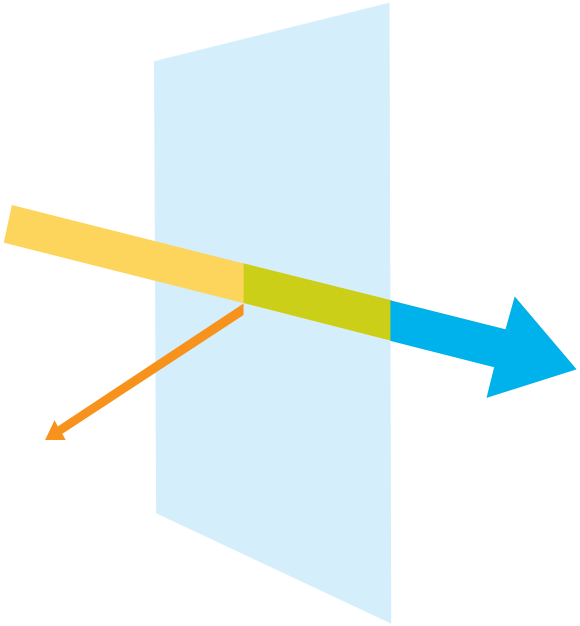
Coatings on Glass

Technology Roadmap Workshop



Workshop held in
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January 18-19, 2000

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Table of Contents

1. Introduction and Summary 2

2. Invited Lectures 5

Flat Glass - Richard J. McCurdy, Pilkington Libbey-Owens-Ford Co. 5
Containers - Clem McKown, Elf Atochem 8
Glass Fiber - Les Campbell, Owens Corning 11
Specialty Coatings on Glass - Carl Lampert, Star Science 13
Online Coating of Float Glass and Its Relationship to Coating Chemistry - Roy Gordon, Harvard University 17
Surface Chemistry of Commercial Glasses - Carlo Pantano, Pennsylvania State University 20
Theoretical Approaches to Modeling Glass Coatings and Interfaces - Michael Teter, Cornell University 25

3. Flat Glass Breakout Group 28

4. Container Glass Breakout Group 42

5. Coatings on Glass Fiber Breakout Group 51

6. Specialty Coatings on Glass Breakout Group 59

Appendix A: Coatings on Glass Workshop Agenda 72

1. Introduction and Summary

Coatings applied to glass surfaces are an essential part of manufacturing in all segments of the glass industry. Without coatings, many glass products would not have the properties that make them so useful; many would also be impossible to make. Examples can be found throughout the industry:

- Because of its abrasiveness, glass fiber could not be formed into products such as fiberglass insulation and composites for automobiles without protective and lubricating coatings.
- The dramatic increases in energy efficiency achieved by low-E and solar-control glass (a nearly twofold increase in the R value of a dual-pane window over uncoated glass) are due entirely to sophisticated application of multiple coatings.
- The high throughputs of today's container lines (up to 700 bottles / minute) would not be possible without lubricious coatings; coatings also increase the burst strength of glass containers threefold.
- New products at the forefront of the industry, such as "smart windows" and flat-panel displays, rely on coatings to achieve their functionality.

The glass industry vision document, *Glass: A Clear Vision for a Bright Future* (Jan. 1996), recognizes that the "development of innovative uses of glass is a linchpin of the industry's future." Examples of some of the many innovative glass products that use coatings are given in Table 1-1. *The Glass Technology Roadmap* (Sept. 1997), includes a partial list of industry-wide product categories essential to broadening the market for glass products. Of the 10 products, at least 7 will likely require coatings (Table 1-2). This report also points to the importance of coatings in the glass industry, listing the following key coating-related barriers that inhibit the greater utilization of glass:

- Lack of basic understanding of the properties of glass at the molecular level [and] its interactions with other materials.
- Sub-optimal measurement and control of processes.
- Limited processes for economical and effective online coating.

Table 1-1. Current products that use coatings and their functions.*

Current Products	Function
Low-E window glass	Energy-conserving windows
Solar control + low-E glass	Windows in large buildings, hot climates
Photovoltaics	Solar electricity
Flat-panel displays	TV, computers
Electrochromic mirrors	Automatic rear-view mirrors in cars
Touch-panel controls	Appliances
Anti-reflection	TV, picture framing
Anti-static	Copiers
Defogging	Supermarket freezers, windows in vehicles
Anti-abrasion	Bar-code readers
UV protection	Reduced fading of fabrics and art work

*Source: R. Gordon, Harvard University.

Table 1-2. Industry-wide product categories essential to broadening the market for glass products: categories involving coatings.*

• Sun Power (solar lenses and mirrors; photovoltaics)
• Structural Applications (thermal insulation; fireproof materials; flooring; foam glass roofing
• Electrical / Electronic Products (flat-panel displays, laser materials)
• High-Strength Glass (flexible / bendable glass, lightweight glass, self-healing glass)
• Composites (fiberglass reinforced composites, glass-polymer composites)
• Optical / Photonics (opto-electronics, optical security devices)
• Biological / Medical Devices (glass bone implants, controlled release products)

*Source: *Glass Technology Roadmap*, Sept. 1997.

Coating is an integral part of glass manufacturing, not simply an "offline" process applied by end users. Consequently, coating places demands on the entire manufacturing process. Glass temperature and speed are closely linked to the deposition efficiency achieved by online coating methods in the float glass industry. Offline deposition methods, such as sputtering, rely on a high degree of cleanliness and reproducibility in the glass surface, which is tightly linked to initial manufacturing conditions. Similarly, line speeds used in the container industry must be compatible with the speed of the deposition chemistry, and container temperatures must be carefully controlled to achieve the appropriate coating properties. In the glass-fiber industry, water-based coating solutions also serve to cool the fiber to a temperature at which it can be wound.

