Designing polymer surfaces via vapor deposition

Chemical Vapor Deposition (CVD) methods significantly augment the capabilities of traditional surface modification techniques for designing polymeric surfaces. In CVD polymerization, the monomer(s) are delivered to the surface through the vapor phase and then undergo simultaneous polymerization and thin film formation. By eliminating the need to dissolve macromolecules, CVD enables insoluble polymers to be coated and prevents solvent damage to the substrate. Since de-wetting and surface tension effects are absent, CVD coatings conform to the geometry of the underlying substrate. Hence, CVD polymers can be readily applied to virtually any substrate: organic, inorganic, rigid, flexible, planar, three-dimensional, dense, or porous. CVD methods integrate readily with other vacuum processes used to fabricate patterned surfaces and devices. CVD film growth proceeds from the substrate up, allowing for interfacial engineering, real-time monitoring, thickness control, and the synthesis of films with graded composition. This article focuses on two CVD polymerization methods that closely translate solution chemistry to vapor deposition; initiated CVD and oxidative CVD. The basic concepts underlying these methods and the resultant advantages over other thin film coating techniques are described, along with selected applications where CVD polymers are an enabling technology.

Ayse Asatekin[1], Miles C. Barr[1], Salmaan H. Baxamusa[1], Kenneth K.S. Lau[2], Wyatt Tenhaeff[1], Jingjing Xu[1], and Karen K. Gleason[1,*]
[1]Department of Chemical Engineering, MIT, Cambridge MA 02139
[2]Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104
*E-mail: kkg@mit.edu.

Chemical vapor deposition for polymer thin films

In chemical vapor deposition (CVD) polymerization, vapor-phase monomers react to form pure solid films directly on the surface of a substrate. Thus, polymerization and coating occur in a single processing step. This enables the formation of highly cross-linked coatings as well as copolymers of incompatible monomers. Thus, a key niche for CVD is the modification surfaces with polymers having limited or no solubility, as is the case for poly(tetrafluoroethylene) (PTFE) and many other fluoropolymers, electrically conducting polymers, and highly cross-linked organic networks.

The substrate compatibility afforded by CVD is essential for implementing polymeric surface modification layers in practical applications such as medical implants, membranes, and microfluidic devices. For example, consider a tissue paper substrate which cannot survive exposure to harsh solvents or high temperatures. A 40 nm thick CVD PTFE renders the surface of the tissue non-wetting (Fig. 1a,b), a dramatic demonstration of the "gentleness" of CVD polymerization. During the CVD treatment, the tissue remains at room temperature, in
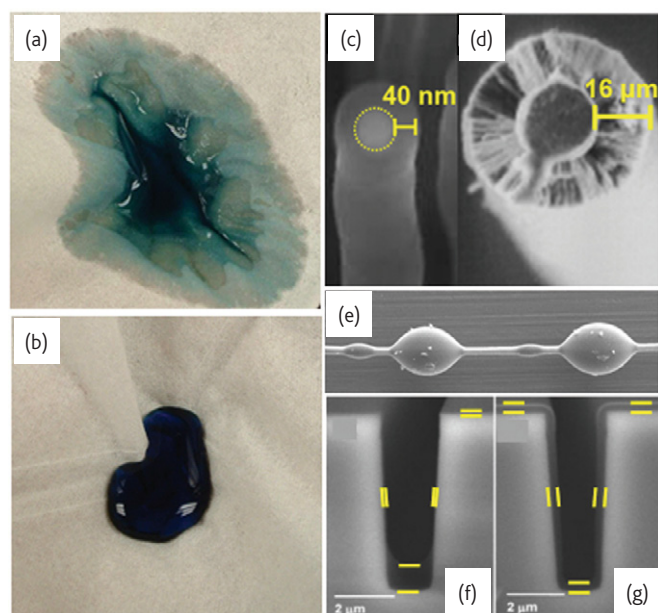

Fig. 1 *Demonstrations of the substrate compatibility and conformality of CVD polymer coatings. A tissue before (a) and after (b) CVD surface modification of a tissue with a 40 nm thickness of CVD poly(tetrafluoroethylene) (PTFE). Without surface modification, the tissue absorbs dyed water. After modification with PTFE, it exhibits hydrophobic behavior. This demonstrates the ability to coat even such delicate substrates without altering bulk properties and damaging the underlying structure. Conformality is achieved via CVD PTFE (c) at the nanoscale by growth on multiwall carbon nanotubes[48] and (d) at the microscale on a 25 micron diameter wire[61]. Solution silicone coating of a similar wire (e) results in dewetting. When microtrenches are solution coated with acrylate polymers, the coating is non-conformal (f), as compared to conformal iCVD acrylate coating (g)[1]. Reproduced with permission from: (a,b,f,g)[11], (c)[48], (d)[61]. © (a,b,f,g) Wiley VCH 2008, (c) American Chemical Society 2003, (d) American Institute of Physics 1996.*

stark contrast to the conventional high-temperature (~400°C) sintering step used in applying PTFE to non-stick cookware.

