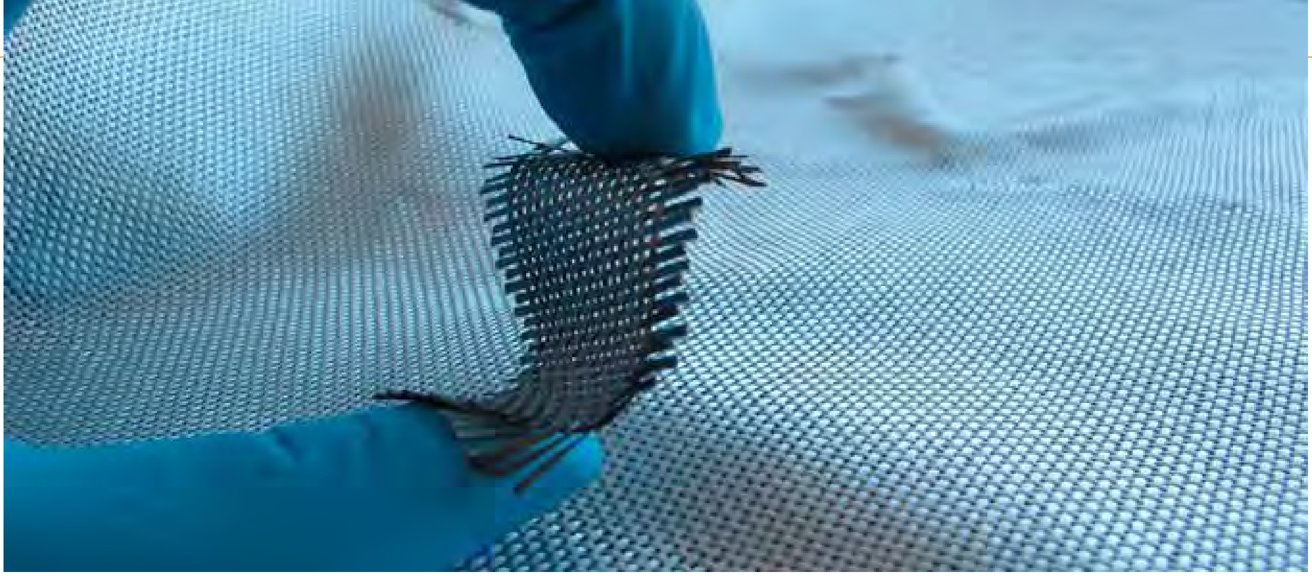


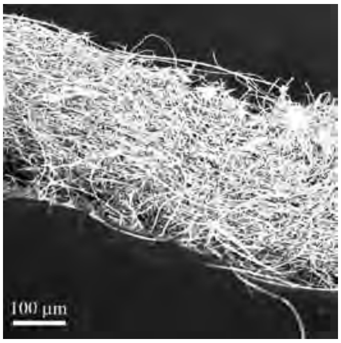
(Credit: NCSU.)

Tungsten–coated quartz fiber woven fabric.

Nanoscale ceramic surface modification of textiles by atomic layer deposition

By Jesse S. Jur and Gregory N. Parsons

Advances in ceramic surface treatments offer new opportunities for textile modification.



(Credit: Jur; NCSU.)

Figure 1. Scanning electron microscope image of a nonwoven textile cross section showing its characteristic porous structure. Compared to planar substrates often used in microelectronics, the structure of a textile presents unique challenges for ceramic surface modifications.

