the oxidizing agent has a naturally nanoporous morphology due to the effusion of gaseous byproduct during the polymerization. By coating this nanoporous film on a microstructured paper mat, a hierarchically structured electrical conductor can be made, whose high surface area could be advantageous for applications such as sensors with high sensitivity or supercapacitors.65

Particles are an important class of substrates, as this factor is common for high surface area sensors or pharmaceutical powders. Exterior coatings on microparticles have been demonstrated using iCVD and pCVD, and the presence of polymer around the particles has been confirmed indirectly by functionalizing the polymer with a fluorescent dye. Direct confirmation of the exterior coating can be seen in the crosssection micrograph in Fig. 10d. While the iCVD process is conformal to all exposed areas of substrate, the potential for “bald spots” on particles exists where the particle meets the deposition stage. This can be avoided by agitating the particles in a specially-designed rotating bed CVD reactor or on a vibrating stage. Particles as small as 5 μ have been coated using pCVD.52,76

Alternatively, particles can be used as a lithographic mask rather than a substrate. Casting monodisperse micro- or nano-spheres as a monolayer on a silicon substrate creates a colloidal template. A subsequent iCVD coating deposits film in the interstices between the particles, and stripping the template reveals a well-ordered array of polymer nanobowls as seen in Fig. 10e. The stripping process consists of rinsing the particles off of the substrate with a solvent; this rinse can also dissolve the polymer off of the surface. To avoid this problem, the templated substrates were first exposed to vinyltrichlorosilane vapors, which reacted with the substrate to present vinyl groups at the surface. The subsequent iCVD coating then polymerized through these vinyl bonds, resulting in polymer chains that were covalently grafted to the surface. This process enhanced the adhesion of the film to the substrate considerably, and the patterned polymer survived subsequent rinses. This colloidal templating has been used to pattern several iCVD polymers, including PHEMA, PV3D3, PPFA, and PPFM.77

Applications of iCVD and oCVD

There are several applications for which the advantages of CVD and polymeric materials intersect. We will briefly review here some applications of iCVD and oCVD targeted toward such applications.

Biological protection

One of the characteristics of iCVD is that the substrates are never exposed to extreme conditions of solvent or heat. This has led to the development of a protective coating for sensors used in biological applications. Coating a sensor of this type represents a unique challenge, since any coating must be both biocompatible and permeable to analytes of interest.78 Moreover, the coating process cannot damage or degrade the device, which eliminates many solvent, plasma and polymer grafting schemes. By using pCVD, thin films of PHEMA can be crosslinked in situ. This results in a thin hydrogel film whose mesh size, as governed by its crosslink density, is small enough to allow for the permeation of water and small-molecule analytes, such as metal ions and sugars, to the sensor surface while preventing the transport of biofouling macromolecules such as proteins. By changing the substrate temperature during deposition, the mesh size was tuned between 2–6 nm. The films are stable and reversibly swellable in aqueous media and more resistant to non-specific protein adhesion than bare silicon.

Most importantly, the pCVD process is gentle enough to coat a delicate optical sensor without changing its response to its target analyte, sodium. Fig. 11a shows the response of the coated and uncoated optode. Neither the response magnitude nor the response time was noticeably affected by the pCVD process or the resultant hydrogel film. This is expected as the optode was maintained at room temperature during the deposition via contact with the cooled stage and was never exposed to potentially damaging solvents.76

Drug delivery

Conformal polymer coatings around pharmaceutical particles are important for targeted drug delivery in the human body. The absence of solvents in iCVD allows individual drug microcrystals to be coated without aggregation or dissolution.
As coatings can be applied at room temperature, temperature-sensitive therapeutic drugs can be encapsulated by a polymer film without thermal degradation. An iCVD copolymer, poly(methacrylic acid-co-ethylenedimethacrylate) (P(MAA-co-EDMA)), has been used to conformally coat ibuprofen microparticles. Due to the methacrylic acid moieties, this polymer has a pH-dependent swelling behavior; at acidic conditions the methacrylic acid is protonated and does not swell significantly. The release of the water-soluble drug particles encapsulated in P(MAA-co-EDMA) can thus be triggered by a change in pH. Fig. 11b shows that the polymer film significantly hinders the release of the encapsulated ibuprofen at acidic pH, but at neutral pH the film does not affect the dissolution rate of ibuprofen. This iCVD film thus acts as an enteric coating and could be used to prevent the dissolution of pharmaceuticals in the acidic environment of the stomach while allowing for release in more neutral environments.

Microfluidics

Another natural application of conformal polymer thin films is in the area of microfluidics. Microfluidic devices have drawn extensive interest recently because of their potential applications in biomedical devices, high-throughput screening and studies of chemical and biological reactions. In a typical device, microfluidic channels are patterned onto a polymer substrate by casting the polymer onto a silicon master containing the negative image. These channels are then sealed by bonding the polymer substrate to a flat surface. Depending on the material, the bonding process can require potentially damaging high temperatures, electric fields or oxygen plasmas.

By conformally depositing an iCVD nanoadhesive on the patterned substrate, the bonding method can be decoupled from the choice of device material. This decoupling allows for material selection based on the desired functionality of the microfluidic device rather than the limitations of the bonding method. The nanoadhesive is a thin film of PGMA, which can then be bonded to any surface containing a primary amine. This was demonstrated by coating a patterned poly(dimethylsiloxane) (PDMS) substrate with a 50 nm iCVD PGMA film and bonding to a flat PET surface coated with poly(allylamine) (PAA). The PAA was deposited using a plasma process. The bonding occurred by lightly pressing the two layers together at 70 °C for 12 h and allowing the epoxy to react with the amine. Because the bonding temperature is below the glass transition temperature for both polymers and the reaction produces no gaseous byproducts, defects at the bonding surface are avoided. Such defects can lead to bond rupture even at low stresses. All of the devices bonded with the iCVD nanoadhesive withstood 50 psia channel pressure. Fig. 11c shows that channels as small as 200 nm were successfully fabricated using this technique.