Coating processes can require very large energy expenditures and have significant associated waste and environmental issues. The need for substantial improvements in coating manufacturing technologies is dramatically illustrated by the following examples:

- In the deposition of coatings on float glass, a best-case yield of around 70% is achieved using online methods (which are the most economical) such as chemical vapor deposition. Without coating, the yield is typically 75–80 % (i.e., 20–25% of the glass is rejected, ground, and remelted). In some cases, however, application of coatings can reduce the total yield to less than 50%. Such high reject rates represent an enormous cost in energy. On average, roughly 3.8×10^{10} Btu / year must be expended to remelt this glass.
- The efficiency of reactant utilization in online float-glass coating techniques can be as low as 10%, necessitating the installation of multi-million-dollar chemical scrubbing units or incinerators and sending more than two million pounds / year of waste to landfills.
- In the fiberglass insulation industry, which produces 1.9 million tons of material annually (1995), an average of 375 Btu per pound of insulation is expended in drying and curing coatings applied to the fibers using aqueous processing methods. Thus, approximately 1.4×10^{12} Btu / year could be saved if non-aqueous coating technologies could be developed.
- In the textile fiberglass industry, where almost none of the material is recycled, between 5% and 20% of the glass that is melted becomes "basement" scrap (coated fibers resulting from quality-control rejection or trimming), amounting to almost 100,000 tons of material annually that must be landfilled due in part to non-recyclable organic coatings.
- In the container industry, hourly replacement of mold-release coatings used to ensure defect-free release of the newly formed container from the mold, causes 1.5 % of all glass containers to be recycled and remelted (54 million containers in the U.S. alone).

Clearly, there is considerable room for improvement with regard to energy utilization, process efficiency, and waste reduction in these manufacturing processes.

The Technology Roadmap Workshop grew out of a collaboration between the glass industry and the U.S. Department of Energy's Office of Industrial Technologies (OIT). The two-

day workshop was held January 18–19, 2000 in Livermore, California and brought 42 experts from the glass industry, universities, and the national laboratories together to identify key targets for improvement, technology barriers, and research needs relevant to the manufacturing of coated glass products. It was sponsored by DOE/OIT and PPG Industries and conducted in collaboration with the Glass Manufacturing Industry Council (GMIC).

The workshop began with overviews of coatings manufacturing by representatives of each of the primary segments of the glass industry: flat, container, fiber, and specialty. In addition, four plenary speakers from academia reviewed important scientific and engineering concepts relevant to glass coatings: chemistry of online coating deposition; surface interactions; characterization techniques; and theoretical approaches to modeling coatings. The heart of the workshop consisted of two breakout sessions in which the participants divided into groups representing each of the four industry segments. In the first session, performance targets and technological barriers to achieving them were identified, while in the second session, a list of research needs required to meet these goals was compiled. The breakout sessions were linked by plenary gatherings at which summaries of the work of each group were presented. During each breakout session, members of the groups also compiled a list of individuals who were not able to attend the workshop but who would be interested in reading the report.

In spite of the great diversity of products and functions involving coatings, a substantial number of common threads were revealed during the discussions of the breakout groups, pointing to the possibility for collaborative work within the industry. Examples of key needs that span the industry include:

- Data bases of information concerning film properties (optical, mechanical, electrical, etc.) and deposition chemistries.
- A pilot-scale facility for developing new coating processes.
- Computational methods for rapid screening of potential coating materials.
- Rapid prototyping methods for evaluating coating processes.
- Fundamental data concerning deposition processes.
- Improved understanding of surfaces and interfaces.
- Low-cost deposition methods.
- Sophisticated sensors and process control.

In addition to these needs, participants identified 135 specific research needs in the four focus areas, of which about half were considered priority items. These research needs were analyzed to determine the time frame in which each research activity is expected to have an impact on the industry, either on a commercial product or on a manufacturing process. Research time frames correspond (roughly) to 0–5 years for near term; 5–10 years for mid term; and > 10 years for long term. In addition, some research is expected to be ongoing during all time periods and be able to produce useful results at all stages.

In closing remarks at the end of the two-day session, many participants expressed satisfaction with the openness of the discussions that occurred among members of a normally secretive industry. However, there was also hope that the momentum not be lost, but be used to pursue mutually beneficial collaborative research opportunities. It was also suggested that the group consider meeting again, possibly at a technical meeting (there are several devoted to coatings research) to review progress toward the goals identified during the workshop.

2. Invited Lectures

Flat Glass (Richard J. McCurdy, Pilkington Libbey-Owens-Ford Co.)

Approximately 550 million square feet of flat glass is coated annually in North America, either by the manufacturer or an end user. Most is used for architectural purposes. The coatings used can be divided into roughly two types: low-emissivity ("low-E") coatings, which improve the energy efficiency of glass used in architectural and automotive applications and specialty coatings, which enhance the electro-optical, catalytic, or conducting properties of glass. The latter were primarily the subject of the Specialty Coatings Breakout group and are reviewed in the Specialty Coatings section that follows. This section focuses on coatings that are produced in high volume and are currently a major value-added market for the flat-glass industry, such as low-E coatings.

Flat glass is coated either offline by magnetron sputtering in vacuum or online by chemical vapor deposition (CVD). The first low-E coatings were deposited by sputtering (Figure 2-1), a well-established method for manufacturing a wide range of thin films. Glass is sputter coated after it has been cut and tempered and is usually in its final shape. In sputtering, the coating species is formed as the recoil product of the collision of a heavy ion with a target of the coating material. The principal advantages of sputtering are the ability to deposit both pure metals and metal compounds (nitrides, oxides, etc.) and the ready availability of precursors, which are typically targets, manufactured from highly pure metals and various reactant gases. Sputtered coatings are better reflectors of unwanted UV and IR radiation than CVD coatings, making them desirable for automotive applications where reduction in heat loads is critical. Unfortunately, sputtered coatings are also relatively soft (the most energy efficient coatings are silver-dielectric multilayers or "stacks") and cannot be bent, so they can only be used in laminated form on vehicle windscreens. An additional disadvantage is that sputtering is essentially a batch process, which adds steps to the manufacturing process and increases costs. Finally, sputtered coatings cannot be used in any exposed exterior application, such as the exterior surface of an integrated glass unit in a building.

