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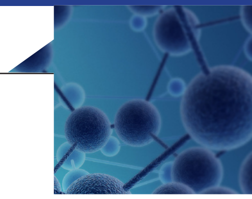
Can highly engineered nanomaterials seamlessly integrate into age-old production processes? Aeonclad Coatings thinks so.



Interactions at the Edges

Can highly engineered nanomaterials seamlessly integrate into age-old production processes? Aeonclad Coatings think so...

Nanotechnology is generally defined by at least one dimension of a material being less than 100 nm or by its surface area. The ratio of exposed surface to total mass is higher for nanomaterials than other forms of solid matter and this fact drives many of the unique properties that make the field of nanotechnology so exciting. Directing interactions at interfaces provides incredible opportunities to create entirely new products for almost every industry.

Plasmas in Industry: A Primer

Highly controlled plasmas are used in semiconductor processing to create finely tuned computer chips. Changing the gas mixtures, power, and a few other variables, plasmas can radically change how the silicon wafers will be modified. Using plasmas, chips can be etched in patterns laid out in photoresist, the photoresist can be removed by selectively burning the resist, and new material laid down by plasma deposition. Plasmas can perform all the functions without a mechanical tool ever touching the surface. However, the precision required to repeatedly create nano scale features comes at a great price as finished semiconductor chips are some of the most costly materials on a per pound basis. High performance requirements, high costs, and rapidly evolving technology all combine to create a situation where the annual tonnage of semiconductors are necessarily small.

The market for plastics could not be more different than semiconductor. The volumes are usually high, costs low, life cycles are long, and performance can be uninspiring.

The only intersection between the worlds of plasmas and plastics has been the limited application of plasmas to slightly oxidize the surface of semi-finished plastic goods for various uses. One illustration is the preparation of plastic sheets for printing by coronal plasmas. The surface energies of rolls of plastic can be economically altered by simply striking a plasma over the sheet as it traverses from one roll to another. While cheap, these kinds of alterations have limited ability to fundamentally change how a material behaves.

Plasmas in Industry: A Primer

What if the interaction between disciplines could be profitably exploited whereby the knowledge, equipment, and performance from semiconductor industries could be married to the high volumes, low costs, and stable product demands of commodity markets? How could pharmaceuticals benefit from perfectly formed thin films to improve patient experiences and outcomes? Can highly engineered nanomaterials seamlessly integrate into age-old production processes? These questions will all be explored in this article.

PECVD Intro

Interactions happen at interfaces. This simple statement defines why interest and innovation in thin film technologies has exploded in recent years. One of the most efficient means to create thin films is with plasma enhanced chemical vapor deposition (PECVD).

Plasma processes are not new and can result in items as disparate as fluorescent lights to semiconductor chips to stars. Surface modification by plasmas is also well known and can be performed at pressures ranging from atmospheric to sub-Torr with tradeoffs on many fronts. Corona plasmas generally operate at around one atmosphere of pressure so tend not to have involved material handling requirements. They are economical when slight modifications are needed to clean a surface or improve receptivity prior to bonding, but have limited ability to fundamentally change how the surface interacts.

Vacuum plasmas can utilize a wide range of chemistries with the major limitation being the vapor pressure of the working gas. For plasma etching or light surface modification this is usually not a problem since the desired results can be achieved with low molecular weight molecules.

