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Perspective

Solvent-free Modification of Surfaces with Polymers: The Case for Initiated and Oxidative Chemical Vapor Deposition (CVD)

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Introduction

Applications employing surface modification by polymers include, but are not limited to, electronic, biomedical, and energy devices; food and drug encapsulation; and textiles and membrane functionalization. Surface modification by polymers offers a number of advantageous characteristics such as mechanical robustness, excellent electronic and optical properties, tunability of the surface density of chemical functional groups, ease of processing, scalability, and low cost.[1] As new requirements for devices become more complex, it is increasingly difficult to fulfill these combinations of needs, which can include conformal coverage over nonplanar substrates, patterning with nanometer-scale resolution, and responsiveness to the environment. Synthesis of new polymeric materials and/or development of new processes for polymer film fabrication are often required for the desired surface modification of new devices, products, or materials.

In general, a polymer is a long chain molecule composed of repeated units of one or more types of monomers. The molecular weight of a polymer chain ranges from a few thousand to more than a million grams per mole. Thus, polymers are typically nonvolatile. As the polymer is heated, decomposition typically occurs before vaporization. Consequently, after polymer synthesis, film formation is typically achieved by a second step involving either (1) liquid processing, such as spin-coating, dip coating, or ink-jet printing, followed by evaporation of the solvent, or (2) melt application, followed by a cooling period. However, there are several important limitations associated with liquid-phase processing.[2] For example, the solvent used during the deposition process can significantly alter the properties of the underlying polymer, making the stacking of different polymer layers extremely challenging.[3] Additionally, liquid-phase processing can degrade substrates, inducing undesirable phenomena including shrinkage, bleaching, swelling, and wrinkle formation. Fragile substrates, like paper and fabric, may experience sharp declines in mechanical properties and ultimately disintegrate or dissolve. Finally, polymeric materials are difficult to purify. Indeed, limiting the presence of impurities attributed to residual solvent content can be crucial for some applications, including noncytotoxic biomedical applications and high-purity electronic applications.[2]

Vapor-phase processes are anticipated to dramatically improve or eliminate difficulties arising from solvent usage.[1,2] Since polymers have limited volatility, the alternative strategy is to carry out the polymer synthesis reactions and the film deposition, simultaneously, in a single-step process, known as chemical vapor deposition (CVD).[1,2] In such process, the monomers are introduced at the vapor phase and, thus, can be typically purified to a significantly higher degree than the resulting polymer. One well-known method for implementing this idea is plasma-assisted CVD, by which plasma excitation activates vaporized monomers to form a polymer-like film on the cooled surface of the substrate.[1] However, due to nonspecific chemistry and damage produced by the energetic plasma, the organic layer obtained is typically highly cross linked, contains dangling bond defects, and possesses a lower density of organic functional groups than would be expected based on the monomer structure.[4] The retention of surface functionality can be improved by lowering the plasma power at the expense of slower film growth rates.[4,5]

Recently, initiated CVD (iCVD) and oxidative CVD (oCVD) resulted in the synthesis of polymeric films displaying full retention of the organic functional groups present in

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Table 1. Advantages of iCVD/oCVD Process

Process Characteristic	Advantage
Solvent-free	Easy stacking of polymeric films Limited damage to the substrate Copolymerization with immiscible monomers Reduced waste generation
Vapor-phase	Conformal coverage One-step film formation Extremely low level of impurities Tunable film properties
Uniqueness of iCVD/oCVD	Retention of organic functionality Applicability of various monomers Scalable Mild, low power processes
Use of polymeric materials	Low cost Flexible Wide variety of functional groups Well-known structure-property relationships

the monomeric reactants. For iCVD and oCVD, a volatile initiating agent or oxidizing agent, respectively, is introduced along with the gaseous monomers.[6,7] The initiator decomposes easily by low-power activation with either a hot filament or ultraviolet (UV) irradiation.[1,2] The oxidizing agent reacts directly with the monomer as the first event in the oxidative step growth polymerization reaction mechanism.[7,8] With these solvent-free processes, a number of functional films including biocompatible,[9] functionalizable,[4,5,10] superhydrophobic,[11–13] and electrically-conductive polymeric films[7,8] were successfully fabricated. In this perspective, we will review the competitive advantages of the iCVD and oCVD processes (Table 1), and explore their utility and future directions and prospects in device applications.