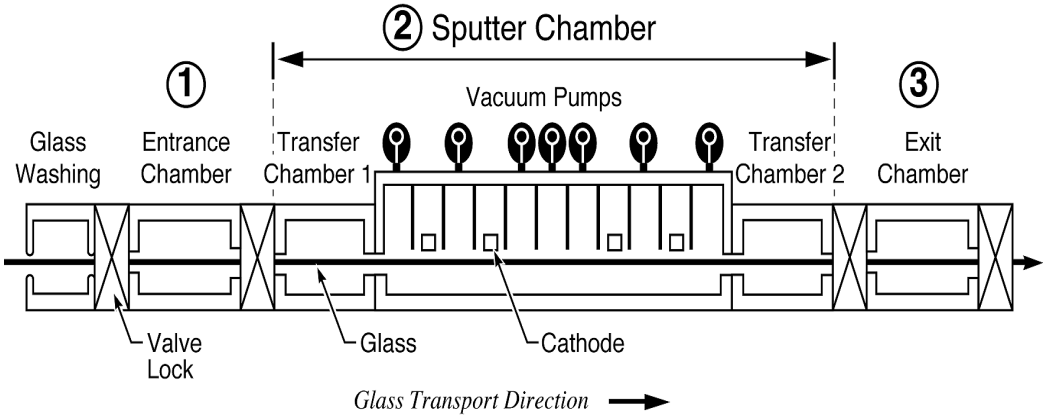

Figure 2-1. Schematic of a continuous-batch sputter-coating reactor.

Chemical vapor deposition, also called pyrolytic coating, was developed as an online method of depositing films directly on the hot glass while it is still on the float line (Figure 2-2).

In CVD, precursor compounds (both gases and liquids) are vaporized in a reactor that spreads the resulting gas mixture uniformly over an advancing, newly formed glass ribbon. Chemical reactions occur in the gas above the glass and on the growing surface of the deposited film. The first coating manufactured in this way was tin oxide (SnO_2), which is deposited from an organotin compound such as dimethyltin dichloride ($(CH_3)_2\ SnCl_2$,) and oxygen. The online CVD process is fast and cheap because the glass is coated as it is formed. Temperature control is easier because the large thermal mass of the system also keeps the temperature relatively uniform across the ribbon. Glass that is coated online is flat and properly annealed, which minimizes post processing. CVD coatings also adhere more strongly to the glass than sputtered coatings because they are deposited at higher temperature (600–700 °C). Strongly adhered coatings maintain their integrity when the product is bent and tempered.

Unfortunately, CVD currently lacks the broad applicability of magnetron sputtering to deposit a variety of materials and compositions. Because the substrate glass moves about 1 ft/s as it travels down the float line, only 1 – 1.5 s are available for the coating to form. This requires very fast deposition chemistry (600–1000 Å/s), which to date has only been achieved for a limited number of materials. The optical properties of CVD coatings, while very good for most architectural applications, are at present not sufficient for the most demanding applications. In particular, lower solar transmission can be achieved by sputtered coatings. As a result, automotive solar control is dominated by sputter-deposited coatings.

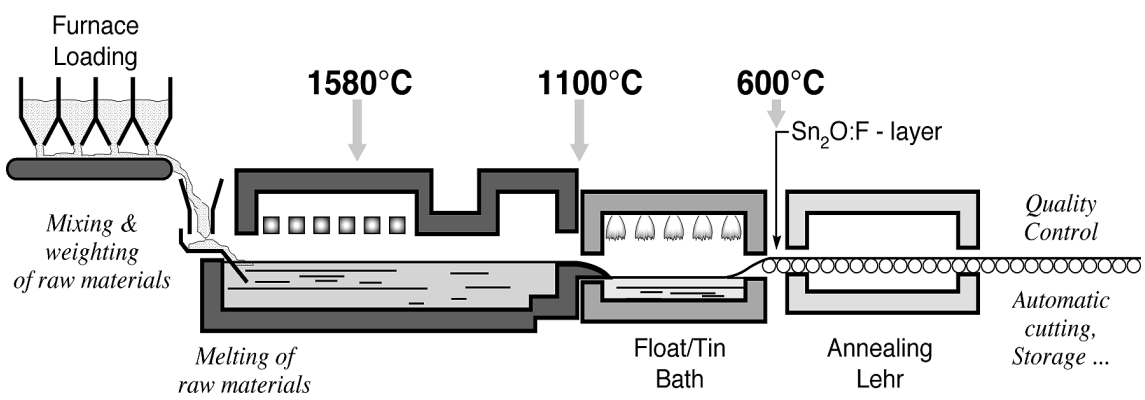

Figure 2-2. Schematic of a float bath production line showing one possible online coating reactor used to deposit fluorine-doped tin oxide.

Coated flat-glass markets are strong and growing. The current markets for coated flat glass are dominated by architectural applications. Coated glass for energy-conserving windows constitutes a roughly $600 million market for the raw glass alone; the total value of the final manufactured product (primarily dual-pane glass units) is in the billions of dollars. Automotive applications, including windshields and mirrors, constitute a smaller but growing market. Miscellaneous applications include freezer doors and copier glass. In addition to these established markets, there are numerous opportunities for developing future energy-efficient or multifunctional products, if economic manufacturing processes can be developed. Examples of these include glass for photovoltaic cell substrates; electrochromic glass for active windows; antireflective (AR) glass that is conductive, contrast enhancing, or for large area displays, as well as AR architectural glass; and self-cleaning glass. Many of these applications, as mentioned above, currently fall into the category of “specialty coatings” and have very limited markets today. However, solving problems in the production of high-volume coatings such as low-E glass could make these materials economically attractive.