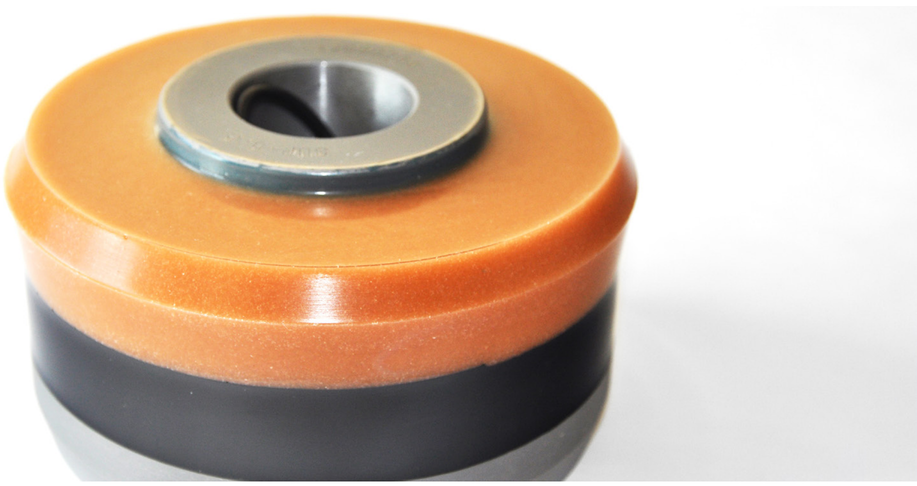
For plasma deposition, especially at room temperature with functional films, the vapor pressure can be a gating item. Best results are usually had with monomers exhibiting at least 1 Torr vapor pressure at 25C. Monomers in this pressure range include perfluorohexane, allyl amine, allyl alcohol, acrylic acid, glycidal methacrylate, and many others. Changing the plasma conditions impacts how much chemical functionality of these monomers is retained in the resulting thin film and using low power settings greatly advantages the deposition reaction versus ablation from high energy ions. What if the high performance vacuum plasmas from the semiconductor industry with their limited volume capacity could be brought to a wide range of materials at scales measured not in millimeters of wafer but in train loads? Combining the chemical precision of plasma enhanced chemical vapor deposition with the raw tonnage of carbon black production has not only been impossible but beyond the pale of consideration. However, recent advances in engineering have borrowed heavily from multiple disciplines to create just the situation where this is feasible.

Consumer materials with controlled interaction

Creating warm clothing is a basic human task and as such is older than recorded history. Synthetic fibers and nanotech coatings have all increased the range of options for garment manufacturers but the full potential of interface engineering has not been realized. Besides synthetics, the natural world also provides a number of promising raw materials, one of the most highly sought after are the down clusters from waterfowl, namely ducks and geese.

One could be forgiven for not making the connection between goose down and processes associated with computer chips but a chance encounter brought these two worlds together. A researcher for the clothing company Patagonia knew of the market for water repellant, super insulating down and upon learning of the ability to use PECVD on natural materials, inquired if PECVD could be used with high grade goose down. Down's high surface area, natural variability, and unique mechanical properties created a series of challenges to processing in high volumes. These hurdles were overcome because it was discovered that not only could down be made highly water resistant by plasma deposition but also that its compressed specific volume increased 30-50%. Specific volume, or fill power as it is known in the industry, is the key metric for down quality and insulation potential. Plasma deposition using benign siloxane materials allowed Patagonia to launch their Encapsil line of down products with an unheard of fill power of 1000 cubic inches per ounce. Managing the feather-environment interface for surface energy, water resistance,

Image 1: A mud pump piston utilizing AeonCoat™ PTFE integrated into the polyurethane at 10%. As a result of even dispersion and bonding, the lubricious properties of PTFE have led to increased product life of 3x-10x depending on the drilling environment.