Characteristics of Initiated and Oxidative CVD Processes

CVD of inorganic films is a well-established technology; especially in the semiconductor industry.[2] Any improvement in the CVD processes leads to enhancements in semiconductor device performance. These process improvements were empowered by a deep understanding of the relationship between reactor parameters and the properties of deposited films.[2] Currently, CVD of inorganic materials is a fully mature technology for industrial manufacturing and is accepted as a scalable technology for device fabrication. Recent studies demonstrate that the desirable characteristics of CVD for inorganic materials remain valid for organic films grown by iCVD and oCVD.[14–16] For example, film properties can be easily and systematically tuned by changing process parameters, such as the feed gas ratio, the process pressure, the process temperatures, and the overall flow rate of feed vapors.[14,15] The iCVD process has proven to be scalable to large batch and semicontinuous roll-to-roll reactors.[17] Control of the flow profiles inside the process chamber enables uniform film growth over 12 × 12 in. square substrates; additionally, precise, real-time control of film thickness is possible at the nanometer scale.[3,17]

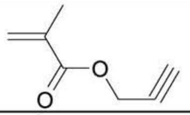
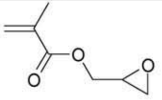
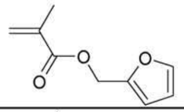
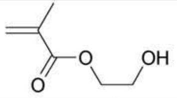
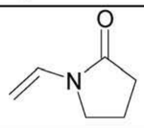
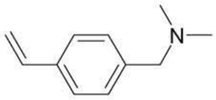
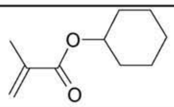
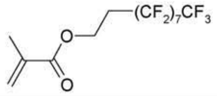
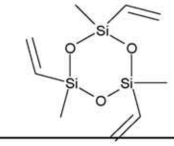
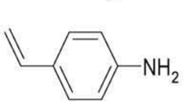
iCVD is a low-energy, low-temperature process that allows for selective activation of the initiator molecules to form radicals. In contrast to what happens in plasma-assisted CVD processes, monomers in iCVD remain intact without degradation of their organic functional groups.[2,18] For iCVD, the polymer growth rate can be optimized independently of the degree of organic functional group retention, allowing both high-film growth rates and 100% retention of functionality to be achieved simultaneously.[18]

The underlying kinetic mechanism of iCVD applies broadly for many different types of vinyl monomers. Operating conditions for depositing new polymers can be predicted based on knowledge of the vapor pressure of the monomers.[14,15] Thus, a wide variety of monomeric materials can be polymerized using the iCVD process; indeed, more than 50 different polymeric film compositions have been reported in the last decade.[1] These coatings include functionalizable,[4,5,10] biocompatible,[9] pH-responsive,[19] temperature-responsive,[20] superhydrophobic,[11–13] antibacterial,[21] antibiofouling,[22] and dielectric films.[23] Table 2 summarizes a partial library of iCVD and oCVD polymer films. CVD copolymers can be freely synthesized, even from monomers which would not mix in the liquid phase. For instance, copolymers of the hydrophilic monomer hydroxyethylmethacrylate (HEMA), and the hydrophobic monomer perfluoroalkylmethacrylate (PFMA), were first achieved via iCVD.[24] Both random and alternating iCVD copolymers have also been synthesized.[19,24,25]

Since initiators readily decompose to form reactive radicals, iCVD is a low-power process. Energy is typically supplied either through resistive heating or through ultraviolet (UV) light irradiation, and should be sufficient to activate the initiator but insufficient to decompose the monomers.[26] This requirement can also be achieved under conditions of very low-power plasma-assisted CVD.[27] In addition, typical iCVD process pressures (50 to 1000 mTorr) do not require the use of a high-vacuum apparatus; a basic rotary pump is sufficient to operate the CVD reactor. To promote adsorption of the monomer species onto the growing surface, near-ambient substrate temperatures (15–40°C) are typically used,[1,17] enabling the coating of delicate substrates such as paper, fabrics, membranes, and plastics without damage.[8,21] Thus, iCVD polymerization is ''gentle'' process, because solvents are avoided and both the process power and substrate temperatures are low.

In addition, vapor-phase processing permits the gaseous precursors to diffuse into small features, making it possible to achieve conformal coverage of complex substrate architectures even at the nanometer scale.[28] Conformal coverage is highly desirable for a variety of device applications,[10–12,29–32] including the formation of diffusion barriers, dielectric films, and encapsulation layers.[29] In contrast, liquid-phase polymer solutions often wick into geometric features, distorting the original profile of the surface.[28] Figure 1 compares scanning electron micrographs (SEM) of trenches coated using iCVD, spin-coating, and pulsed plasma-assisted CVD, respectively. The liquid-

Table 2. Partial Library of Monomers and Initiators used in iCVD or oCVD Process

Name of Monomer	Chemical Structure	Function/Application
PMA (propargyl methacrylate)[4,5]		Functionalizable with N_3- functionality
GMA (glycidyl methacrylate)[10,30]		Functionalizable with amine functionality; e-beam patternable; UV-curable
PFM (pentafluorophenyl methacrylate)[36]		Functionalizable with amine functionality
FMA (furfuryl methacrylate)		Diels-Alder reaction with vinyl group
HEMA (hydroxyethyl methacrylate)[3,9,34]		Biocompatible, water swellable hydrogel
VP (vinyl pyrrolidone)[22]		Biocompatible / anti-fouling
DMAMS (dimethylaminomethyl styrene)[21]		Anti-bacterial
CHMA (cyclohexyl methacrylate)[28]		Dielectric
PFA (perfluorodecyl acrylate)[12,13]		Low surface energy superhydrophobicity
V_3D_3 (trivinyltrimethyl cyclotrisiloxane)[23]		Low-k dielectric material
AS (4-aminostyrene)[10]		Bio-functionalizable with epoxy/COOH