Since economics drive technology in the glass industry, the push is toward faster and better online coating processes. Like much of the glass industry, flat-glass producers face the dual challenge of increasing the market share for coated products while minimizing cost. For offline coating, this means developing new materials and improving cathode technology to enable faster growth rates, deposition of new materials at commercial speeds, and formation of new structures with increased abrasion and corrosion resistance. Online deposition holds great promise for exploiting the large economies of scale enabled by the continuous float-glass process. However, critical challenges include: 1) the need for thickness insensitive thin-film designs to maximize yield for 4-m ribbon widths; 2) development of new CVD chemistries compatible with short residence times (high ribbon speeds typical of float-line operations); and 3) flexible reactor designs that yield high deposition efficiencies while allowing for facile interchange between products.

Because glass production volume is high, growth in the markets for coated glass depends primarily on a favorable cost-benefit comparison with uncoated glass, both at the supplier and end-user levels. However, continued enhancement of the value of coated glass by developing new products as well as reducing its cost will also play an important role. Realization of future products in online coating technology must include the development of new coating materials through the development of new precursor materials, faster deposition methods (both CVD and sputtering), and modeling to improve understanding of the deposition process. Good process control at higher temperatures will also be required. Many technical barriers stand in the way of achieving these goals, including lack of critical data needed to model coating processes, poor understanding of the phenomena controlling coating properties, and a need for durable online process control.

Containers (Clem McKown, Elf Atochem)

More than 95% of all glass containers manufactured in the United States (36 billion / year on 300 production lines) are produced with one or more coatings. Worldwide, the percentage is somewhat lower, but is still about 75%, yielding a total of over 180 billion coated glass containers each year.

The glass container market is flat and threatened by competition from plastics. The glass container industry has responded with fewer glass container producers, fewer glass container plants, and fewer, faster glass production lines. Between 1979 and 1992, 48 container plants closed, in part, because of increased energy costs and environmental compliance difficulties. As a result, the industry has found it difficult to develop the technology necessary to improve its products. The industry is a mature one, using relatively cost-effective coating technologies. Thus, radically new developments are needed to initiate major changes in the appeal and competitiveness of glass containers.

Coatings are applied for several reasons. First, they increase the yield of production lines by providing a lubricious surface that eliminates scratching and line jams. This characteristic is particularly important, since it permits the very high processing speeds used today (the fastest lines now produce 700 bottles / min). Specifically, coatings reduce the slip angle from greater than 30 degrees to less than 10 degrees and increase scratch resistance from less than 0.1 kg to much greater than 30 kg. Second, they increase and preserve the strength of the bottle by reducing the likelihood that defects in the glass will lead to breakage. Coatings raise the burst pressure of glass containers by over threefold, from less than 10 bar to over 30 bar. This increased strength is critical because glass containers are typically handled at least five times before they reach the distributor: production, stock, transport to the filling plant, filling, and transport again to the seller. Finally, because of the improved break-resistance imparted by coatings, they allow container weight to be reduced, which is an essential part of reducing manufacturing energy consumption and increasing the competitive position of glass relative to plastic. This reduction is substantial and can be as much as 25%. It is not an exaggeration to say that modern glass containers could not be produced without the use of coatings.

Typically, two coatings are applied to glass containers, a hot-end coating (HEC) and a cold-end coating (CEC). The HEC protects the glass surface from damage and provides the substrate for the CEC. The HEC is usually 10 nm of a hard ceramic material, while the CEC consists of ~ 50 nm of an organic material. Neither coating alone is sufficient. The ceramic material is applied at the hot end using chemical vapor deposition (CVD) and is either tin oxide or titanium dioxide. These materials are applied immediately after forming when the container surface temperature is between 450–600 °C. A range of precursors can be used, including monobutyltin trichloride, tin tetrachloride, dimethyltin dichloride, and titanium tertrachloride. Applied on single line at full production, the average rate of application is about 200 bottles per minute, but can be as fast as 700 bottles per minute on the fastest lines. The process is shown schematically in Figure 2-3. The HEC has several critical requirements. It must be: 1) fast (only 1-5 ms are available to coat the container) and highly efficient (≥ 50%); 2) low cost; 3) provide a coating of uniform thickness; 4) low maintenance and easy to use; 5) safe and noncorrosive; 6) insensitive to ambient conditions; and 7) leave no coating on the threads of the container. These requirements make development of new HEC materials and processes extremely challenging.

The CEC typically consists of partially oxidized polyethylene, which is spray-deposited from a dilute (1%) aqueous emulsion, or stearate, which is deposited as a vapor. This coating is about 50-nm thick and is applied at a glass temperature of 135–165 °C, after the container is annealed. This temperature is very critical; if it is too high and an anhydrous film forms, the label will not stick to the container (Figure 2-4).

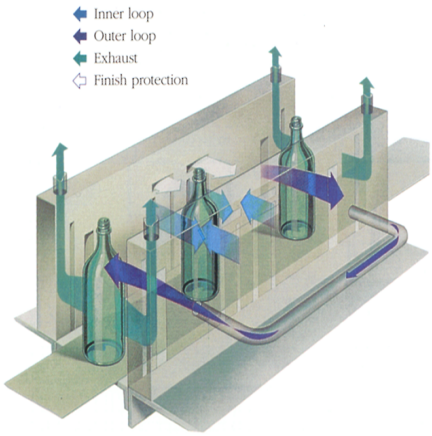

Figure 2-3. Schematic of a hot-end container-coating process (Source: C. McKown, Elf Atochem North America).