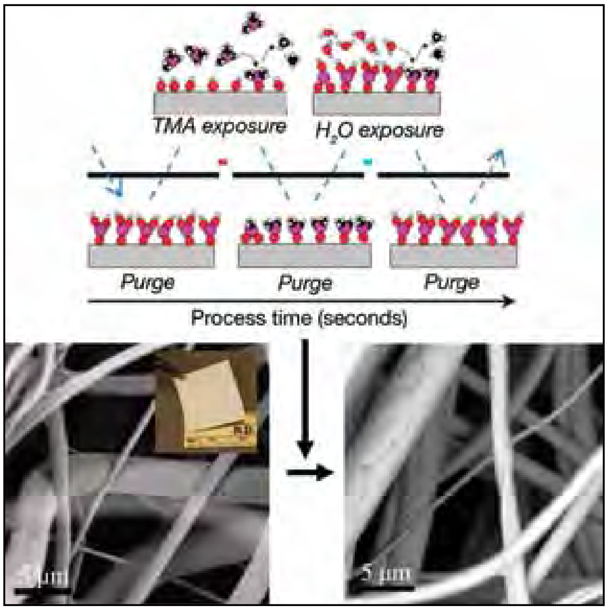
Recent opportunities to merge traditional inorganic materials processing with organic fibrous textiles are creating new possibilities in electrical, optical and mechanical applications for textiles. Textiles are made of low-cost natural or synthetic fibers and have unique flexibility, strength and durability with a large accessible surface area. Herein we describe inorganic surface modification techniques that are applicable to the textile industry and how these ceramic modifications could extend the range of textile applications.

First, it is important to distinguish between traditional versus nontraditional textile materials. Traditional textiles most often are woven or knitted structures and commonly used for clothing and many durable fabrics. The processes for their manufacture can be slow, about 1 to 2 meters per minute. Nonwoven fabrics, typically referred to as nontraditional textiles, have shown increasing adaptability for high speed of production, up to 1,000 meters per minute.[1]

Nonwovens extend the strength, flexibility, breathability, optical appearance and feel of textiles. They can be engineered for low-cost, customizeable solutions, which has expanded markets for them into an untold number of durable and disposable products, including carpet backing, personal care materials, air and water filtration, automotive interiors and cleaning wipes. Nonwoven processes are modified easily to alter fiber diameter, density and orientation, and, therefore, are used for many technical textile products (Figure 1). Thus, the nonwovens sector provides broad opportunities for innovation in the textiles industry.

Atomic layer deposition of nanoscale coatings

A critical component to all textiles, including nonwovens, is the ability to modify the fiber surface.[2,3] Surface modifications on roll-goods expand the materials' capabilities for adhesion, surface wetting, product feel or "hand," wear resistance, biocompatibility or chemical stability, for example. Most modifications used now



(Credit: Jur; NCSU.)

Figure 2. ALD produces conformal, nanoscale ceramic coatings on textiles. The process involves a sequential, low-temperature reaction of chemicals on a surface to form a ceramic coating. A single cycle of trimethylaluminum and water, separated by an inert gas purge, is shown at the top. Multiple cycles result in an increased thickness of the textile.

are carbon- or amine-based. Ceramic materials have electronic or mechanical properties that are difficult to achieve with polymers. Therefore, advances in ceramic inorganic surface treatments offer new opportunities for textile modification.

Carbon-based modifications involve wet-chemical-processing schemes that penetrate throughout the textile to modify the entire surface area. In contrast, many ceramic surface modification techniques, such as plasma or vapor coating methods, modify the topmost surface of the fabric more than the underlying fibers. There are aqueous techniques such as sol–gel and electrochemical processes, but those processes often need high temperatures or undesirable solvents or other chemicals. Uniformity and thickness control also limit the material efficiency.[4–7]