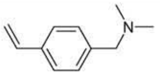
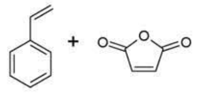
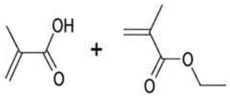
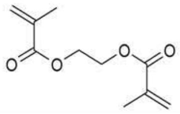
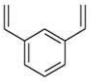
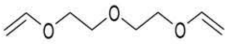
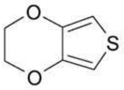
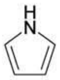
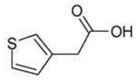
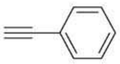
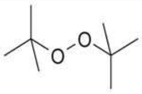
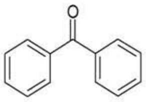
(Continued)

phase spin-coating process results in essentially no coverage of the trench sidewalls and a thick film layer puddled at the bottom of the trench. In the case of the plasma-assisted CVD process, the film thickness varies significantly with position along the trench; this is a consequence of the uneven distributions of the electric field and the concentrations of the reactive species.[28] In part, the conformality of the iCVD process is a consequence of its reliance on neutral species to achieve film growth. The degree of step coverage can be tuned using iCVD polymer deposition parameters.[28]

Mechanistic Understanding and Quantitative Modeling

The polymerization reaction mechanism underlying the iCVD process consists of three stages: (1) Introduction and

Table 2. (Continued)

Name of Monomer	Chemical Structure	Function/Application
NIPAAm (*N*-isopropylacrylamide)[20]		**Temperature sensitive**
MA-alt-St (maleic anhydride-alt-styrene)[19]		**Bio-functionalizable with amine pH-sensitive; water swellable**
MAA-co-EA (methacrylic acid-co-ethyl acrylate)		**pH sensitive** **Bio-functionalizable with amine**
EGDMA (ethyleneglycol dimethacrylate) [27,34]		**Crosslinker in iCVD** **Crosslinked polymer for nanotube fabrication**
DVB (divinylbenzene)		**Crosslinker in iCVD**
DEGDVE (di(ethylene glycol) di(vinyl ether)		**Crosslinker in iCVD** **Anti-fouling**
EDOT (3,4-ethylene - dioxythiophene) [8,16,17]		**Electrically conducting**
PPy (pyrrole) [37]		**Electrically conducting**
TAA (3-thiopheneacetic acid) [37]		**Electrically conducting** **Functionalizable with amine** **Sensor application**
PA (phenyl acetylene) [38]		**Electrically conducting** **Semiconducting**
TBPO (t-butylperoxide)		**Thermal initiator for iCVD**
Benzophenone[29]		**Photo-initiator for iCVD**

mixing of vaporized monomer and initiator molecules; (2) decomposition of the initiator to yield radicals and the delivery of the reactive radical species and monomers to the surface of the substrate, and (3) polymerization and formation of a thin solid film on the cooled substrate.[1,14] The core concepts for the iCVD process[14,15] are derived directly from the solution-phase free-radical polymerization process, which has been extensively studied and for which the process-composition-property relationships are well-understood.[2] Free-radical polymerization is a chain reaction involving extremely reactive radicals with very short lifetimes. The reaction mechanism consists of three steps: (1) Initiation, which increases the number of free radicals; (2) propagation, which increases the molecular weight of the growing chains and maintains the number of free radicals, and (3) termination, which decreases the number of free radicals.[1,14] Generally, free radicals are formed from the decomposition of initiators rather than direct radical formation from the monomers. The radicals then attack the reactive sites, typically the vinyl functionalities of the monomers, and start the growth of polymeric chains. This growth continues

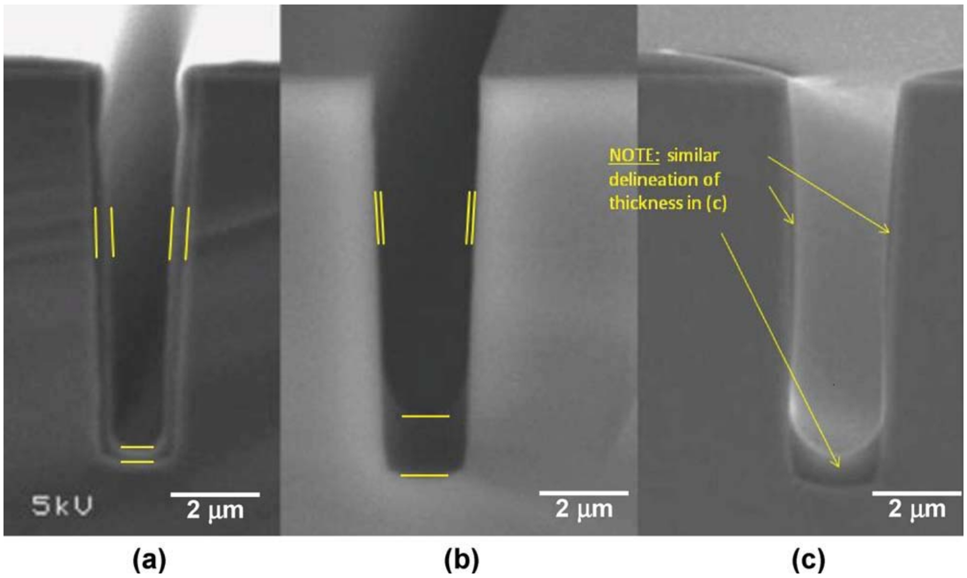


Figure 1. Films deposited by (a) iCVD, (b) spin-coating, and (c) pulsed plasma-assisted CVD.

