Nanotechnologies Expand Glazing Options and The Complexity Of Specifications

ABSTRACT

If controlling materials on a nanometer scale qualifies, the glass industry had decades of experience in that field before the term "nanotechnology" became a buzzword. Sputter coating, long used to control reflectivity and emissivity, applies materials to a substrate "atom by atom." Nanotechnology actually refers more to manipulation of materials on a molecular level to achieve a property or performance differing from that of the bulk material. The term encompasses inactive systems, such as coatings stacked to produce optical interference; and active systems, including examples of photovoltaic and photochromic technologies. Nanotechnology applications presently used to enhance glazing systems, and future opportunities, are discussed.

The current profusion of nanotechnology-dependent glazing products significantly enhances a designer's ability to optimize the functionality of the built environment. It also significantly complicates the design and specification processes. Architects and engineers will increasingly rely upon computerized performance simulation to optimize glazing system designs and specifications.

INTRODUCTION

Nanotechnology today is not all about carbon nanotubes and Bucky balls (fullerenes), intriguing as those structures may be. Many materials behave differently as single molecules than they would in bulk. The precision with which we can deposit, align, and bond those molecules determines the extent to which we can utilize the interactions between them.

Dr. Helmut Hohenstein presented a paper at Glass Processing Days 2003 entitled "Coatings with Nano-Particles for Windows and Facades." He mentioned some initial goals of surface modification. The topics of the day were UV-filtration, corrosion-resistance, abrasion-resistance, anti-fogging, and "self-cleaning" surfaces utilizing hydrophobic and oleophobic coatings. These coatings were primarily protective in nature. Some were of interest more as treatments for wood window framing than as active surfaces on glazing.

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Even then, however, the promise of nanoscale manipulation of molecules was evident. Hohenstein listed photocatalysis among “innovations as a motor for technical progress.” Switchable liquid crystal glazing panels had been in commercial production for over a decade. Photovoltaic panels were recharging sailboat batteries. Highly reflective glazing, one of the earliest thin-film technologies, was already out-of-style. Low-emissivity coatings incorporating thin films of metallic oxides were the norm in insulating glass specifications. Coating stacks engineered to generate optical interference tailored for spectral-selectivity had long been available on both glass and plastic film substrates. For decades, the glazing industry had been controlling materials on the molecular scale. Yet, we were then only beginning to call that “nanotechnology,” and market the concept.

Still, today, nanotechnology in glazing applications relates exclusively to thin films and active coatings. Conveniently, float glass production affords economical access to glass substrate in a wide range of temperatures. That facilitates deposition of coatings by temperature-dependent processes.

Five years ago, Dr. Hohenstein began by quoting Wolfgang Pauli, an Austrian quantum physicist who said, “God has created the bulk, but the devil fiddled with the surface.” The following review supports the conclusion that, currently, the devil is very active.

GLAZING INDUSTRY NANOTECHNOLOGY

Mirrors:

Glass coating technologies originated with mirror production utilizing metallic coatings and protective paints. The discovery that extremely thin metal coatings are transparent led to production of optical beam splitters, transparent mirrors, and reflective glazing for architectural applications.

Decades later, with the proliferation of computers and cell phones, came the need for specifiers of metallic thin film coatings to consider the effects of the EMI /RFI shielding properties of the glazing system. These properties vary significantly among coatings. Any shielding that does occur is likely to be beneficial in terms of data security, and detrimental to cell phone communications.

Transparent conductive coatings:

With the capability to deposit thin films of metals and metal oxides on a glass surface comes the ability to control the electrical conductivity or resistance of that surface.

Transparent conductive surfaces coated with materials such as indium tin oxide (ITO) are commonly used to establish fields or deliver current that enables many chromogenic glazing products to function. Most chromogenic technologies rely upon transparent conductors.

Transparent conductive coatings have also been utilized to generate heat to eliminate frosting on the insulating glass doors of refrigerated food display cases, and in transportation applications such as defrosting mirrors or windshields.

The potential exists for heat generated in this manner to be utilized to initiate reversible reactions in other layers or other coatings, possibly one located on the opposite surface of the substrate. Inducing thermo-catalytic reactions in chromogenic glazings would be one example of that type of application.