Vapor deposition avoids the undesirable effects of de-wetting and surface tension arising from liquid phase coating processes (Fig. 1e,f). Practical applications often involve non-planar substrates having micro- and/or nano- scale features, motivating the desire for polymeric thin films displaying uniform thickness over the geometric features present in the substrate, so called conformal coatings. Conformal coverage by CVD polymers (Fig. 1c,d,g) results from the arrival of reactants to the surface by non-directional vapor phase diffusion combined with the limited probability of the reactants "sticking" to the surface during a single collision[1]. For textiles, papers, and non-woven mats, conformal coverage results in the "shrink-wrapping" of the individual fibers comprising the substrate, thus retaining high surface area and breathability in the final coated product.

Processes for CVD polymers can readily transition out of the laboratory into commercial applications as a result of the same characteristics that make the CVD of inorganic films a mainstay of integrated circuits manufacture[2]. These desirable attributes of CVD include uniformity, scalability, purity, and ability to systematically tune film properties. Real-time monitoring using interferometry or a quartz crystal microbalance permits films to be grown to the precise thickness desired.

CVD polymerization chemistry

Chemical vapor deposition (CVD) of polymers combines the organic synthesis of polymers, typically performed in the liquid phase, with the formation of coatings from the vapor phase, widely used in the formation of inorganic thin films. The first method in forming organic films by CVD was plasma enhanced CVD (PECVD), where plasma excitation creates the active species that initiate polymerization. However, PECVD involves a complex mechanism where highly active species such as free radicals and ions are involved[3,4]. However, chemical control and functionality retention are typically limited. This led to efforts to better control the chemistry and side-reactions during CVD polymerization, through alternate reaction and initiation schemes[5,6].

The chemical mechanisms established for traditional polymer synthesis have been directly translated into CVD platform technologies for both chain growth and step growth polymerization[6]. Such selective chemical strategies are essential for devising low-energy, low-temperature CVD processes. Indeed, the chemical composition of the CVD polymer films deposited using a selective strategy is often indistinguishable from conventionally synthesized materials. For example, vapor deposition polymerization (VDP)[7] and molecular layer deposition (MLD)[8] use CVD methods to perform step growth polymerization reactions, by introducing the monomers into the reaction chamber in vapor phase and allowing them to adsorb and react on a cooled substrate. In VDP, both monomers enter the chamber

simultaneously, whereas MLD uses a sequential, alternating sequence of monomers for better control over film growth[5,8]. In some cases, CVD polymerization of well-defined linear macromolecules has no solution chemistry analog. This is the case for CVD poly(p-xylylene) films and their various functionalized forms[9], commonly termed "parylenes", which have been widely commercialized for printed circuit board and medical device applications[10]. Each of these methods is able to form thin, conformal, functional films by proper control of operating parameters, but suffer from various setbacks. For example, MLD is a very slow process that requires extensive control over changing monomer flow rates. Both VDP and MLD suffer from issues in precursor delivery, as the monomers involved are often of low volatility. Parylene monomers are often expensive, and new chemistries generally require custom synthesis.

This review focuses on two more recent techniques of CVD polymerization: initiated CVD (iCVD) and oxidative CVD (oCVD)[11,12]. The first of these methods closely translates free radical polymerization to vapor deposition, whereas the second is used to form coatings of conducting polymers. Both methods benefit from high chemical control and functionality retention, and are able to form conformal coatings on various substrates[11,12].