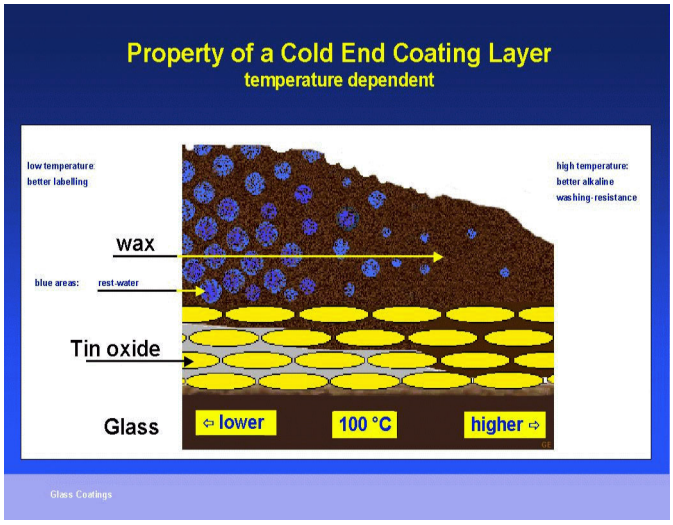

Figure 2-4. Effect of temperature on cold-end coating layers (Source: C. McKown, Elf Atochem North America).

Other coating processes have been attempted but failed in the marketplace. Coatings to provide improved strength, one-step coatings that eliminate the HEC, energy-absorbing and fragment-retention coatings, colored and decorative coatings, and post-coatings for reusable glass containers fit in this category. None of these is used by manufacturers currently, primarily because of their higher cost, but for other reasons as well. For example, coatings to strengthen

the glass, of great interest to the manufacturers of glass containers because they could improve the performance of glass relative to plastics, were developed (separately) by Elf Atochem, AGTS, and IPGR in the 1990s. Ultimately, these were not successful because of their relatively high cost (0.7–2 ¢/bottle) and the fact that they only increased the burst pressure without also improving the impact pressure. The market for these also declined when much of the carbonated beverage market (principally, soda) converted to plastic (PET) containers. One-step coatings were applied at the cold end and found to be inferior to the dual HEC/CEC coatings.

On the positive side, however, there appear to be no technical barriers to achieving significant improvements to the properties of glass containers, such as increased break resistance, fragment retention, higher strength, and energy absorption, even within 5 years. Much of the technology already exists. However, it must be made cost effective.

Glass Fiber (Les Campbell, Owens Corning)

Coatings play an essential role in the manufacturing of products from glass fiber. Because of its abrasiveness, glass fiber is almost useless unless it is first coated with a water-based solution of compounds known as "sizing." In the absence of such coatings, fibers virtually self-destruct. Consequently, sizings are applied to fibers almost immediately after they are formed. Sizing is the most important factor in differentiating one product from another. These coatings not only increase fiber durability, but also add significant value to the product. Many different products are made from glass fiber, including yarns, wet- and dry-use chopped fibers, mats, panels, and milled products. In general, the direct consumer of glass fiber processes it into a composite part (e.g., fiberglass); fiberglass insulation is another product and also requires the use of sizing. This wide variety of products led to the more than 100 sizing compositions on the market, each containing from 2 to 10 components.

Figure 2-5 illustrates the process of manufacturing glass fiber and the application of sizing. In a typical fiber-forming machine, the coating applicator is located just below the fiber-forming bushing. Glass fibers leave the forming die at a temperature of over 1000 °C and are rapidly cooled by the aqueous sizing solution to a deposition temperature of less than 100 °C. Less than 0.5 ms are available for applying the sizing since the fibers are being pulled at speeds greater than 1000 m / min. The filaments are then formed into a multifilament strand and wound into a package; there can be as many as 4000–6000 fibers in a bundle. Fibers may also be chopped.

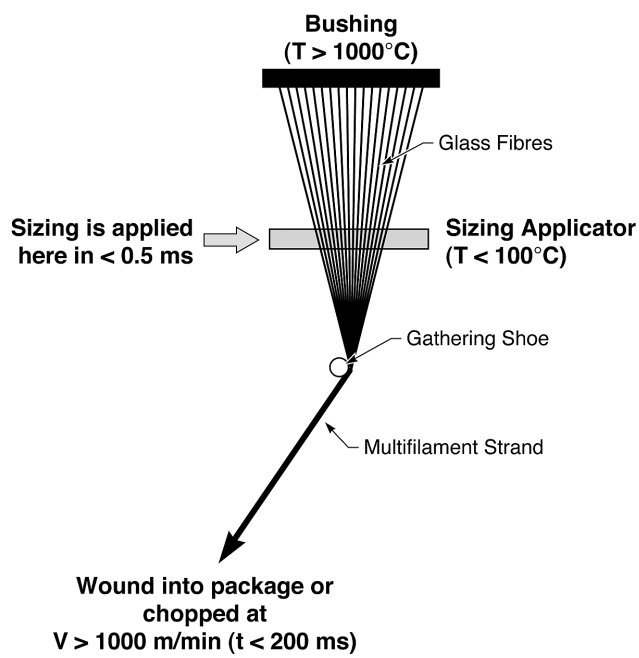

Figure 2-5. Schematic of the fiber drawing and coating process.