Conducting inorganic–organic composites

The conducting polymers synthesized by oCVD can be chemically functionalized as well. PTAA can be functionalized through its carboxylic acid group, but films of this material typically have poor mechanical properties and low conductivities. PPY, on the other hand, has been shown to be stable
over a 20-year period. Conducting copolymer thin films of poly(thiopheneacetic acid-co-pyrole) (P(TAA-co-Py) can be synthesized by oCVD by simultaneously flowing both monomers into the reactor during deposition. This yields a stable, conducting film with built-in chemical functionality. Hybrid inorganic–organic thin film conductors were created by attaching silver nanoparticles to the carboxylic acid moiety via the conjugated linker molecule 4-aminothiophenol. The thiol creates a linkage to the silver nanoparticle while the amine reacts with the carboxylic acid to form an amide bond. Fig. 11d shows that the attachment of silver nanoparticles increases the conductivity of these copolymers across all tested compositions, in one case by as much as 1000 ×. The high surface area of the silver nanoparticles is a potential avenue into resistance-based sensing on these composite thin films. The integration of silver nanoparticles in the film is a direct result of the ability of oCVD to make conducting thin films with chemical reactivity.

**Chemical sensing**

The reactivity of iCVD thin films can be used as a platform for the solventless synthesis of self-sorting surfaces. An iCVD film of PPMA deposited on top of a thin layer of crosslinked poly(allylamine) (PAAm) can be patterned by capillary force lithography (CFL). In CFL, a nanostructured mold is gently pressed onto a polymer thin film; heating the polymer above its glass transition temperature induces capillary flow of the iCVD film into the mold interstices. The important feature of the iCVD polymer is that it consists of linear, non-branched chains. Plasma methods induce crosslinking, which would impede the capillary flow into the mold interstices. The CFL process patterns the iCVD PPMA and exposes the underlying PAAm; the result is an orthogonal bifunctional surface. The PPMA is present in the negative pattern of the mold and the underlying PAAm is exposed in the positive pattern of the mold. The alkyne-functional PPMA reacts selectively with azides and the amine-functional PAAm reacts selectively with N-hydroxysuccinimide. Red and green fluorescent dyes with azide and hydroxyxuccinimide groups, respectively, present in the same aqueous mixture self-sort on the patterned PPMA/PAAm surface due to this selective reactivity. The composite image in Fig. 11e shows the self-sorted dyes on the surface after the reaction.

The reactivity of iCVD thin films can also be utilized as a chemical transducer in a sensing device. This has been accomplished by using iCVD to conformally coat microelectromechanical switches. The switches themselves are microcantilevers whose deformation can be transduced into an electrical signal. The conformal nature of iCVD is ideal for coating the complex cantilever geometry. The volume expansion of the iCVD polymer thin film upon reaction with an analyte induces a stress that causes the cantilevers to bend. This mechanical deflection generates an electrical current when the bending cantilever contacts an interdigitated electrode, thereby generating a current.

Chemical selectivity was accomplished by using an iCVD film of poly(maleic anhydride-alt-vinyl pyrrolidone) (P(MA-alt-VP) as the anhydride moiety reacts readily with amines to form an amide bond. In order to generate large stresses, the volume expansion of the film due to reaction with an analyte was constrained by incorporating the crosslinker di(ethylene glycol) divinyl ether into the film. The high degree of compositional control in iCVD allows the polymers to be engineered to generate a large stress upon reaction in the analyte, which in turn generates a large deflection in the cantilever. Fig. 11f shows the coated cantilever before exposure to the analyte as well as the deformation induced by exposing the coated cantilever to the analyte. Without the use of the crosslinker, it was found that the cantilever did not bend sufficiently to contact the interdigitated electrode.

**Current stance and future outlook**

Our work in iCVD and oCVD has been motivated by the desire to integrate the possibilities of CVD processing with the promise of polymeric materials. Free-radical and oxidative polymerization chemistry have been accomplished by iCVD and oCVD, which has led to a rapid expansion of available polymers. Understanding the film growth mechanism on complex substrates has enabled deposition on fibrous substrates down to the nanoscale as well as trenches on the microscale.

The scalability and proven industrial usage of CVD processes suggests that iCVD and oCVD may be more than research curiosities. Scale-up has been achieved by converting a large-scale plasma chamber into an iCVD reactor. Appropriate process conditions for the large reactor were determined by dimensionless analysis. Roll-to-roll processing in this large chamber was also demonstrated, with deposition rates on moving substrates equivalent to those on stationary substrates. Other research groups are studying mechanistic and reactor design aspects. Proposed modifications include the use of an axisymmetric reactor and replacing the filaments with a “hot-zone” packed with glass beads to promote heat transfer.

The most recent advances in iCVD and oCVD have included several demonstrations of practical utility, each of which utilize at least one of the unique aspects of iCVD or oCVD—systematic control of polymer composition or properties, conformal coatings around complex geometries, and functional and reactive coatings. For these applications, iCVD and oCVD can serve as platform technologies for further fundamental research and development. Future work in iCVD and oCVD will center on integrating the previous research into device applications and prototypes in areas such as chemical or biological sensing, biological activity, stimuli-responsive films and organic electronics.

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