In *initiated CVD (iCVD)* an initiating species, such as tert-butyl peroxide, and a chain growth monomer are simultaneously introduced through the vapor phase. Inside the iCVD reactor chamber (Fig. 2a), heated filament wires are suspended a few centimeters above the substrate. The modest temperature of the filaments (~250°C) results in selective formation of free radicals from the initiator without cracking of the monomer. Adsorption and polymerization

then proceed on a cooled substrate. In the absence of an initiator species, film growth is negligible[13]. The iCVD method has proved exceptionally versatile for chain growth polymers including PTFE[14], acrylates[15-18], methacylates[19,20], styrenes[21, 22], vinylpyrrolidone[23] and maleic anhydride[21,22] (Fig. 2b). A variation on the iCVD method, involves the simultaneous vapor phase introduction of a photosensitive initiator along with a vinyl monomer. Upon excitation by a UV light source, a *photoinitiated CVD (piCVD)* polymer layer deposits[24]. As in the case with other CVD depositions, the range of polymer structures that can be deposited by iCVD is limited by the delivery of the precursors into the vacuum chamber and onto the substrate surface. The precursor molecules need to have a high enough vapor pressure to achieve a reasonable and steady flow rate into the reactor. This limits the use of monomers and initiators with high molecular weight or polarity.

Most iCVD and piCVD reactors are pancake shaped vacuum chambers into which monomers are evaporated and metered by mass flow controllers or needle valves (Fig. 2a)[11]. Vertical barrel style reactors[25] and larger scale roll-to-roll systems[18] have also been described. In all cases, reactors must be designed to ensure uniform gas flow to achieve uniform film thickness. One or more monomers can be delivered to the reactor, and their delivery rates can be varied throughout the deposition process, making it possible to form copolymers, terpolymers and gradient chemistries with simple control[13,26,27]. The total pressure in the reactor, filament temperature and stage temperature can also be used to tune and optimize the deposition process[15,16,28]. iCVD reactors are often equipped with viewports that allow *in situ* monitoring of the deposition process,
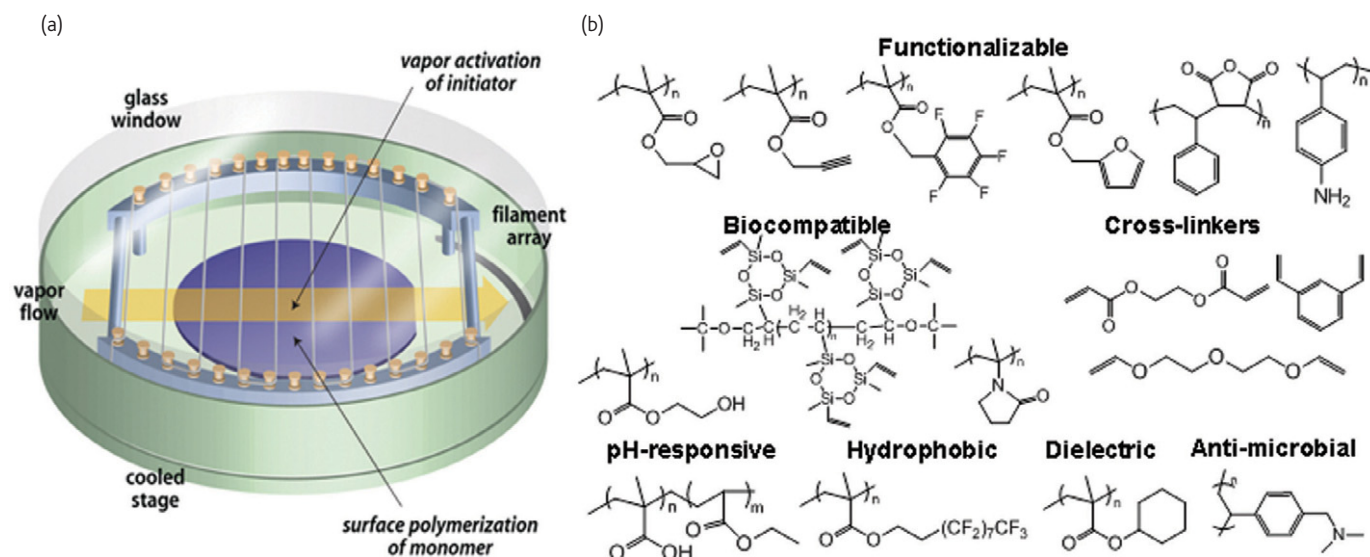

