Low-Energy, Solventless Coating Processes

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ABSTRACT

GVD Corporation is commercializing solvent-free, chemically-pure polymer coatings formed by chemical vapor deposition (CVD). GVD's all-dry coatings currently range from fluorocarbons to silicones to electrically-conductive polymers. These novel coatings are deposited from the vapor phase, obviating the need for harmful VOCs, and are spectroscopically-indistinguishable from conventional solution-polymerized coatings. GVD's PTFE (polytetrafluoroethylene, also known as Teflon®) coatings, for example, show no evidence of the oxidative damage and cross-linking associated with conventional plasma deposition processes. Critically, GVD's clean PTFE process uses none of the solvents or surfactants (e.g., PFOA) incorporated into spray-on PTFE formulations. The waste effluent from GVD's process is treated using a standard scrubbing approach. GVD's coatings can be deposited at room temperature such that even facial tissue can be coated with ease.

Keywords: coating, solventless, low-energy, vapor deposition

1 INTRODUCTION

Polymer coatings are an essential ingredient in almost every industry [1]. Specialty coatings like fluorocarbons and silicones, for instance, are widely employed in applications ranging from wire insulation, biocompatible coatings for medical implants, semi-permeable membranes, and optical devices, to circuit-board protection. Intrinsically-conductive polymer coatings have significant potential in organic electronics, including light-emitting diodes (OLEDs) and photovoltaics (PVs) owing to their chemical tunability, processability, and optical transparency.

Conventionally, these coatings are applied using liquid-based dip, spray, ink-jet or spin-coating methods. Polymer formulations are dissolved in a solvent or, where no solvent is available, emulsified as a powder in a liquid medium, applied to the part, and then cured/dried with heat to drive off excess solvent or dispersion media. There are several challenges with this approach:

- **Residual solvent or surfactant.** Residual contamination from solvents or dispersion media can have adverse effects of the performance of the coating and the environment. For example, perfluoro-octanoic acid (PFOA) is a key processing agent and surfactant traditionally used in making fluorinated nonstick and stain-resistant coatings (Teflon®, Scotchgard®). Recently, PFOA has been linked to cancer and birth defects in animals and is in the blood of 95% of Americans, including pregnant women. PFOA has also been found in the blood of marine organisms and even in Arctic polar bears. The EPA has mandated the near-elimination of the chemical by 2015, which requires re-formulation of many fluorinated coatings [2,3].

- **Solvent waste.** Transfer efficiencies of polymer to the part are often low, resulting in wasted solution. Moreover, recycling of the solution requires energy (pumping, filtration) and the solvent is rarely recovered after the part is cured.

- **High energy utilization.** The curing process necessitated by most dip/spray processes is energy-intensive. Teflon® PTFE, for instance, requires a curing temperature of 370°C (700°F).

- **Lack of process control.** For many applications, particularly those in emerging industries like microelectronics, MEMS, and nanotechnology ("small tech"), the coating placement, volume, and thickness are critical. Dip and spray processes do not give the required precision or controllable, consistent coverage needed for predictable results and dependable device performance. In many cases, small features (microns or below) are obscured or overcoated or suffer degradation from surface tension effects when the solvent is driven off. Real-time thickness monitoring is rarely implemented. Lack of control also results in higher reject rates due to uncoated or partially coated areas, variations in thickness, or unintended deposition on nearby components. Overapplying expensive coatings increases costs and requires extra cleanup time.

2 GVD POLYMER COATINGS

GVD is commercializing a low-energy, solventless chemical vapor deposition (CVD) process which allows a variety of polymer coatings to be produced, including polytetrafluoroethylene (PTFE or Teflon®) and crosslinkable silicones. In GVD's process, as shown in Figure 1, a precursor gas is thermally decomposed over a hot surface to produce reactive molecules. These species migrate to the surface of the part and polymerize to form the desired coating.