The meniscus-like shape of the spin-coated film clearly shows the effects of solvent surface tension, while the decreased film thickness at the external trench corners and increased thickness in the internal trench corners in the pulsed plasma-assisted CVD film suggest competition between etching and deposition. The iCVD film is continuous and of comparable thickness around the top, bottom, and sidewall of the trench. Copyright 2008 Wiley InterScience.[28]

through the rapid addition of monomers. The chain reaction is terminated either by radical-radical recombination or by the transfer of reactive radicals.

For conventional free-radical polymerization, all of the mechanistic steps occur in a single phase (e.g., the solution phase), and at a single temperature; however, iCVD involves both gas-phase and heterogeneous elementary reactions, which take place at different temperatures. For the iCVD process, vaporized initiator and monomer species flow into the reaction chamber (Figure 2a). The initiator is dissociated into free radicals either at or near a hot filament.[24] These radicals are then transported to the substrate, where they react with monomers adsorbed onto the surface of substrate. To promote adsorption, the substrate is maintained at a low temperature. The continuing adsorption of monomers feeds the polymerization reaction. Chain growth is terminated by recombination with a radical initiator or a radical from another polymer chain.

As the chain length of the polymer grows, it becomes less volatile, leading to the postulate that the polymerization reaction occurs only at the surface of the substrate.[14,15] Accordingly, the rate of polymerization is dependent on the surface concentration of the monomer. The dimensionless ratio of a monomer's partial pressure to its saturation vapor pressure (P_M/P_{sat}) has proven to be a useful predictor of the concentration of monomer adsorbed on the surface.[14,28] Values of $P_M/P_{\mathrm{sat}} < 1$ are employed to avoid the condensation of monomers. Interestingly, the same relationships established to quantitatively predict the surface adsorption isotherms of small molecules, such as H_2 and CO, were found to also describe the adsorption of much larger vinyl monomers, such as butyl acrylate ($CH_2 = CHCOO(CH_2)_3CH_3$). In particular, V_{ad}, the total volume of the adsorbed monomer, depends on the gas-phase concentration given in the form of the ratio P_M/P_{sat} through the Brunauer-Emmett-Teller (BET) equation.[14,15]

$$\mathbf{v}_{ad} = \frac{V_{ml}c\left(\frac{P_M}{P_{sat}}\right)}{\left(\mathbf{1}-\frac{P_M}{P_{sat}}\right)\left[\mathbf{1}-(\mathbf{1}-c)\frac{P_M}{P_{sat}}\right]} \tag{1}$$

where, V_{ml} is the adsorbed volume for a monolayer. The constant c is typically used as a fitting parameter, but can also be obtained using

$$c = \exp\left(\frac{\Delta H_{des} - \Delta H_{vap}}{RT}\right), \tag{2}$$

where ΔH_{des} is the enthalpy of desorption of a monolayer from the substrate and ΔH_{vap} is the enthalpy of vaporization from the liquid adsorbate. When P_M/P_{sat} is much less than unity, a simple linear relationship exists between the surface and gas-phase monomer concentrations since $V_{\mathrm{ad}} \approx V_{ml} \cdot c \cdot (P_M/P_{\mathrm{sat}})$. The surface concentration of monomer [M], can be described by

$$[\mathbf{M}] = \frac{\rho_M}{Mw_M} \cdot \frac{V_{ad}}{V_{ml}} \tag{3}$$

The number-average molecular weight of iCVD polymers was also found to increase linearly with increasing P_M/P_{sat},[14] a trend which is also generally observed in liquid-phase radical polymerization.[15] These observations clearly demonstrate that after accounting for the differences between the filament and substrate temperatures and for the adsorption isotherm, the deposition mechanism of the iCVD process shows a striking similarity to the reaction kinetics of liquid-phase free-radical polymerization.[14,15] This implies that the well-known characteristics of free-radical polymerization in the liquid phase are directly applicable to interpret, develop, and