Fig. 2 (a) Schematic of a typical iCVD reactor. (b) Some functional monomers polymerized by iCVD and piCVD. (a) Reproduced with permission from[15]. © American Chemical Society 2006.
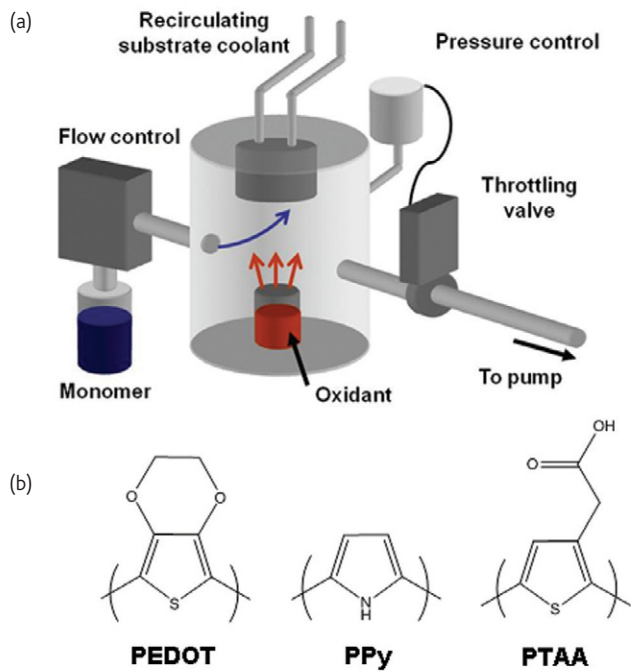
Fig. 3 (a) Schematic of a typical oCVD reactor. (b) Chemical structures of conducting polymer deposited by oCVD. PEDOT: poly(ethylenedioxythiophene), PPy: polypyrrole, PTAA: poly(3-thiopheneacetic acid).

such as laser interferometry[11,29] to monitor the growth rate or spectrometers to analyze the gas phase composition in real time[29]. This confers great control over the iCVD deposition process, and makes it possible to deposit films of a wide range of thicknesses with high precision.

The method of *oxidative CVD (oCVD)* enables the step growth of electrically conducting polymers such as poly(ethylenedioxythiophene) (PEDOT). For oCVD, the oxidant and monomer are delivered to the substrate through the vapor phase (Fig. 3a). Adsorption and spontaneous reaction proceed directly on the substrate. No additional excitation of reactants is required. Conducting polymer layers synthesized using preapplied oxidant in combination with vapor phase monomers has been termed vapor phase polymerization (VPP)[30,31]. Since the need for a solid state dopant typically utilized to achieve solubility is avoided, CVD results in high conductivity layers (>1000 S/cm). Simply by changing the substrate temperature, both the electrical conductivity and the work function of oCVD PEDOT can be systematically tuned[32,33]. Other conducting polymers, polypyrrole (PPy) and poly(3-thiopheneacetic acid) (PTAA), have also been deposited by oCVD[34]. oCVD precursors need to have a high enough volatility to be delivered into the vacuum chamber without decomposition. This, in addition to the commercial availability of functional precursors, limits the range of chemistries that can be achieved by oCVD.

In both of the processes described by Figs. 2 and 3, the CVD process builds film from the substrate up, affording the opportunity to engineer the interface between the growth surface and the polymeric coating. In particular, covalent bonding at the interfaces is desired for promoting adhesion, and in the case of conducting polymers, for potentially influencing electronic transport. For substrates containing an aromatic
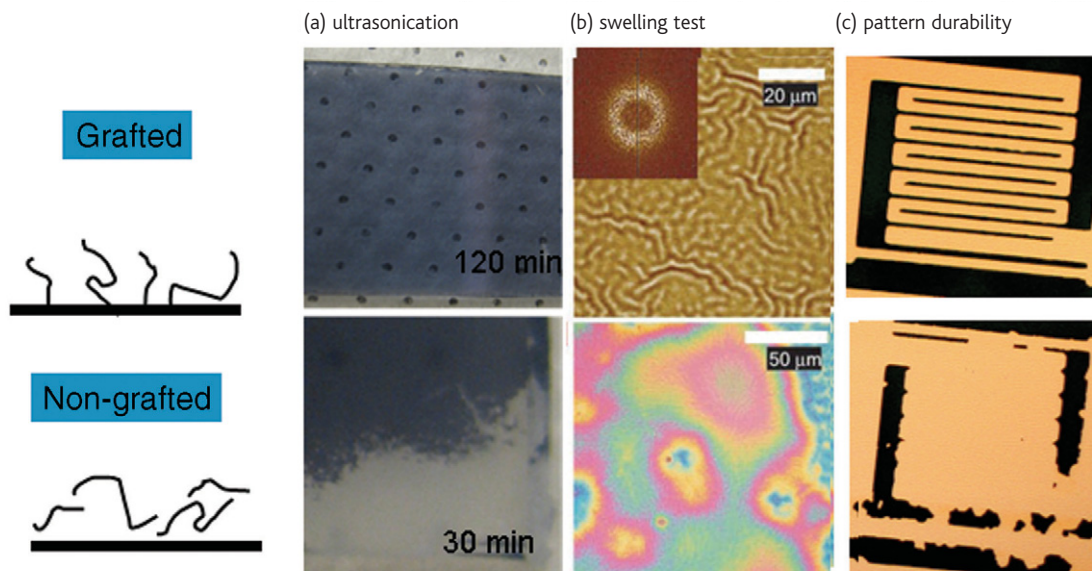