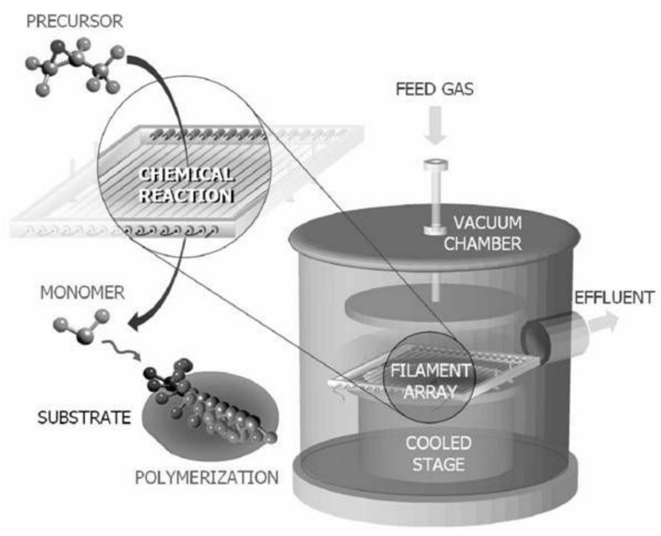

Figure 1: Chemical vapor deposition (CVD) process for producing polymer coatings.

The precursor is activated when it contacts a heated element in the chamber. The element requires a lower energy input (5-400 Watts) than most domestic bread toasters. This is possible because precursors and operating conditions are selected to favor chemical pathways which require minimal energy input and low temperatures.

Importantly, the temperature of the part being coated is independently controlled and remains cool (25-35°C) to promote adsorption. The cooled stage also allows deposition on a wide variety of substrates, including those that may be temperature-sensitive. The chamber is maintained at low pressure (~1 Torr or 10^{-3} atm) during coating, which means that the concentration of precursor gas is minimized. No curing step is required after the deposition process, and no solvents are used during processing.

Since it requires no solvents, GVD's coating process lends itself particularly well to polymers which have high chemical and thermal stability and infusibility (inability to fuse, melt, or dissolve). Two examples of these polymers follow.

2.1 GVD Polytetrafluoroethylene (PTFE)

PTFE is well known for its hydrophobicity (water-repellency), lubricity, nonstick/release properties, and chemical inertness. It finds ubiquitous use in industries ranging from cookware to clothing to biomedical prosthetics. However, PTFE's chemical and thermal stability also renders it intractable to conventional polymer processing. Hence, the ability to make PTFE thin films of precise dimension and coverage has traditionally been very limited. Conventional processes rely on spraying or dipping of liquid PTFE emulsions, followed by sintering at >300 °C in an inert atmosphere. This makes coating of temperature-sensitive substrates, such as fabrics and plastics, very difficult. The capillary action of liquid media can also damage micron-scale features and prevent conformal coating. Finally, obtaining a uniform emulsion of PTFE powder usually requires a surfactant, which has historically been PFOA.

In contrast, GVD's process is able to produce conformal PTFE thin films of high purity and controlled thickness down to the submicron scale without solvents and without curing [4]. GVD's coatings are chemically identical to bulk PTFE, as shown analytically by Fourier-Transform Infrared Spectroscopy (FTIR) and ^{19}F Nuclear Magnetic Resonance (NMR) spectra (see Figures 2 and 3).

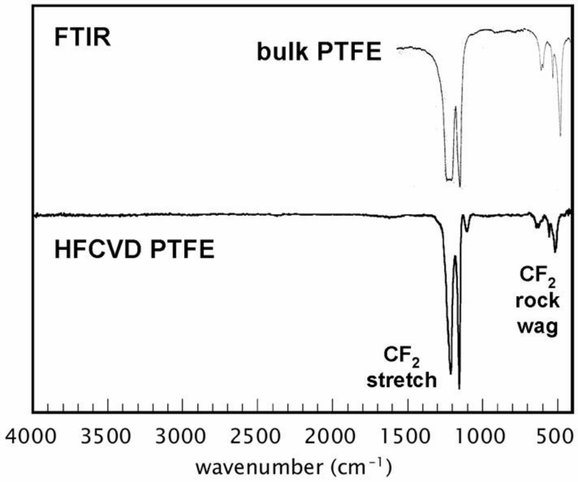

Figure 2: Comparison of FTIR spectra of bulk PTFE (top) and a PTFE coating using GVD's process (bottom).