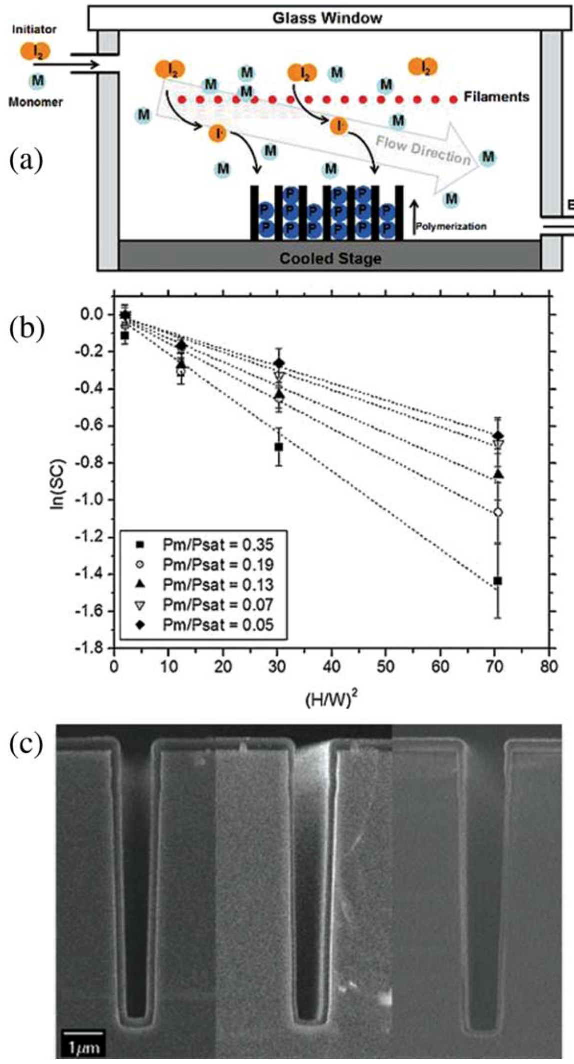


Figure 2. (a) Schematic of the deposition reactor with the anodized aluminum oxide (AAO) template and the iCVD process. During deposition, radicals attack the monomer molecules adsorbed in the pores of the template, initiating the polymerization, (b) step coverage of PEGDA films vs. trench aspect ratios at various P_m/P_{sat} values, and (c) SEM images of PEGDA films deposited at P_m/P_{sat} values of 0.05 (left), 0.13 (middle), and 0.35 (right) on trenches with aspect ratios of 5.5. The observed step coverages are approximately 0.8 (left), 0.65 (middle) and 0.5 (right).

(a) Copyright 2009 The Royal Society of Chemistry.[34] (b-c) Copyright 2010 Wiley InterScience.[29]

optimize the iCVD process for polymer deposition. For example, in a free-radical copolymerization process, the composition of the resulting copolymer is generally different from the feed ratio of the monomers due to steric hindrance and differences in the reactivity of the monomers. In liquid-phase free-radical copolymerization, reactivity ratios are well-known for each monomer pair. Copolymer film deposition is also possible using iCVD; final film compositions and calculated reactivity ratios for copolymers deposited using the iCVD process match extremely well with results from liquid-phase free-radical copolymerization.[25]

The step coverage of iCVD polymerization is also a function of the concentration of the surface-adsorbed monomer (Figure 2b and 2c), and, hence, P_M/P_{sat}. At lower P_M/P_{sat}, a higher degree of conformal coverage was obtained.[28] This dependence implies that the step coverage is determined by the interaction between the reactive vapor-phase species and surface-adsorbed monomers. This study also demonstrated that the sticking coefficient of the reactive species in the vapor phase, which are typically initiator radicals, plays a critical role in controlling step coverage.[28] The step coverage *SC*, can be described using the sticking coefficient, Γ

$$\ln(SC) = -0.48(\Gamma)\left(\frac{L}{W}\right)^2 \tag{4}$$

where L and w are the length and width of the trench, respectively. Better step coverage (e.g., SC approaching unity) is obtained with lower sticking coefficient and P_M/P_{sat} values. These lower values ensure a uniform concentration distribution on the trench surface, and the corresponding uniform film growth rate enables high-step coverage of trench features with high-aspect ratios.[28] Another recent study demonstrated that the concentration of vinyl bonds at the surface determines step coverage and confirmed that increasing P_M/P_{sat} increases the sticking coefficient.[29] In addition, the sticking coefficient was demonstrated to be insensitive to the initiator concentration, which suggests that the highly-volatile initiator radicals are not adsorbed to any appreciable degree on the substrate, and the step coverage is governed by the chemisorption of the initiator radicals onto the adsorbed monomer sites.

Similar phenomena are operative during oCVD and, thus, the conformality of these polymer films is also highly dependent on the physical nature of the oxidizing agent used.[8,33] For example, Fe(III)Cl_3 oxidant is directly evaporated by heating a cell inside the reaction chamber. The flux of the evaporated oxidant is directional, which results in poor step coverage on the standard trench structure. On the other hand, Cu(II)Cl_2 decomposes during evaporation to form a gaseous oxidant Cl_2, which can freely diffuse into the trench structure, resulting in much better step coverage of the conducting polymer film.[8] A similar result was obtained with a volatile oxidizing agent Br_2, with excellent step coverage of the conducting polymer film.[33]

Analysis based on the dimensionless Reynolds number, thermal Peclet number, and mass Peclet number guided the scale-up of the iCVD process, enabling uniform deposition over a 30 cm by 30 cm area.[17] A roll-to-roll iCVD process was also performed with the scaled-up reactor, and polymer films produced at rolling speeds of up to 60 mm/min were identical to films produced using a stationary reactor configuration.[17] This scalability is highly advantageous for further high-throughput studies and the industrial-scale commercialization of the iCVD process.