Fig. 4 Comparison of grafted (top row) and non-grafted (bottom row) oCVD PEDOT films. (a) After 120 minutes of ultrasonication in water the grafted patterns survive, while ungrafted patterns are lost in less than 30 min. (b) AFM images of PEDOT films upon exposure to THF vapor for 15 minutes. The grafted film exhibits uniform wrinkling, which confirms strong adhesion between the film and substrate. Fourier transform (inset) indicates a length scale of 3.9 ± 0.9 µm. In contrast, the non-grafted film shows no uniform wrinkling upon exposure to water vapor for 30 minutes, as seen in this optical microscopy image. (c) Conventional lift-off photolithography leads to high pattern durability and retention with grafted PEDOT films, while the fine features are lost with ungrafted films. Reproduced with permission from[58]. © Wiley VCH 2007.

group, such as poly(styrene) (PS), poly(ethylene terephlate) (PET), or silicon treated with a phenyl silane coupling agent, the oxidant FeCl$_3$ utilized in oCVD creates a radical cation directly on growth surface. From this reactive site, step growth of a conducting polymer brush can proceed directly. The greatly improved adhesion and patternability of these grafted oCVD conductive polymer layers can be seen in Fig. 4. Grafting enables high-resolution (60 nm) oCVD patterns, even on flexible substrates[35].

Grafted films of vinyl polymers can also be formed by iCVD. One way of achieving such tethered thin films is to incorporate vinyl groups on the substrate surface, often by a surface treatment prior to deposition[36]. Another strategy is using a volatile type II photoinitiator such as benzophenone, which creates free radical sites on the surface of the substrate upon exposure to UV light[37]. This results in the growth of chains covalently bound to the substrate surface. In both cases, the durability and adhesion of the coatings are significantly enhanced.

In iCVD and oCVD, the adsorption of the monomer onto the surface usually limits the rate of CVD polymerization. Thus, low temperature substrates, which promote adsorption of the reactive species, lead to rapid CVD polymer film growth (100's of nm/min). The dimensionless ratio of the partial pressure of monomer to its saturation pressure, P_M/P_{SAT}, is a key figure of merit for CVD polymerization. Adsorption isotherm studies of vinyl monomers indicate monolayer coverage is reached for P_M/P_{SAT} ~0.4, while condensation of a liquid phase corresponds to a value of unity for P_M/P_{SAT}. Typically, iCVD operates within the range of $0.2 < P_M/P_{SAT} < 0.8$, allowing the desirable process window for the deposition of new monomers to be predicted solely from vapor pressure data. This simple correlation has led to the rapid development of new iCVD polymers (Fig. 2). The adsorption process serves to concentrate the monomers on the surface to liquid-like concentrations, whereas the gas-phase monomer concentrations are several orders of magnitude lower. Increasing the density of monomers at the surface corresponds to faster iCVD growth rates and also to deposited polymeric chains of higher number average molecular weight[15,16].

Simultaneous control of surface concentration for two monomer species is required for copolymerization[21,26,38,39]. Random copolymer compositions can be predicted utilizing surface concentrations and conventional analysis of reactivity ratios, which confirms the concept of heterogeneous polymerization is occurring a nearly liquid-like adsorbed surface layer[38]. When the reactivity between unlike monomers far exceeds those for either homopolymerizations, perfectly alternating iCVD polymer films result[21]. CVD copolymerization is well suited for deposition from monomers which have no convenient common solvent. For example, photoinitiated CVD readily achieved smooth films of random copolymers from highly hydrophobic and highly hydrophilic comonomers[26,40].