Low emissivity coatings:

The concept of applying metal oxide films to reduce the emissivity of glass surfaces was a logical extension of reflective glass coatings technology. Emissivity modifiers originated as a mechanism for retaining heat gain in passive solar heating applications. That was initially accomplished through use of metal oxide films such as ITO (indium tin oxide) or TiO_2 to minimize emissivity without creating excessive visible reflectivity. These products transmit almost the entire solar spectrum, but prevent loss of energy absorbed and re-radiated at IR wavelengths.

Interference Stacks:

Two categories of interference-based spectrally-selective band-pass filters are marketed for glazing materials, coating stacks and coextruded films.

Coating Stacks. Low emissivity metallic coatings were eventually modified to create optical interference, enabling the coating designer to better tailor the wavelengths of electro-magnetic energy that are reflected. The goal is to limit the transmitted energy to visible light by reflecting the NIR waveband, thereby rejecting almost half of incident solar energy.

Until recently, this goal was most effectively accomplished through use of "dual silver" coatings interspersed with dielectric layers. Because the transmittance curves of these products approximate a bell curve centered in the visible light spectrum, they commonly exhibit a green cast due to reduction of transmittance at either extreme of that waveband.

Coatings of this category are now commonly applied to both glass and plastic film substrates. They provide more reduction of cooling load, with less loss of daylighting, than any prior technologies.

Coextruded Films. Coextruded films are spectrally selective (NIR & IR reflecting) interference stacks typically consisting of over 200 layers of polymers with discrete indices of refraction.

All-polymeric solar reflecting films reflect NIR energy while maintaining high visible light transmission and color neutrality. This feature allows color design flexibility in solar reflecting laminates (Boettcher 2003). Under normal circumstances, the coextruded film would be protected by a low-iron glass to the outboard, and any higher-absorption strata of the glazing system would be kept inboard of the film to avoid dual-pass absorption.

The precision with which these films can be engineered permits them to have transmittance curves that are uniquely rectangular. Therefore, the transmitted light is uncommonly white, visible transmittance is uncommonly high, and the rejection of NIR radiation is uncommonly efficient.

Abrasion-resistant glazing:

Glass with scratch resistance an order of magnitude greater than that of tempered and chemically strengthened glass is now on the market. The manufacturing process begins with ion beam milling of the glass substrate to smoothen the surface. Then, a pyrolytic diamond-like carbon (DLC) coating is applied by chemical vapor deposition. Current uses include display cases, tabletops, vending machines, and public transit system windows. Gradual decomposition of the DLC in ultraviolet exposure limits exterior use of this product.

Stain-resistant Glazing:

A similar technology, marketed through the shower enclosure industry, produces a surface that is resistant to the surface erosion and deposit accumulation that commonly occur in that application. The production process involves milling the glass substrate with an ion beam in order to smoothen the surface and modify the sodium (Na) and sulfur (S) concentrations at and near the surface. Typically, to minimize risk of unwanted reactions with the substrate, ions of an inert gas would be used. Argon (Ar) is the predictable choice, although other inert gas ions could be substituted, at higher cost. The “self-cleaning coating is then applied to the milled surface.

Minimally, according to the patent (Veerasamy 2001), the hydrophobic coating includes a diamond-like carbon layer and a fluoro-alkyl silane (FAS) compound. Both the ion beam milling process and the DLC deposition resemble the manufacture of the abrasion-resistant product and, similarly, the stain-resistant coating is abrasion resistant. It too ultimately would be subject to depletion by UV radiation if installed in an exterior application.

Superhydrophobic Coatings:

Hydrophobic coatings, utilizing nanoscale technologies, have long been marketed as windshield treatments and for similar uses. These coatings reduce the surface tension of the substrate, increasing the contact angle of water droplets.

Nanoscale glass powders developed by John Simpson at Oak Ridge National Laboratory (2007) form water-repellant coatings for applications on glass and other surfaces. The base material is a phase separating borosilicate glass. It is crushed, the glass phase matrix is etched away, and the residual particles are treated to attain a non-polar state. This technology may enable more economical production of durable superhydrophobic coatings.

Superhydrophilic Coatings:
Hydrophilic coatings often function as effective anti-fogging agents on windshields or eyewear. Some such coatings are not permanent. Others, based upon titanium dioxide, depend upon frequent UV exposure to function optimally.