Example applications of conformal CVD polymers

This section provides examples of some specific technologies that can benefit from the integration of CVD polymers. Desirable attributes of CVD polymers include outstanding

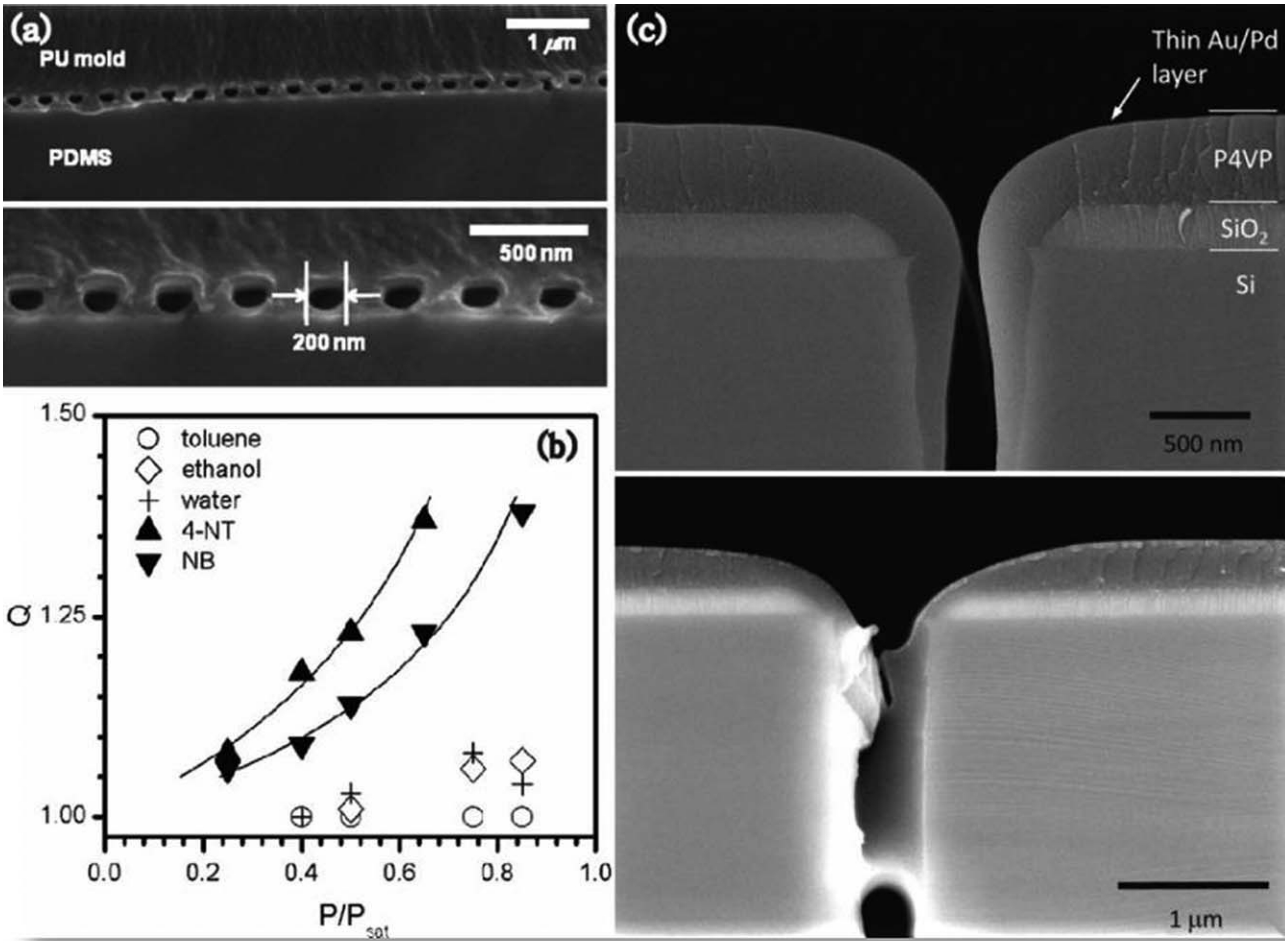


Figure 3. (a) Cross-sectional image of a 200 nm nanochannel formed by a nanoadhesive applied onto a PDMS surface and a poly(urethane) surface and without the alternation of the channel design,[28] (b) equilibrium swelling ratios of P4VP with nitroaromatics and potential interferents,[29] and (c) SEM images of P4VP-coated trench substrates (top) before, and (bottom) after exposure to nitrobenzene. The image in the bottom figure shows that the contact between the polymer sidewalls in the trench interior is permanent.[29]

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step coverage over complex substrate architectures combined with a wide range of possible surface properties (Table 2). Indeed, some applications are uniquely enabled by ultrathin, conformal iCVD and oCVD polymer films.