Changing the proportion of comonomers fed to the CVD reactor over the course of the deposition results in compositional graded layers. The photoinitiated CVD copolymerization of the fluorinated monomer pentafluorophenylmethacrylate (PFM) with hydroxyethyl methacrylate (HEMA) allowed growth of graded films having the PFM nanoconfined within 10 to 20 nm of the surface. Having the reactive PFM primarily at the surface allows for its complete reaction with amines, while the underlying HEMA layer retains desirable swelling characteristics for the overall layer[26].

Selected applications of CVD polymers

CVD polymer thin films are promising in several applications where thin, conformal, functional, and responsive films are desired on surfaces. Selected applications, of the many possible, are described below.

Surface engineering

The retention of organic moieties in the CVD polymer films provides synthetic control over the functional groups displayed at the surfaces. These moieties provide systematic control over surface properties such as wettability, lubricity, adhesion, and biocompatibility. Additionally, the functional groups impart chemical and biological specificity to the surfaces. Specific chemical sites on CVD polymers have proved useful in subsequent surface attachment of fluorescent dyes[41], bioactive molecules[41,42], and inorganic nanoparticles[34,36]. CVD copolymerization with monomers with multiple vinyl groups results in controllably cross-linked films which are resistant to solvent damage yet remain mechanically flexible[42-44]. Multifunctional surfaces have been designed through both CVD copolymerization from multiple monomers and via patterning strategies on multilayer CVD polymer stacks[36,41,45,46].

In addition to imparting specific functionality, CVD polymers can be used to simply alter the surface energy of various substrates. Low surface energy surfaces can be formed using iCVD films such as PTFE[47,48] and other fluorinated polymers[17,49]. Such coatings have applications in areas such as stain resistant fabrics, anti-wetting applications, and microelectromechanical systems (MEMS).

Highly hydrophilic coatings such as hydrogels, on the other hand, are of interest as fouling resistant and biocompatible coatings in biomedical applications. Poly(hydroxyethyl methacrylate) (PHEMA) hydrogel thin films deposited by iCVD have shown promise for such coatings for preventing fouling of sensors that would easily be damaged by other coating methods[50]. The CVD hydrophilic/hydrophobic copolymers displayed compositional heterogeneity at the molecular-length scale also proved successful in disrupting the adsorption of the protein Bovine Serum Albumin (BSA)[40]. In addition, iCVD PHEMA has been demonstrated as non-cytotoxic surfaces for the growth of human cells, providing evidence that iCVD is a clean synthesis process that does not entrain unreacted monomer or initiator in the deposited polymer film[51].

iCVD can also be used to coat microparticles to encapsulate them for controlled release, and change their surface chemistry.
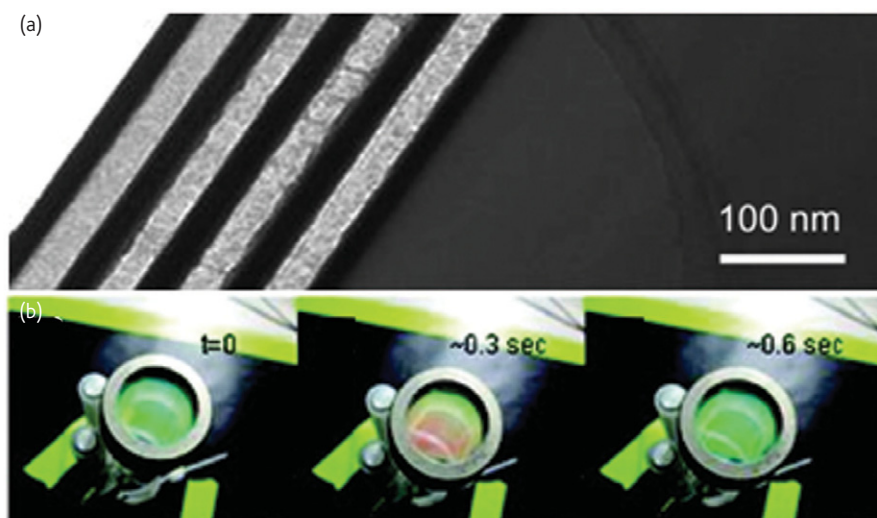
Figure 5. (a) Cross-sectional TEM image of a Bragg mirror constructed of nine alternating layers of PHEMA gel (white) and titania (dark). (b) Change in the color of a window coated by such a Bragg stack: Green color in dry state (left), red color upon exposure to 1 mol% water in N_2 (middle), and recovery of green color upon N_2 purging (right). Reproduced with permission from[55].
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The encapsulation of pharmaceuticals can be difficult with solution methods, as especially small particles tend to aggregate during this process. Furthermore, many drug molecules are fragile and potentially soluble. The solvent-free, room temperature iCVD is ideal for the encapsulation of such drug particles[39,52,53].