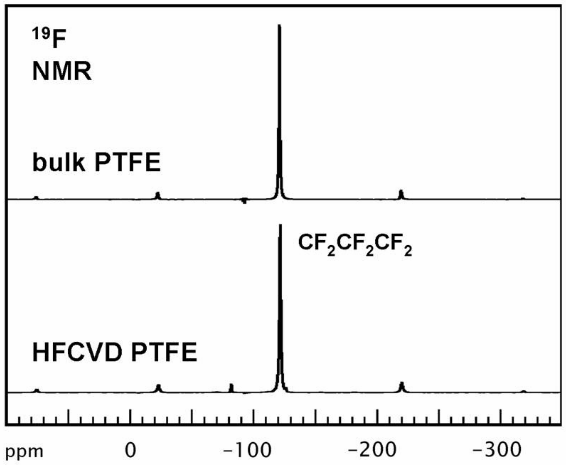

Figure 3: Comparison of ^{19}F NMR spectra of bulk PTFE (top) and a PTFE coating using GVD's process (bottom).

GVD's polymer coating process produces ultra-thin conformal coatings, as illustrated in Figure 4. This is important for applications or devices in which small, complex geometric shapes require uniform coating. These include, for instance, microelectronics circuitry, microelectromechanical systems (MEMS), neurological probes, and many emerging nanotechnology applications.

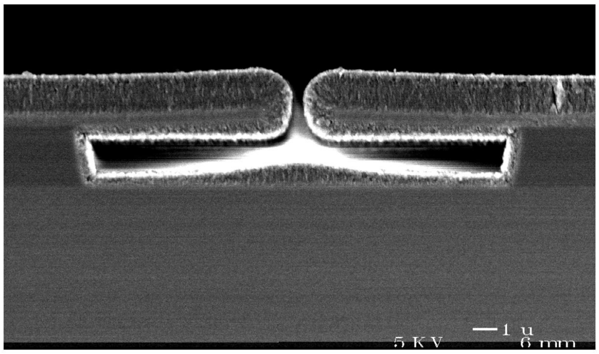

Figure 4: Silicon overhang structure coated with PTFE demonstrates thinness, conformality and lack of film stress achievable with GVD's process.

One of the key advantages of GVD's process lies in its chemical flexibility. Many conventional polymerization techniques can be used to customize both the coating composition and process characteristics. For example, initiation of the polymerization process can be performed using chemical additives similar to those used in bulk processing. The effect of the initiator on PTFE growth rate is demonstrated in Figure 5. Very high deposition rates can be achieved, making the process highly efficient and economically attractive for high-throughput applications, such as coating on moving-web substrates.

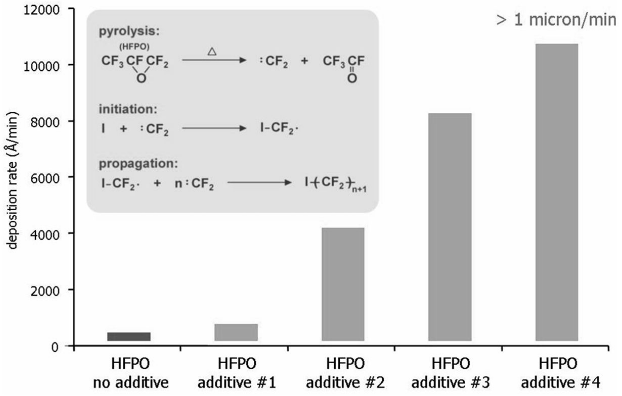

Figure 5: Effect of initiator additives on the growth rate of PTFE, with polymerization mechanism also shown.