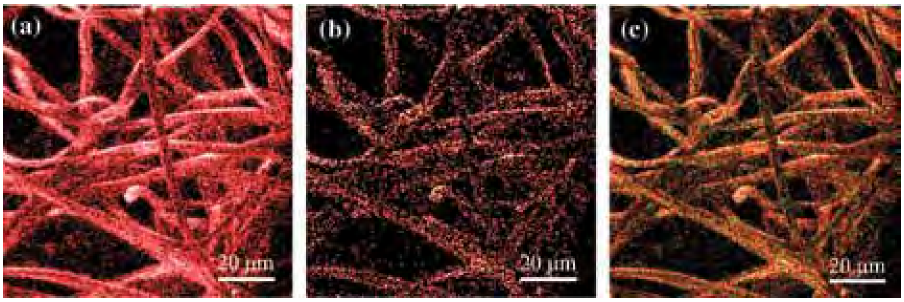
Recent studies of vapor-phase methods based on atomic layer deposition are promising for uniform, low-temperature fiber surface modification.[8–10] The ALD method sequentially exposes a surface to two vapor-phase reactants, allowing a nanoscale inorganic coating to build up one layer at a time (Figure 2). The low-temperature, surface-driven reaction is compatible with many natural and synthetic fiber fabrics.[8-10] Because the process is driven by surface reactivity, it often proceeds at very low temperature and routinely achieves extremely conformal coatings. Operating at low pressure (about 1 to 2 torr) allows for long vapor diffusion lengths, which also helps achieve conformal coatings in trenches between fibers with aspect ratios in excess of 5,000.

A common example of an ALD coating is the deposition of aluminum oxide from trimethylalumninum and water. For a single ALD cycle, the fabric surface is exposed to TMA first, followed by a nitrogen purge to remove the vapor product, then water, then nitrogen again. This cycle results in about 0.1 nanometer of growth, and repeating the cycle adds about 0.1 nanometer each time Therefore, precise coating thicknesses can be achieved by performing a desired number of reactive cycles. A key difference between ALD and other surface chemistry processes, for example, electrochemical deposition, is the range of materials that can be deposited, including oxides, nitrides and pure metals. Layers of dissimilar materials also are possible with the proper precursor exposure sequences.

From electronics to textiles

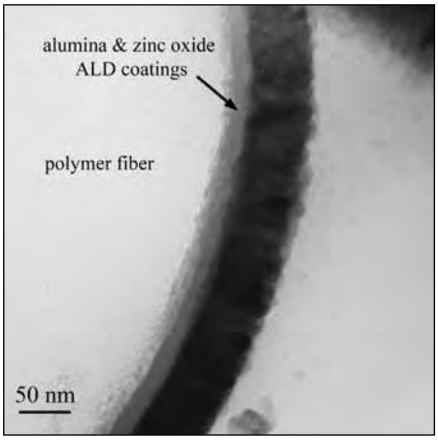
ALD dates back to its development in the mid-1960s in the USSR, and it later gained popularity for research in Finland in the 1970s and 1980s for applications as electroluminescent displays.[8] In the early 2000s, ALD found a home in the semiconductor transistor industry. Like many technologies explored for advancing Moore's law,[†] the range of applications for ALD expanded, because of its ability to produce nanoscale, pin-hole-free layers that are conformal on surfaces with complex architectures. Currently, ALD is used in research projects ranging from renewable energy technologies to biocompatibility coatings for implants.[9]

When used to apply coatings to organic materials, ALD is a low-tem-



(Credit: Jur; NCSU.)

Figure 3. Time-of-flight secondary ion mass spectroscopy mapping of an Al_2O_3 ALD-coated nylon nonwoven fabric. The images are mappings of (a) CN- and (b) AlO- and (c) a combined overlay (AlO- shown in green) distribution on the coated fabric.



(Credit: Jur; NCSU.)

Figure 4. Cross-section transmission electron microscopy image of a multilayered nanoscale ALD coating on a polymer fiber.

[†] Moore's law—named for Intel cofounder, Gordon Moore—says that the number of transistors on an integrated circuit will approximately double every two years.