Optoelectronic devices and sensors

CVD polymers integrate directly into vacuum processing schemes for the fabrication of inorganic optoelectronic devices which demand high purity films and interfaces. Purity is also paramount for biomedical device coatings, where residual solvent rather than the polymer coating itself can be responsible for lack of biocompatibility and poor electrical insulation characteristics[54]. Integration of organic CVD functional surfaces provides chemical and biological specificity not achievable in inorganic materials. While most devices are fabricated from inorganic layers have fixed properties and dimensions, incorporation of organic materials opens the possibility for incorporating responsive behavior. Changes in film thickness can result from swelling upon exposure to a specific analyte, or switching of the surface energy can occur in response to a change in temperature, external field, or pH. These responsive layers can transduce chemical and biological events into electrical and/or optical responses.

In an example of such an application, hydrogels formed by CVD have been incorporated into flexible and responsive Bragg mirrors that change color between red and green. Bragg mirrors consist of multiple alternating layers of materials with different refractive indices. Their color arises from the constructive interference of interfacial reflections, and depends strongly on the refractive index and thickness of each layer. CVD in a single reactor has been used to form alternating layers of organic poly(2-hydroxyethyl methacrylate) (PHEMA) gel by iCVD

and inorganic titania by hot filament CVD. PHEMA is hydrophilic and swells when exposed to water, shifting the color observed from green to red (Fig. 5). The response is reversible, and the thinness of the device (300 nm for nine alternating layers) leads to very fast response times, on the order of tenths of a second[55].

CVD polymerization was also used in the manufacture of micrometer scale resistive sensors. In these applications, the swelling of a thin, CVD-deposited polymer layer to the analyte of interest is converted into a change in electrical resistance. The ultra-thin CVD layer decreases the diffusion resistance and enhances the response time, while enabling a significantly smaller sensor size. One demonstration of such devices uses an inorganic microcantilever coated with a CVD-polymerized layer that reacts with amines. This results in the swelling of the polymer, which causes the cantilever to deflect and complete a circuit[56]. Another sensor design involves microtrenches coated with a conformal layer of poly(4-vinyl pyridine) (P4VP) (Fig. 6). On top of the polymer coating, a thin, non-conformal gold/palladium layer is formed. Upon exposure to nitroaromatic explosives, P4VP swells, bridging the trench and completing the circuit.

Patterned functional and responsive surfaces

Hydrogels with weak acidic or basic groups exhibit pH-responsive swelling that varies often to a much greater extent than in the case of neutral hydrogels. This property has benefits in many applications, including drug delivery and responsive membranes. CVD polymerization has a significant advantage in the coating of soluble drugs, which would be impossible using solution methods[39,53]. The ability of CVD to form very thin, defect free coatings also finds use in the formation of the selective layers of composite membranes, including pH responsive
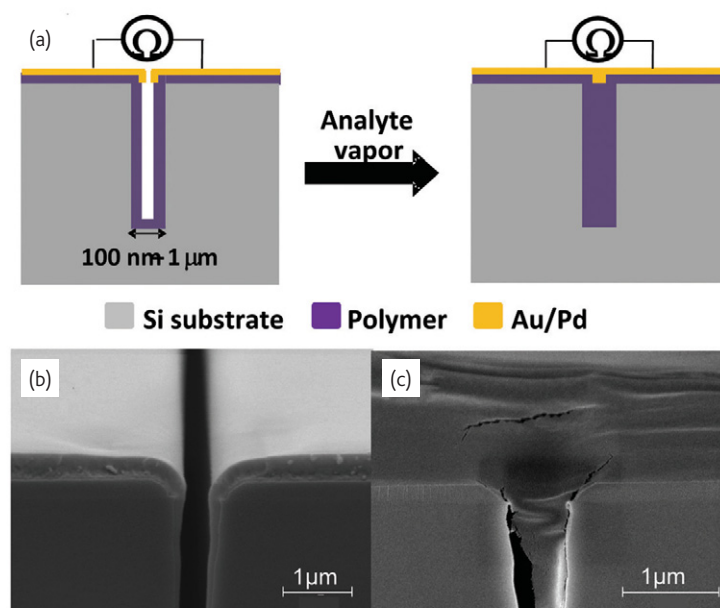
Fig. 6 (a) Operating principle of sensor based on CVD polymer coated microtrenches. Microtrenches are conformally coated by a functional polymer, followed by non-conformal deposition of Au/Pd. When exposed to analyte vapor, the polymer swells, completing the circuit. (b) SEM of microtrench coated with P4VP and Au/Pd. (c) SEM of microtrench after exposure to nitroaromatic vapor. Upon swelling of P4VP, the two sides of the trench meet, and the circuit is completed, turning the circuit "on".