Researchers at the Massachusetts Institute of Technology have developed an anti-fogging coating by alternating layers of silica particles and polyallylamine hydrochloride to create a surface that is superhydrophilic, anti-reflective, and durable (Bravo, Zhai, et al. 2007).

Self-Cleaning Glass:
Several of the "self-cleaning" coatings predicted by Hohenstein (2006) are now in the marketplace. In addition to a hydrophilic property, most also utilize photocatalysis to decompose organic contaminants. The usual basis of these coatings is titanium dioxide (TiO_2) applied pyrolytically.

The photocatalytic action is activated by ultraviolet radiation. That action breaks down organic deposits in contact with the coating, causing them to lose adhesion and making them more likely to be rinsed off of the hydrophilic surface by rain, or more easily removed by washing.

The coating's hydrophilic quality speeds water evaporation and minimizes spotting.

The self-cleaning products function well to reduce the maintenance costs of sloped glazing, and improve workplace aesthetics. Even so, they have scalar limits. Therefore, advertising representations have been edited to moderate consumer's expectations.

Anti-reflective glazing:
Anti-reflective coatings function by progressing from low to high indices of refraction through one or more coating layers. Pyrolytic and cold-applied sputtered stacks and baked-on dip coatings are commercially available. Visible transmittance of these products ranges from approximately 1% to less than 0.5%. Low-iron glass, with anti-reflective coatings, is virtually invisible from most angles under many lighting conditions. Use of anti-reflective glazing is becoming common in display cases, storefronts, sports venues, and other vision-critical applications.

LED Glazing:
LED lights embedded in glass laminates can be powered by transparent conductors. In the current version, small spot LEDs are embedded in the interlayer of a glass laminate. These products are commercially available, and are used for pathway identification and decorative lighting.

Oak Ridge National Laboratories researchers are developing large area organic LEDs. These "OLEDs" are designed to be formed into thin, flexible sheets. Electrodes composed of carbon nanotubes and magnetic nanowires enhance their electroluminescence efficiency and reduce the energy required for their operation (ORNL 2007).

The potential exists for large area translucent LED construction. If adequate radiation resistance is achieved in OLEDs, or inorganic substitutes are developed, it may become possible to utilize translucent wide area LED glazing as a diffuser in skylights. In that application, sources of diffuse natural daylighting could become artificial light sources at night, enabling designers to provide more consistent distribution of lighting than might be practical otherwise. The laminate construction might incorporate a reflective coating on the #2 surface, outboard of the LED, to limit solar energy transmittance and maximize retention of artificial light.

A designer in Australia has addressed the radiation resistance issue by offering a jalousie window in which the louvers incorporate both transparent OLED and transparent photovoltaic coatings (Curtin 2008). The photovoltaics store electricity in batteries concealed in the window frame. Four hours of direct sunlight will sustain a 60 watt light for approximately six hours. The jalousey design allows the louvers to be oriented to maximize solar absorptance. They are removable for replacement, or use as portable lights.

Solar-photovoltaic (PV) Glazing:
Much of the presently commercialized glazing-related nanotechnology, and much of the research momentum now, is associated with solar photovoltaic applications. Numerous technologies now compete for market share; including amorphous silicon; “micromorphous silicon“; cadmium indium diselenide (CIS);copper, indium, gallium and selenide (CIGS); and a CIGS variant, CIGSSe. Research continues to improve each of the competitive technologies.

Silicon nanoparticles have successfully been utilized both to enhance the PV efficiency of conventional silicon wafer PV cells and as a substitute for silicon wafers in PV coatings, permitting reduction of silicon content and fabrication costs (Beard, Knutsen, et al. 2007).

Flexible copper indium gallium selenide (CIGS) photovoltaic films now constitute only a small segment of the global photovoltaic market, but they are gaining market share rapidly. These films typically operate at lower PV efficiency than that of the silicon-based technologies, but they are versitile and significantly less expensive to manufacture.

Holographic Screens:
Transparent holographic screens, originally developed for aviation “heads up display” (HUD) applications, can now be laminated onto and into glazing panels. The ability to make transparent store windows display projected images potentially could benefit retailers.