Micromechanical and electrical systems (MEMS)

Micromechanical and electrical systems (MEMS) hold promise in a broad variety of applications including, but not limited to, the following: useful tools for the rapid diagnosis of diseases, programmed drug delivery devices for personalized administration of medicine, chemical and biosensors, and electronic actuators.[1] Integration of signaling, actuation, and transducing units in the confined area offered by MEMS devices requires that feature dimensions become increasingly smaller.

Bonding is regarded as one of the most difficult steps in MEMS fabrication processes.[10,30] While fusion bonding and anodic bonding ensure strong adhesion, these processes require high temperatures and high-electric fields, which are not compatible with common organic substrates. Oxygen plasma bonding is only applicable to silicon-containing substrates. Application of traditional adhesives to organic substrates is possible, although coverage is nonconformal, which results in deformation of the original channel design.[30] Thus, an ultrathin adhesive with conformal coverage is highly desirable for MEMS bonding applications, and has motivated the new concept of a nanoadhesive using iCVD polymer films containing adhesive functionalities.[10,30] Pairing amine with epoxy functionalities resulted in iCVD nanoadhesive coatings able to define MEMS channels as small as 200 nm with adhesion strengths exceeding 50 psia (Figure 3a).[30] More recently, an improved iCVD nanoadhesive demonstrated a longer adhesion lifetime in an aqueous environment with an adhesion strength higher than 150 psia.[10] This process is applicable to almost any substrate, including common organic substrates such as PTFE, polystyrene (PS), poly(ethylene terephthalate) (PET), and polycarbonate (PC), allowing much cheaper organic substrates to be used for MEMS device fabrication.[10,30]

Nitroaromatic sensors for explosive detection

Nitroaromatic compounds, including 2,4,6-trinitrotoluene (TNT), form one of the most common classes of explosives.[31] Thus, nitroaromatic sensors are of paramount importance, but the fabrication of high-sensitivity sensors is extremely challenging due to the low-vapor pressures of these compounds. In addition, the transducing process of the sensor needs to be simple enough for commercialization, especially for portable devices. For this application, a new nitroaromatic sensor was developed using iCVD polymer on a trench structure (Figure 3b and 3c).[31] In this device, a chemically-sensitive polymer film was conformally deposited on an electrically-insulating trench substrate. A nonconformal, electrically-conductive metal layer (gold/palladium) was deposited on top of the polymer. The polymer film used in this study was iCVD poly(4-vinylpyridine) (P4VP).[22] P4VP demonstrates a selective volume expansion when exposed to nitroaromatic compounds (Figure 3b). The volume expansion is reversible and quantitatively proportional to the nitrobenzene concentration. When a P4VP film is applied to the trench structure, as shown in Figure 3c, exposure to nitroaromatic vapors forces the gold layers on opposite sides of the trench to contact and create an electrical short, which is easily detectable by measuring the electrical resistance of the circuit. A prototype sensor device was capable of detecting nitrobenzene at a concentration of 493 ppm.[31] With optimized geometry, the calculated detection limit is predicted to be approximately 1 ppb, which is comparable to current state-of-the art systems.[31] The conformal coverage of iCVD P4VP enables the fabrication of this sensor and the unique selective volume expansion of the polymer determines the performance of the device. Since the trench structure and the transducing portions of the sensor are relatively easy to fabricate, this sensor has a great potential as a portable explosive detector.

Membranes

Membranes are of great importance in our daily lives. A wide range of commercial applications includes the purification of drinking water, gas separation, desalination of salt water, and wastewater treatment.[1] Membrane performance is a function of pore size, surface chemistry, and functionality. To control these properties, modification of membrane surfaces has been extensively studied. Conformal coverage of membrane pores is one of the most important attributes motivating surface modification using iCVD. In addition, ultrathin layers are typically desired, since the presence of thicker films on the pore sidewall will alter the design of the membrane's porous structure. Such ultrathin and conformal coatings are difficult to achieve with liquid-phase processes due to surface tension limitations.

Uniform surface modification using iCVD poly(1H, 1H,2H,2H-perfluorodecyl acrylate) (PPFDA) was achieved inside high aspect ratio capillary pores of fiber-on-end membranes.[13] The very low-surface energy of PPFDA (9.3 mN/m) gave rise to significant changes in contact angle on both the top and back sides of the membrane, clearly indicating that the reactants traveled through the pores. X-ray photoelectron microscopy (XPS) confirmed that that the fluorine peak from PPFDA was detected on the back side of membrane. Electron microprobe analysis performed on a membrane cross section confirmed the presence of iCVD PPFDA as thin as 10 nm along the entire length of pores with aspect ratios approaching 80:1.[18]