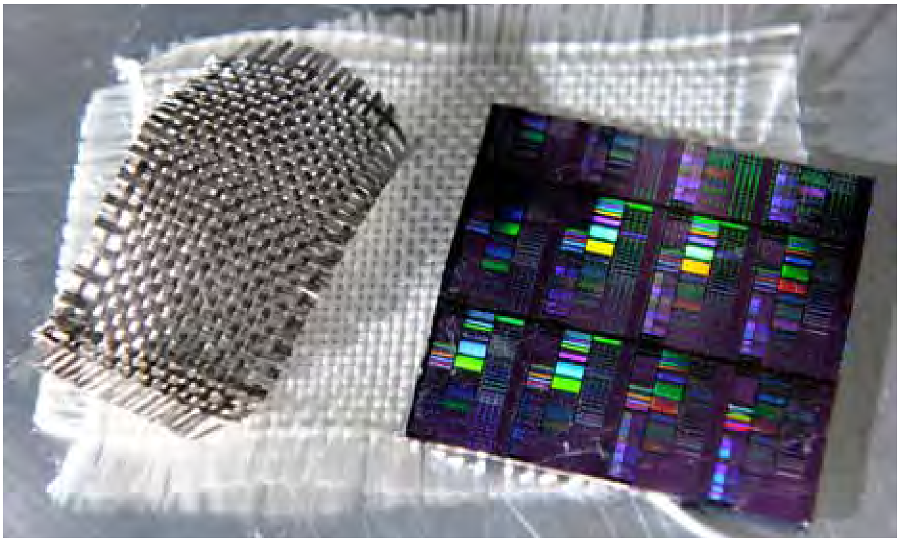
perature means for ceramic compound nucleation. (ALD coatings also are useful for preventing moisture penetration into organic devices.) ALD nucleation on polymers depends on the chemical makeup of the substrate material, the process temperature and precursor chemistry.[11–14] High-quality (i.e., crystalline, dense and conformal) coatings are formed by controlling the interface nucleation (Figures 3 and 4).

On textile substrates, ALD produces a uniform, conformal coating throughout the polymer fiber matrix. This allows fabrication of some interesting constructs, including high-surface-area frameworks for catalysis, biocompatible fabrics, fabric capacitors and chemically stable nanofibers.[11–15] Other vapor- or liquid-phase coating methods lack the nanoscale control, uniformity and material breadth that ALD achieves.

Because many ALD-processed materials have been examined for electronic devices, the application of these same materials for the fabrication of electronic devices using textiles (Figure 5) is of particular interest. Because of the ubiquitous use of textiles throughout society, there are benefits to be gained by adopting new electronic-textile (e-textile) technologies.[16]

One example is the use of electronic-active textiles to monitor a condition or activity of the human body. Research efforts are developing new technologies for imparting electronic behavior into textiles that can sense changes in the body with clothing.

ALD offers a route for producing inorganic conducting and semiconducting materials, which serve as the building blocks for most responsive sensor and other device architectures. In addition, the nanoscale surface coverage of ALD offers the ability to fabricate device layers that take advantage of the high surface area and strategic structure–property relationships available through the use of a textile substrate. This is important in the formation of responsive materials with electrical behavior that changes when flexed or exposed to certain chemicals, that is, fabrics that act as platforms for "all-fiber-based" electronic devices.



(Credit: Jur; NCSU.)

Figure 5. Many of the same materials used in semiconductor processing are being applied to textile materials. The swatch on the left shows a tungsten coating on a woven fabric. On the right is a semiconductor chip constructed on a silicon wafer.

Properties of modified textiles

ALD has been shown to produce nanoscale conducting and semiconducting coatings on a range of textiles of varying fiber diameters, construction and polymer-type.[17] Materials such as ZnO and TiO_2 show the same behavior on textile substrates as they do on planar substrates, including properties such as photoluminescence and photoconductance. Tungsten coatings of less than 30 nanometers on nylon, cotton and quartz fibers show high electrical conductance.

In general, the specifications for electronic behavior of conductive materials remain an open question, and new evaluation techniques are necessary. For example, standard four-point probe methods are not compatible with porous fiber substrates. A four probe measurement is needed to eliminate parasitic and contact resistance effects during measurement, but insufficient contact between the fiber and the sharply pointed probes leads to inconsistent evaluation and a nonuniform potential drop.