Sizing is a multifunctional material that contains several constituents. All sizings are an aqueous chemical system containing 0.05–10% solids. Water has a key role in the application of sizing. Besides being a carrier and diluent, water cools the hot fiber and allows the application

of small quantities of sizing materials to large surface areas. It wets glass easily, helping to bring the sizing to the glass surface and, as a lubricant, it reduces direct fiber-to-fiber contact. The solid constituents in a sizing are a film former (the “glue” that holds filaments within a fiber bundle together); a coupling agent (promotes adhesion between the fiber and the composite matrix); lubricants, both cationic and nonionic (provide abrasion resistance); and other additives, such as antistatic compounds, emulsifiers, chopping aids, wetting agents, and antioxidants. Film formers are typically polymers such as polyvinyl acetate, polyurethanes, polyolefins, polyesters, and epoxies. When emulsified, these high molecular weight and otherwise water-insoluble compounds can be deposited on glass. Organosilane coupling agents such as $(OH)_3Si(CH_2)_3NH_2$ react with silanol groups (Si-OH) on the surface of the fiber to form Si-O-Si bonds. Cationic lubricants, positively charged molecules that are attracted to a glass surface, are very effective in reducing fiber breakage. Nonionic lubricant acts like surfactants; they soften the strands and plasticize the film former.

Compromises and tradeoffs are common in glass fiber manufacture, so a successful sizing must be a balanced chemical system that gives the product its most desired properties. Sizings are chosen to help form a composite material and give it the required strength. Thus, promotion of strong bonding between the fiber and the resin matrix is of paramount importance.

The multifunctional nature of sizings combined with the complexity of the chemistry makes it very difficult to optimize the composition and deposition of a size. While the effect of individual components in the size is known at least qualitatively, the relationship among these components in solution and their combined effect on strand integrity, wet-out rate, and mechanical properties is often unclear. The chemical reactions that occur during fiber formation, coating deposition, drying, and the various stages of composite manufacturing, must be much more fully characterized. Even some of the most basic facts about the coating process, such as the percent of the fiber covered by sizing, are not known well; however, it is known that variables such as coverage are strongly linked to key fiber properties such as tensile strength.

The future of size chemistry depends on advancing the technology. New sizing concepts must be developed to add significant value to glass-fiber products. Areas ripe for exploration include the use of nonaqueous sizes, which may yield better fiber coverage. Improvements in the existing technology, such as development of more effective silane coupling agents and higher molecular-weight polymer emulsions, could substantially improve fiber properties. While pursuing these developments, however, the industry must continue to keep its manufacturing processes environmentally friendly in an era of increasing regulation.

Specialty Coatings on Glass (Carl Lampert, Star Science)

Specialty coatings is a broad area that encompasses a wide range of specific functionalities for coatings on glass. These include electrochromic materials, conductive coatings, reflecting or antireflecting films, and catalytic materials, as well as several others (see discussion of the Specialty Coatings working group, page 63). While these materials have small niche markets today or are still in the development stages, the potential for major growth exists. Cost is a significant inhibitor and points to the need for economical mass production methods, which generally means either online or continuous batch forms of manufacturing. Thus, the challenges faced by the special coating industry today presage ones that the flat-glass industry will likely confront in the near future because of its role as the producer of economical coatings on large-area glass.

Dr. Carl Lampert of Star Science (Santa Clara, CA), described the markets and challenges in the area of specialty coatings by dividing his presentation into three parts: switchable glass for glazing (which includes "smart windows" and electrochromic materials), display glass, and fire-retarding glazing. Coatings are an essential part of the first two technologies and may be able to play a role in the third.

Smart switchability is the ability to electronically control certain features of windows and mirrors so that they darken selectively on command. They can thus be used to provide visual and thermal comfort, glare control, daylight management, and reduced energy consumption caused by overcooling or excess solar transmission. Electrochromic coatings are the most common materials of this type and respond to electronic control. Other types of switchable media include electronically switchable liquid crystal displays and electrophoretic films, thermally sensitive thermochromics and thermotropics, and photosensitive materials. Currently, tin oxide and indium-tin-oxide (ITO)-coated float glass are used to fabricate electrochromic windows. Many major glass manufacturers have entered the electrochromics field and are attempting to scale up production as well as develop new technologies. Recently, for example, electrochromic glazing over 1 m^2 in size was demonstrated. There is also some significant government-supported research in this area (see for example the following web pages: U.S. Dept. of Energy Office of Building Technology, State and Community Programs (www.eren.doe.gov/buildings); Lawrence Berkeley National Laboratory Windows and Daylighting Group (windows.lbl.gov); and National Renewable Energy Laboratory Center for Buildings and Thermal Systems (www.nrel.gov/buildings/windows)).

Electrochromic automotive mirrors are perhaps the largest application of these materials today. In this application, the mirror darkens automatically at night with the approach of bright headlights. While these materials are typically found on high-end vehicles in the U.S., it is not difficult to see how electrochromic materials could become an important part of energy-efficient building construction. Unfortunately, their complex structure (see Figure 2-6) leads to high manufacturing costs. In most commercial electrochromic devices, the electrochromic material is either an organic coating (for automotive mirrors) or tungsten oxide (WO_3). Other examples of electrochromic products include E-control glazing, electrochromic windows for the Airbus, dispersed liquid-crystal glazing, and encapsulated dispersed-particle products.

In addition to the complexity of the manufacturing process, manufacturers of electrochromic materials face other substantial technical problems. Seals and protective coatings play a vital role in protecting the glazing; in fact, seal integrity dictates the lifetime of the device.

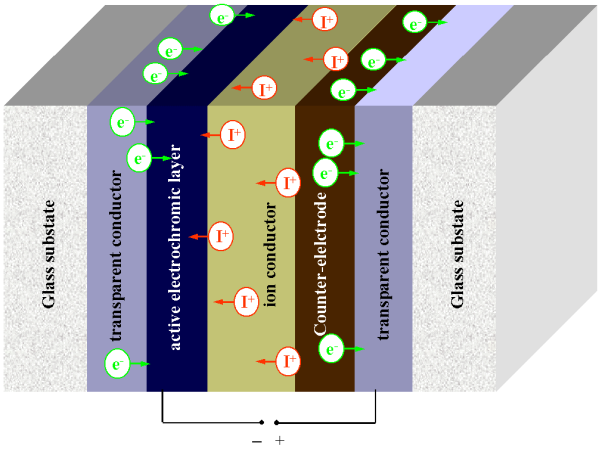

Figure 2-6. Schematic of the construction of an electrochromic device (Source: M. Rubin, Lawrence Berkeley National Laboratory).