The high degree of conformal coverage achievable via iCVD can be utilized to fabricate free-standing nanotubes using a membrane as a template. A film of poly(ethylene glycol diacrylate) (PEGDA) was deposited on polycarbonate membranes that were later dissolved in chloroform.[29,34] By altering the pore geometry of the membrane, various kinds of nanotubes were obtained. The nanotubes were 8 μm long, with 70 nm-thick walls. The diameters of the nanotubes ranged from 400 to 800 nm. The high degree of conformal coverage and robustness of the iCVD polymer film enabled the fabrication of these 3-D polymer structures.[29]

The membrane-templated nanotubes were also used to encapsulate sensory material. Biocompatible hydrogel nanotubes were used to encapsulate optode sensors; incorporation of the optodes was confirmed by transmission electron microscopy (TEM).[32] The hydrogel layer conformally covered the optode material with a thickness of 50 nm. This conformal encapsulation is crucial to prevent leaching of active compounds from the optode. This sensor system exhibited a significantly elongated lifetime after injection into a mouse. Without the encapsulation, 60% of the optode intensity was lost within an hour after *in vivo* injection of the sensor. More than 90% of the signal intensity remained after the same time span using the encapsulated nanosensor.[32] Thanks to the biocompatibility and excellent step coverage of the encapsulant hydrogel, the injectable sensors hold great promise for continuous *in vivo* monitoring of chemical imbalances. With proper selection of an iCVD polymer film, this process can be applied to a variety of other sensor and drug delivery applications.

Superhydrophobicity: Controlling surface energy

Superhydrophobic surfaces are highly desirable due to their widespread applications for self-cleaning, water-repellent, and antifouling surfaces.[1] In general, hydrophobicity is a function of both the chemistry and the morphology of the surface.[12] High-surface areas and low-surface free energies are desirable for superhydrophobic surfaces, and numerous methods have been suggested to achieve these properties. For this purpose, iCVD and oCVD were applied to deposit polymer films onto various complex substrate architectures, including electrospun fibers,[12] carbon nanotubes (CNTs),[11] paper,[8] and membranes.[13] All of these substrates retain their high-surface areas as a result of the conformality of the iCVD and oCVD processes. The surface free energies of the nano- and micro- structured substrates can also be rendered extremely low by using fluorinated CVD polymer films. A PTFE film was conformally deposited onto a bundle of multiwall CNTs. CNTs coated with a 40 nm-thick PTFE film exhibited exceptional superhydrophobicity.[11]

Electrospun fibers were also covered with poly(perfluoroalkyl ethyl methacrylate) (PFEMA), and a water contact angle exceeding 175° was obtained with an extremely low level of hysteresis.[12] In this work, the surface structure was systemically controlled by changing the parameters of the electrospinning process, and an optimized surface structure was suggested for a superhydrophobic surface.[12] In another study, a temperature-responsive polymer film was deposited on electrospun fibers using the iCVD process. A reversible contact angle change of more than 120° was observed with each turn-over.[20] A highly porous nanomorphology was conformally incorporated onto a paper mat by depositing an oCVD conducting polymer film.[8] The nanomorphology could be easily obtained by proper selection of the oxidizing agent in the oCVD process; application of the coating resulted in a well-defined hierarchical structure of "electrically conducting paper".[8] The hierarchical structure enormously increased the surface area of the paper mat. Coating the mat with a 20 nm-thick layer of iCVD PPFDA resulted in a water contact angle exceeding 165°. The paper mat also demonstrated an ethanol contact angle of up to 113°; this is one of the best examples of oleophobicity obtained with conducting polymer coatings.[8] Highly porous membranes were also treated with PPFDA coatings using the iCVD process and demonstrated superhydrophobicity with water contact angles greater than 150°.[13]

Since conformal surface coatings can make the surface energy of complex substrates uniform, iCVD polymer coatings can be used to study the effects of surface topography in isolation. Recently, a directional surface structure was fabricated using a conventional photolithography process and tilted-angle deposition of a gold film.[34] By conformally coating the structure using iCVD PEGDA, the surface structure effect could be successfully decoupled from the effect of surface chemistry. Unidirectional liquid spreading was achieved, and it was verified that this effect was solely derived from the asymmetric nanostructure.[35]

Conclusions

iCVD and oCVD are vapor-phase processes that allow polymeric films to be directly deposited from monomeric units in a single step. Mechanistic studies reveal many kinetic analogies to liquid-phase reactions. By tuning CVD process parameters, systematic control is achieved over film properties, including the degree of conformal coverage of complex surface geometries. Scalability of the iCVD process has also been demonstrated and industrial-scale commercialization has been reached for certain applications, while it is within reach for a very broad range of materials and devices. The advantages of iCVD and oCVD polymer films include full retention of functionality, excellent step coverage, damage-free deposition of polymeric coatings onto vulnerable substrates, and exclusion of solvent-oriented damage, which enables stacking of the films. The example applications described in this Perspective and which take advantage of the conformal coverage and the variety of polymer film properties afforded by the iCVD and oCVD processes are illustrative of the tremendous potential offered by this new and evolving technology. These novel solvent-free surface-modifying processing technologies have the potential to enable breakthroughs in a wide range of applications, including flexible electronics, biomedical devices, sensors, MEMS, and membrane technologies.

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