To resolve these issues, investigators have used a technique employing larger probes to improve fiber–electrode contact. By applying a force normal to the textile surface, the fiber mat collapses to maximize fiber–fiber connectivity, ensuring that the entire conductive coating is accessible to current flow. By measuring the coating mass and estimating the material density, a value for coating conductivity is obtained, making it possible to quantitatively compare various coatings and conductive textiles.

The way a textile is constructed may build in a physical anisotropy that can influence the electrical behavior, too. Physical anisotropy is observed easily in woven fabrics where the warp and weft yarns are aligned preferentially based on a weave pattern. For example, consider the visisble texture difference between an undershirt and a dress shirt. In a nonwoven fabric, the fibers are "randomly" distributed, and the texture is less visually obvious.

The anisotropic structures of nonwoven fabrics result in interesting mechanical behaviors of the textile, showing significant differences based on the directions in which the textile is strained. This orientation influences the conductivity of the coated textile as well, because electricity moves down the length of the fiber more easily than it can cross between parallel fibers.

Another unique feature of a textile is that the porous structure allows liquid or vapor to penetrate and pass through. This can be demonstrated in a device design constructed of a textile sandwiched between two conductive-coated textiles, effectively creating a metal–insulator–metal capacitor. Liquid passing through this device fills the void space (air) of the inner textile, resulting in a change in capacitance.

Challenges remain

A major challenge to adopting ceramic modifications to textiles is realizing high flexibility and durability of the ceramic coating. Because the ALD process is based on covalent interactions, the coating adheres strongly to the polymer fiber. New testing methods are needed to quantify the adhesion. The most common test for surface durability is to expose the material to a series of wash cycles using standards defined by the American Association of Textile Colorists and Chemists. However, besides observing the functionality before and after the standardized testing, it remains difficult to assess the wear of nanoscale coatings.

In terms of flexibility, much of the work done on nanoscale coatings on planar, flexible organic devices can be extended to textiles. Research has shown that the critical strain to cracking scales with the thickness of the coating as $1/t_f^{1/2}$ where t_f is the coating thickness.[18] This means that nanoscale films, such as those produced by ALD, are more flexible. The key, then, is to achieve the desired functionality of the coating at these nanoscale thicknesses. Properties can be altered by the nucleation behavior of the ALD coating, making device functionality highly dependent on the processing temperature and polymer type.

An alternative means of producing more flexible and durable coatings is to use more pliable hybrid (organic–inorganic compounds) coatings. Recent work on molecular layer deposition, a hybrid synthesis process similar in principle to ALD, offers interesting possibilities.[9] Likewise, strategic modification of the near-surface polymer by chemical reaction and infiltration with ALD precursors is another means being studied to form a more mechanically pliable hybrid material. Although the mechanical properties of these hybrid coatings may be promising, the research to make these materials multifunctional is needed.

Finally, there is significant emphasis on adaptating ALD to a continuous process, which would allow production approaches commensurate to the profitability of a textile industry. Much of the ability to develop a continuous ALD process results from advancements in the ability to perform ALD at atmospheric pressure.[9,10,19,20] Again, the majority of this work has been in the development of materials processes for flexible organic devices as well as passivation layers for solar cells. Unfortunately, it applies only indirectly to materials processing on textiles.

The complexity of ALD processing on porous materials surfaces, like textiles, is a significant challenge. Although ability to perform ALD modifications on textiles at atmospheric conditions has been demonstrated, much more research is needed to reach the processing speeds required for the textile industry. Back-of-the-line surface modification processes that are less than 20 meters per minute could be considered slow and unprofitable, depending on the margins of the final product.

In summary, the appeal of textile applications outside of traditional textile products is heavily influenced by the ubiquitous use of textiles in society. As new types of textile and nonwoven materials become available, there will be an increasing push to make them useful for diverse new applications, well beyond clothing, furnishings or other common protective structures. Surface modification of textiles will be important to expanding textiles for new uses. Introducing inorganic ceramic materials in textile materials will certainly play a role, especially when the fiber modification can proceed controllably at the nanometer scale, and, most likely, vapor-phase ALD and related processes will help drive these advances.

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