hydrogels[27]. Due to the stresses that arise upon swelling and collapse of responsive hydrogel layers, the durability and adhesion of such coatings is crucial. As described above, CVD films can be attached to surfaces through covalent bonds[27,57]. This treatment prevents the coatings from delaminating through volume changes by over 10 times, as well as ultrasonication[27].

High resolution polymer patterns find use in many fields, including sensors, tissue engineering, and MEMS. CVD films can be patterned by various approaches, including conventional[13,36,43,57,58] and non-conventional lithography[57-59], microcontact printing[42,60], and through the use of masks during deposition[27,59]. Functional groups can be incorporated in the patterns for the attachment of biologically active components[27,36,41].

An example that demonstrates all these attributes is shown in Fig. 7[27]. In this study, a cross-linked polymer containing maleic anhydride groups, poly(maleic anhydride-*co*-dimethylacrylamide-*co*-die(ethylene glycol) divinyl ether) (PMaDD) was patterned using a TEM grid as a mask. Anhydride groups were used to functionalize the gel with cysteamine and attach CdSe/ZnS nanoparticles. The remaining anhydride groups are then hydrolyzed to form the carboxylic acid groups, which results in a pH-sensitive hydrogel that is highly swellable. The patterns are grafted onto the substrate, which was functionalized prior to the CVD step with amine groups that react with maleic anhydride to form covalent bonds. This allows the patterns to survive the high degrees of swelling (over 10 times) experienced upon changes in pH, as well as shear processes such as ultrasonication.
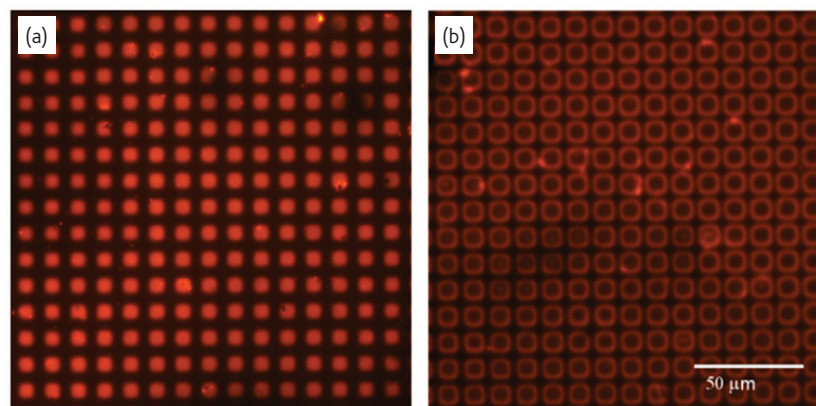

Fig. 7 Fluorescence microscopy images of PMaDD hydrogel patterns functionalized with cysteamine and linked to CdSe/ZnS nanoparticles. (a) Dry, (b) swollen in pH8 buffer. Reproduced with permission from[27]. © American Chemical Society 2009.

Future outlook

Understanding of the chemical kinetics and fluid dynamics of CVD polymer reactors has allowed successful scale-up to batch reactors > 100-fold larger. Because the CVD polymers are compatible with flexible substrates like plastics, papers, textiles, and membranes, scale-up has also been achieved to 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 solvent disposal. Due to the fact that CVD polymerization has to be conducted under vacuum, commercial scale iCVD and oCVD systems can require large capital investments and trained staff. However, an installed system is often economical to operate, especially in specialty applications where the advantages of CVD polymerization such as conformality, thickness control and functional group retention are emphasized.

In conclusion, CVD polymerization bridges all-dry microfabrication technology with the chemistry of functional and responsive organic materials. In a single step, vapor-phase monomers can be transformed through selective reaction for conformal surface modification of micro- and nano- structured surfaces. These heterogeneous processes for functionalizing solid surfaces have only begun to be exploited for novel device applications, such as in flexible optoelectronics, sensors, and biomedical devices. In the future, CVD polymers will find more use in many more fields, including MEMS, drug delivery, modulating cell-surface interactions, microfluidic devices, and membrane separations. mt

Acknowledgements

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