UV radiation tends to degrade the performance over time. To minimize this problem, several new technologies are being investigated, including photoelectrochromics and photovoltaic-powered materials. To reduce costs and simplify the manufacturing process, manufacturers of electrochromics are moving toward laminated construction, processing sizes greater than 2 m^2, and in the long term, monolithic construction. There is still a need for coated flat glass with lower sheet resistance (<1 ohm / square is desirable). Prefabricated (i.e., provided by the flat-glass manufacturer) bi- and tri-layer films are also needed, but these will require new deposition methods (CVD, vapor deposition, or sol-gel). Overall, fewer defects, lower cost, and higher quality are needed to increase the market for these products.

Flat panels and CRT displays make up the major markets for displays and represent a very large market. The worldwide value of the flat-panel market for 2000 is expected to be $18 billion, while that for CRT displays is projected to be $30 billion. These growing markets are thus expected to be a major source of revenue for the glass industry, if glass technology can progress fast enough. The use of display technologies, particularly active-matrix liquid crystal displays and electroluminescent displays, is expected to increase rapidly over the next 5 years (Figure 2-7). Flat-panel displays are used for laptop computers; desktop displays; advertising and public information display; microdisplays, such as cell phones, cameras, gaming, and headsets; internet appliances; and portable TVs. Electroluminescent displays and liquid crystal displays are the predominant flat-panel technologies. CRT displays, which are used in computer monitors and TVs, are actually a larger market than flat panels. As with switchable glazing, the manufacturing trend for flat panels is toward larger processing sizes, better control of defects, and cheaper production. In addition, display glass producers want thinner glass sheets (on the order of 0.1-mm thick), glass whose properties (especially the strain point temperature) approach those of fused silica, better edge quality, and smaller pixel size. These needs are summarized in Table 2-1, which shows that display technologies have considerable commonality with the needs in the switchable glazing area.

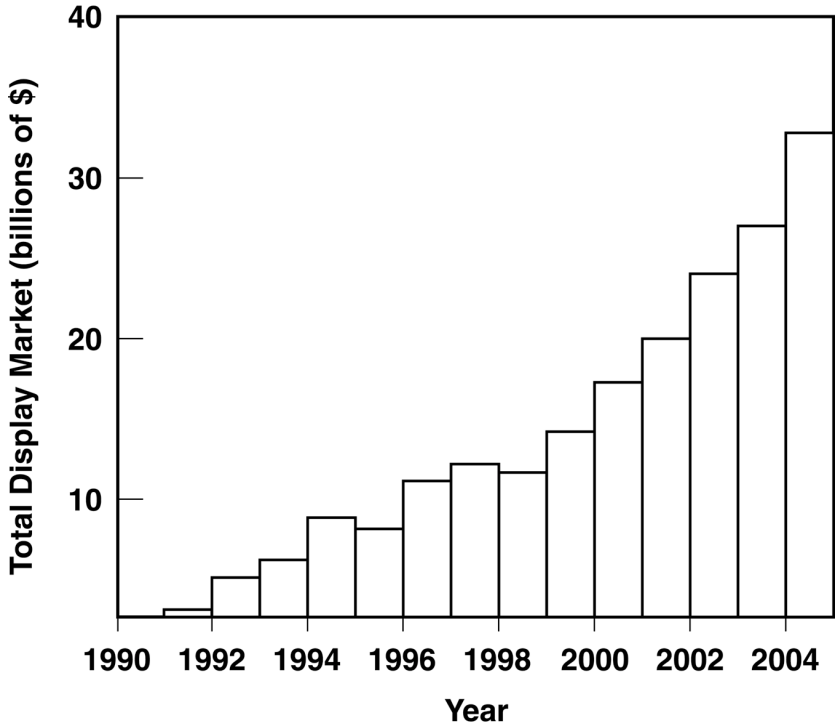

Figure 2-7. Projected total value of the worldwide market for displays (Source: adapted from C. M. Lampert).

Table 2-1. Technology trends and issues in the switchable glazing and flat-panel display industries.

Switchable Glazing	**Flat-Panel Displays**
Moving from small to larger sizes (> 1 m^2). Glass and plastic substrates used. Cost reduction needed (currently \$100 / ft^2). Poor defect control and low yield. More economical, simpler deposition methods needed.	Moving from small to larger sizes (> 1 m^2). Glass and plastic substrates used. Cost reduction needed (\$650 / ft^2 in 1998). Defect control could be improved, but better than for EC. Lower-cost fabrication techniques required.

Tougher fire codes are driving glass producers to produce glass that retards the spread of fire. Float glass is inherently a bad structural material at temperature, having low tensile strength and high thermal expansion; thus, it often cannot withstand the pressure of a fire hose or thermal stresses imposed by a fire. Although there are a number of methods for imparting fire resistance to glass, including the use of wired, toughened, borosilicate, laminated, block, or ceramic glass, several promising approaches include the use of coatings. One type of fire-retarding glass (known as El or F-class glazing) employs multilaminates of between 3 and 23 interlayers that give off water and swell when hot, reducing heat radiation and propagation. Typical E- and G-class glazings currently used provide 20–30 minutes protection, while the

newer El- and F-class glazings last 30–120 minutes. The ideal fire-retarding glass would be a thinner, transparent, heat-radiation-reducing glass that would resist heat exposure for periods greater than 120 minutes. Coatings that form chars, materials with high heats of vaporization, such as hydrogels; and intumescing (swelling) materials are all potential solutions to this problem.