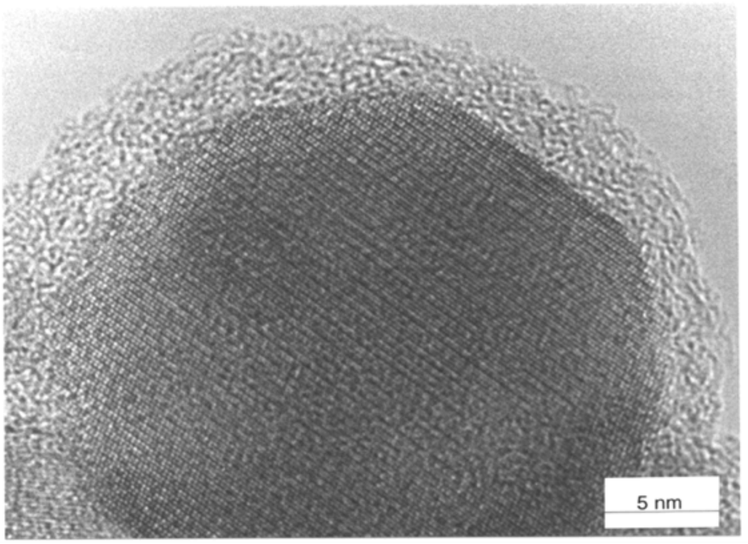


and dielectric properties of goose down is key to this novel product.

Doing Drugs

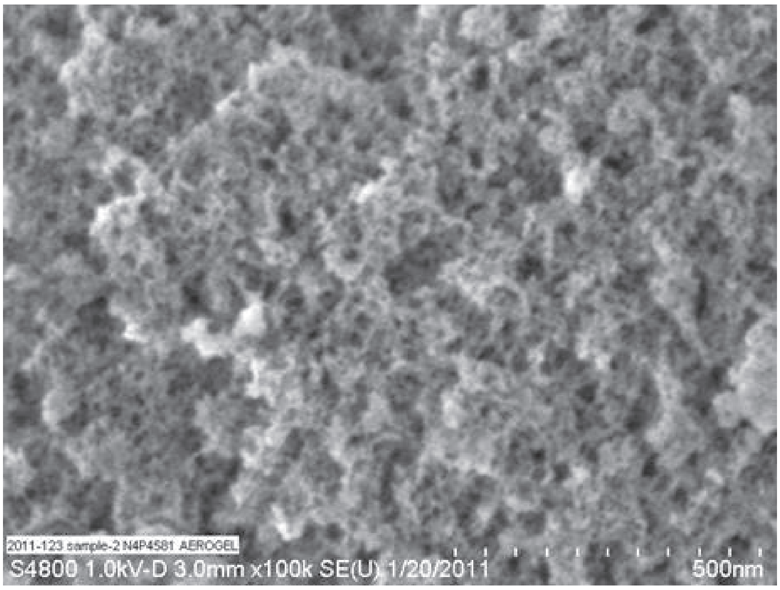
From goose down we now look at another industry with ancient roots, namely pharmaceuticals. Could a phenomenon more closely associated with the hellish temperatures of nuclear fusion be harnessed to improve fragile proteins? In a word, yes. The same precision that enables millions of transistors to be placed on a single wafer can also be used to encase microscopic drug particles with a protective coating. The secret is in modulating power delivery and selecting appropriate chemistries. Studies with enzymes as well as small molecule drugs have shown that not only is it possible to gently plasma deposit thin biocompatible films on these substrates, but also the shelf life, form factor, and absorption are improved. By changing the generally-regarded-as-safe (GRAS) monomers used in the deposition, the poorly soluble drug powders can be made more easily dispersed or rapidly absorbed

Image 2: TEM pic of aerogel dispersion



HRTEM of a 5nm Polyallylamine Film Uniformly Coating a 30nm Fe_2O_3 Nanoparticle

Image 3: AeonClad treated aerogel is highly dispersible and mixable into plastic. It has an average pore size of 50 nm which has been uniformly coated without closing up the pores.



drugs can be converted to controlled release versions. By simply changing power intensity in the plasma, the degree of cross linking in the film is shifted, thereby allowing blended release formulations within a single drug. With very tight control of all the plasma variables, temperature or pH, responsive films can be formed to create a bandage that releases a pulse of antibiotics when warmed or an oral tablet that delivers its payload in the intestines instead of the stomach. In all these ways, PECVD thin films help pharmaceuticals perform in their various environments.