2.2 GVD Conductive Polymer Coatings

Solvent-free deposition allows GVD's intrinsically-conductive polymers to uniformly coat planar substrates and "shrink-wrap" high-surface-area substrates like membranes and textiles [5]. GVD's conductive coatings also graft (permanently attach) themselves to many substrate materials for superb adhesion. Both features are of critical importance to emerging organic electronics applications, such as OLEDs and wearable PV devices. For military use, where rollable PVs are desired for easy storage, organic PVs are also being integrated into fabric tents. Lightweight, organic PVs can be used to re-charge "AA"-size batteries in a few hours, obviating today's need for soldiers to carry many hundreds of batteries into hostile territory. For PV application, GVD's transparent coatings boast optical transmittance values of as high as 89%, and 84% transmittance at higher conductivity (Figure 5). The work function of GVD's conductive polymer coatings can be easily changed to match that of adjacent PV and OLED device layers, improving device efficiency [6].

In multilayer electronic devices, GVD's dry process leaves previously-deposited organic layers undisturbed. In contrast, conventional wet coating processes (e.g., dip- or spin-coating) may erode soluble organic materials, reducing device quality. Ink jet printing is a commonly-used tool for depositing organic materials, but requires soluble organics. Further, the cost of purchasing, processing, and disposing of solvents must be factored into the cost of printed organic electronics. Finally, ink jet is well-suited for printing soluble materials in specific regions, but is perhaps not ideal for printing over large areas which do not require pixelation. GVD has recently installed roll-to-roll deposition equipment (Figure 6) for large-area deposition. This equipment can be exploited for any of GVD's coating technologies described here, including conductive polymer deposition. Hence, GVD's low-energy, solvent-free

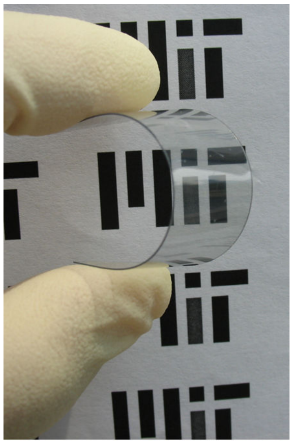

Figure 5. GVD's solvent-free, low-energy, intrinsically-conductive polymer coatings are highly transparent, making them attractive for OLED and PV device application.

Figure 6. GVD has several on-site polymer deposition chambers suitable for coating a range of parts, including a roll-to-roll deposition chamber (shown here).

coating technology is advantageous from both device fabrication and environmental standpoints.

2.3 Other Polymer Coatings

GVD's process can produce a wide variety of other polymers. Some examples are:

- **Crosslinked silicone coatings** useful for biopassivation of implantable circuitry [7,8]
- **Functional coatings**, such as poly(glycidyl methacrylate), which can be used to bind biological ligands to create biofunctional surfaces, as an adhesion promoter, or as a lithographic resist in microelectronics manufacturing [9,10]
- **Crosslinked hydrogel coatings** which allow systematic tuning of surface energy and swelling response [11]
- **Antimicrobial coatings** [12]

2.4 Commercialization

GVD has developed commercial equipment capable of coating parts in a variety of form factors, including small, medium and large batch coaters and a roll-to-roll or conveyor coating system (Figure 6). All coating systems use automated PC-control and offer a full range of safety interlocks and data recording and management options. Both standard and custom systems are available and sold to customers along with a license to manufacture. GVD offers evaluation and development services to test the coating on customers' parts and perform small-scale pilot manufacturing. We are commercializing a number of applications in medical devices, textiles, consumer products, and industrial applications.

3 CONCLUSION

GVD's polymer coating process enables thin coatings of high purity to be produced at low powers, without solvent wastage, and without the need for high-temperature curing.

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