Three-dimensional imaging:
Several research groups are developing three-dimensional imaging technologies. One, a sponsored program at University of Oklahoma, such uses a clear, non-moving, volumetric projection medium into which light-emitting up-conversion fluorescent nano-materials have been suspended (Newman 2008). Precisely coordinated laser beams are projected into that medium, exciting the suspended materials to display the three primary colors, to create full-color volumetric images.

Commercialization of these technologies will enable designers to incorporate three dimensional moving images into shop windows, kiosks, or interior glass partitions.

Interactive Glazing:
By integrating touch-screen technologies, holographic keyboards, and image analysis with the glazing, merchants of the future will be able to make a storefront or kiosk display function like a web page; entertaining, providing information, and processing transactions.

Photochromic Glazing:
Photochromics are chromogenic glazing materials in which the absorptance and/or reflectance of electromagnetic energy increases with exposure to electro-magnetic radiation, typically ultraviolet (UV) radiation. They are presently marketed only as eyeglass lenses. The original product developed by Corning in the 1960s has silver halide crystals embedded throughout the lens material.

Organic molecules exhibiting photochromic response cannot be dispersed in glass because they cannot endure the temperature of the molten glass. Technologies utilizing photochromic response of organic molecules have them dispersed in a plastic medium, or deposited as a surface coating.

Silver halide crystals are durable when encapsulated within glass, but have not been successfully utilized as an exposed surface coating. Organic photochromic coatings are economical and effective, but have generally lacked the durability requisite for architectural applications.

Little resources have been devoted to development of photochromic glazing materials for architectural applications because they respond to sunlight in the same manner in winter as in summer. Therefore, products affording more selectivity are generally preferable.

Electrochromic Glazing:
Electrochromics are chromogenic glazing materials that respond to an electrical field or current with a modification of absorptance and/or reflectance.

In a typical five-ply configuration, a chromogenic electrode layer, an “ion conductor” layer, and a counter electrode are sandwiched between two transparent conductive films. Lithium ions migrate back and forth through a thin medium between the electrode, in which they initiate an electrochromic reaction, and the counter electrode in response to current flowing between the transparent conductive layers. As the surface of the reactive electrode is permeated with lithium ions, it darkens. Transparency increases as the lithium ions are drawn back to the counter electrode when the current is reversed.

Liquid Crystal Glazing:
Liquid Crystal glazing panels have been commercially available for over twenty years. They are comprised of a polymer matrix layer, consisting of microscopic cavities filled with liquid crystal molecules, that is sandwiched between transparent conductors. That assembly is usually encapsulated in the interlayer of a glass laminate.

The threadlike LC molecules have a polarity, and rotate in planes perpendicular to the transparent conductor coatings when an alternating electrical field is activated between the conductors. While the field is active, the laminate is transparent, although a slight haze is visible. When the field is terminated, the LC molecules repose in random jumbled configurations that diffuse light. Therefore, in the power-off state, the glazing transmits about 80% of incident light in a highly diffuse form.

The constant activity imposed by alternating current is essential in the current state of the technology. If the frequency of the alternating current is reduced to about 30 hertz, a visible flicker becomes conspicuous. If direct current is applied, the LC molecules align perpendicular to the field and fuse themselves in place, leaving the panel permanently transparent.

LC glazing panels do reflect and absorb slightly more solar energy than plain glass, but that attenuation is not spectrally selective to a significant degree. The dominant optical effect is forward diffusivity. That suggests that LC panels would be ideal for use as light diffusers in skylights but, historically, durability in prolonged UV exposure has been limited. Therefore, the principle applications have been in interior privacy partitions.

Suspended Particle Devices:
Suspended Particle Devices (SPD) are similar to LC panels, except that the encapsulated particles are inorganic opaque molecules that absorb, rather than scatter, light. These panels can be adjusted from nearly opaque black to a light grey tint.

SPD products have been used to control daylighting from skylights and to adjust the transparency of limousine windows. When SPDs are incorporated in the outboard panel of an insulating glass unit, outboard of a low emissivity coating, significant energy efficiency can be obtained by absorbing direct solar beam radiation during periods of high cooling load, and admitting more daylighting at other times.

Thermochromic glazing:
Thermochromics are chromogenic materials that respond to temperature variance with changed absorptance and/or reflectivity. The optimal response for glazing purposes, by

energy-efficiency criteria, would be for NIR/Visible reflectivity to suddenly increase as ambient temperature increased to a trigger value.