Creating Composites

From consumer goods with relatively minor regulatory oversight to highly controlled medical applications, the sweet spot for PECVD may be the field of extreme performance materials. Many nanotech innovations never reach their full potential because they have a single Achilles heel which limits their broader adoption and in almost every case, surface interactions play a part. Many commodity nanomaterials are used in industries with intense price competition. The synthesis of semiconductor precision with commodity consumer volume and pharmaceutical chemistry can be blended into thin films that enable an explosion of novel material combinations.

Some examples:

PTFE is known for its inertness, lubricity, and temperature stability. These very properties that make it attractive also mean it is very difficult to process with standard equipment and therefore it is almost never found as a filler in other materials. By taking PTFE micropowders and first using plasma to covalently graft functional films on the surface and then encapsulating reactive chemistries around the powder particles, a new form of highly dispersible, easily blended and covalently bondable PTFE is created. These powders can be used to impart lubricity to other plastics without fear of leaching or degrading mechanical properties. The key is masking the highly fluorinated PTFE surface with a reactive film to manage the interaction without degrading the inherent properties of the underlying substrate.

Silica aerogels are the best thermal insulators known with mean pore sizes of 50 nm and surface areas over 1000 m2 per gram. However, these exposed surfaces are highly methylated which makes the aerogel both extremely hydrophobic and very susceptible to attack by organic chemicals. Much work has gone into finding surfactants that can wet out the aerogel but not degrade its structure. Plasma deposition, being a gas phase process, can readily coat high surface area materials regardless of the hydrophobic/hydrophilic nature of the surface. For aerogels, plasma deposition can lay down a protective film that masks the hydrophobic moieties with vinyl acrylic acid, allowing for blending into aqueous phases. Taking this approach one step further, a recent patent has issued describing PECVD treated aerogel for use in polymer composites while maintaining the all-important aerogel structure.

The third and final example to complete the story is that of carbon. PECVD deposition on carbon black, carbon nanotubes, and carbon fiber has all been demonstrated. Carbon black can be aggressively treated to ensure adequate functionalization and carbon nanotubes can be gently encapsulated to preserve the chirality. A thin film of allyl amine can be deposited on carbon fiber to assist in both wetting out and chemical bonding in order to transfer stress between an epoxy matrix and the carbon backbone. Reducing debonding as a major failure mode in this way allows designers to shift the cost-weight-safety factor paradigm in product development.

Final thoughts

PECVD can be applied to a wide range of substrates (synthetic, biological, mineral) over sizes ranging from nano (carbon) to micro (PTFE) to macro (goose down) and with an impressive array of chemistries. Given these options and all the control variables inherent in plasma processing, the number of experimental possibilities demands that a method of rapid iteration is critical. The company AeonClad has not only created systems which allow such rapid experimentation, but has coupled this ability to scalable reactor systems from batch systems handling grams to large continuous powder processors. Rapid evolution at scale allows compelling economics across a range of industries and AeonClad is the leading company working to redefine surface chemistry through PECVD.

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Image 4: Untreated aerogel (on left) vs. treated aerogel (on right) in water.

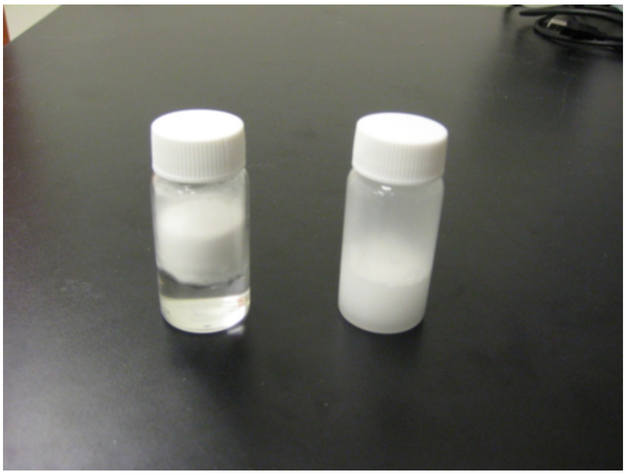

Image 5: Untreated carbon nano fiber (on left) vs. treated carbon nano fiber (on right).