Isolation of a thermochromic glazing panel as the outboard lite of an insulative glass assembly causes the solar-optic performance of the glazing system to be controlled by external ambient temperature.

The first thermochromic glazing products in the stream of commerce may be developed from work done with doped vanadium dioxide films deposited via chemical vapor deposition at atmospheric pressure. Vanadium dioxide (VO_2) exhibits a reversible phase transition from monoclinic to tetragonal at 70° C. Below the transition temperature, VO_2 is semiconductive, but above that temperature it exhibits metallic properties (Parkin 2001). Both reflectivity and absorptance increase. The transition is virtually instantaneous.

Manning and Parkin (2004) have found that doping a sol-gel derived VO_2 film with 2% tungsten makes it thermochromic at 25° C, well within the optimal range for architectural glazing applications.

Use of absorptive (tinted) glass substrates with thermochromic coatings effectively decreases the ambient temperature at which transition occurs. Furthermore, substrate color can be used to spectrally neutralize the visible light transmittance. Therefore, it is likely that these coatings will be available only on substrate glass of carefully selected, or custom, coloration.

A reflective thermochromic product would provide optimal energy efficiency with no external power consumption, no cabling, no external controls, and no programming.

Work relating to atmospheric pressure chemical vapor deposition (APCVD) of such films is underway.

DISCUSSION

Funding:

Federal funding support for nanotechnologies, through the National Nanotechnology Initiative, currently totals approximately $1.5 billion dollars annually, with about one third of that total being invested in fundamental research. It is anticipated that this level of funding will continue through FY 2009 (National Nanotechnology Initiative 2008).

Regulation:

Worldwide, governments have funded a significant portion of the basic research through dedicated nanotechnology initiatives. Simultaneously, worldwide, government regulators have mobilized as their citizens have become alarmed at the prospect of unknown nanohazards.

In part, the underlying apprehension is due to fear of the unknown. To that extent, the public's confidence can be enhanced by the spread of knowledge.

Part of the concern of regulators is justified by the fact that the nanotechnologies present new environmental challenges, and have scant history. Clearly, some glazing-related applications of nanotechnologies, including certain photovoltaics, utilize toxic raw materials. The undeniable public interest in preventing environmental pollution, and ensuring workplace safety, necessitate regulatory oversight.

What is now known collectively as the "nanotechnology sector" constitutes both a potential environmental health hazard and the most promising means of enhancing our environment.

Metrology:

Manipulating individual molecules in a manufacturing environment presents unique challenges, especially in the context of audited and certified quality control systems. In nanotechnologies, the instruments that characterize the quality of our products may be far more complex than the machines that manufacture them. Calibrating those measurements is one of the challenges.

In the United States, the EPA is now promulgating new rules and procedures and NIST is establishing new nanoscale gold standards.

Metrology, standards, regulation, funding, and intellectual property rights, provided by governments, form an infrastructure that will enable continued development of nanotechnologies. The renaissance in engineering inherent in nanotechnology is reshaping and strengthening the relationships between industry, academia, and certain governments.

Trend:

The most significant technological changes in the glazing industry since the advent of float glass production are attributable to coatings. Nanotechnologies presently constitute the dominant pathways toward development of new coatings. New coatings appear to provide the most viable means of enhancing the value glazing products in the future. That suggests that nanotechnologies will be, for a while at least, the dominant technological influence on the glazing industry.

CONCLUSIONS

Utilizing nanotechnologies, the glazing industry is developing new products, offering new benefits. The extent to which those benefits are achieved will depend upon the skill with which architects and engineers utilize new products to optimize fenestration systems for specific applications.

With the advent of myriad new functions available in glazing systems, the tasks of designing and specifying these systems becomes progressively more complex. For some emerging fenestration technologies, standards and specifications lag behind the products in their stage of development. Certain functions of some of the new glazing products cannot be simulated with the software traditionally used to model glazing systems.

In some instances, detailed knowledge of the physics of a new technology is required to engineer a glazing system to function properly in any given application. The requisite expertise may be provided by the manufacturer, the architect, the glazing consultant, the mechanical engineer, or the glazing contractor; but it must exist within the Design Team or the Supplier Team of the project.

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