In concluding, Dr. Lampert pointed out that cost is the biggest driver controlling the development of new coating technologies. Cost includes not only materials and manufacturing costs, but also costs of disposal and coating areas. The need to achieve high yields from manufacturing processes is critical to reducing these costs, so that these and other specialty-coating technologies can become more economical.

Online Coating of Float Glass and Its Relationship to Coating Chemistry (Roy Gordon, Harvard University)

Online coating deposition is a proven way to manufacture high-performance, low-cost, and durable products from float glass. Chemical vapor deposition (CVD) and its derivative methods (such as spray pyrolysis) are the techniques used today to deposit coatings on a float-glass line. High productivity results from online CVD because of the high production volumes possible; large float-glass lines can produce over 300 tons of flat glass per day. CVD has other important advantages, however (Table 2-2). Of particular importance to flat glass manufacturing is the flexibility to deposit a wide range of elements at high rates with excellent adhesion to the substrate. Thus, there is great interest in developing new CVD methods to deposit a wide variety of commercially valuable materials on flat glass. Ultimately, CVD may be the route by which an increased spectrum of value-added coated glass is produced economically.

Unfortunately, development of new CVD processes is far from straightforward and substantial barriers exist to the implementation of new online coating technologies (Table 2-2) Perhaps the greatest challenge of all is that the chemical reactions that produce the film must be quite fast since only 1–2 seconds are available for the coating to form as it moves along the float line (typical float-line speeds are ~ 1 ft/s). Thus, understanding the rates of these reactions is extremely important to the development of effective online processes. In addition to this problem, many potential coating precursors are solids with low vapor pressures, making them difficult to vaporize. Some compounds leave impurities that affect the properties of the film, while others can attack the glass substrate.

Table 2-2. Advantages and disadvantages of CVD.

Advantages	Disadvantages
Most elements can be deposited.	Complex, poorly understood chemistry.
High purities are possible.	Solid sources difficult to vaporize.
Unique materials can be achieved.	Impurities left by some reactions.
Wide variety of physical forms/microstructures.	Some substrates attacked by chemicals involved.
Good step coverage or “throwing power”.	Some substrates damaged by high temperatures.
Substrate-specific (i.e., selective) deposition.	
Low porosity (coatings useful as barrier layers).	
High density.	
Hard coatings.	
Large-scale equipment.	
High deposition rates.	
High productivity.	
Good coating/substrate adhesion.	
Low cost.	

Ideally, an online CVD process would have a number of features, which can be grouped into three areas: precursor properties, vaporization behavior, and process parameters. The ideal CVD precursor would be a liquid or gas at room temperature, inexpensive to manufacture and purify, stable during storage, and unreactive with air. It should also be nonflammable, nontoxic, and noncorrosive. Vaporization behavior is also critical. The ideal precursor should have a vapor pressure of about 30 Torr at a temperature at which the precursor is thermally stable (practically speaking this should be less than 200 °C). Vaporization must be rapid and

reproducible, which is typical of non-associated liquids (but not solids). Once in the gas phase, reactant vapors should not react with each other prematurely, allowing mixing to create a uniform composition. Deposition temperatures should be low enough to avoid substrate damage, and the reaction should produce a pure film with the desired properties. Speed and efficiency are also critical; a high percentage of the precursor, which can be quite expensive, should be converted to film within the limited time available. Finally, the byproducts of the reaction should be stable, unreactive, nontoxic, noncorrosive, and nonflammable. Needless to say, it is extremely difficult to achieve all of these characteristics, a fact borne out by the small number of materials (principally doped and undoped tin oxide, silica, titanium nitride, and compounds containing iron, cobalt, and chromium) that are actually deposited by online methods today.

Obtaining these properties in a CVD process places some restrictions on gas-phase chemical reactions, which can occur at substantial rates under deposition conditions. Reactions that are fast at temperatures over 600 °C but slow at lower temperatures are preferred for CVD because they avoid prereactions. Typically, this means activation energies over 30 kcal/mol but less than about 50 kcal/mol. High activation energies can produce temperature nonuniformities that may produce thickness nonuniformities. In addition, these reactions need to be controllable, meaning that there not be too many branched-chain reactions. Nonbranching chain reactions can give high and controllable reaction rates, while a high degree of chain branching can lead to flames or even explosions. High-speed CVD is also aided by slow homogeneous nucleation of particles in the gas phase, so film growth predominates over particle formation. For example, homogeneous nucleation of silica is fast, which limits the rate at which silica can be deposited, while tin oxide does not readily nucleate in the gas phase and can thus be deposited at relatively high speeds.

Strategies exist for overcoming these obstacles, however. These include:

- Precursor ligands can be chosen so that low-energy decomposition pathways exist. For example, including an ethyl group (C_2H_5) in the compound provides a β-hydrogen elimination pathway that is faster than the reaction when only a methyl (CH_3) group is present.
- Addition of more reactive components to the gas mixture can accelerate the chemistry. For example, silicon dioxide deposition from tetraethoxysilane, $Si(OC_2H_5)_4$, is faster when ozone is added to the reactant gases.
- Moderating agents that slow down gas-phase reactions can also lead to stable film growth. For example, silicon dioxide, which is used to provide a suitable substrate layer for tin oxide deposition, cannot be effectively deposited from silane and oxygen because gas-phase chain reactions lead to uncontrolled (often-explosive) growth of powder. Addition of radical scavengers such as ethylene reduces these rates and allows growth to occur on the surface.

The key to designing high productivity coating processes is to create a knowledge base of precursor properties and their chemical reactions. To obtain this information, experimental and theoretical methods must both be employed to determine the properties of coatings, reactants and byproducts, and chemical reaction rates (Table 2-3). With this knowledge, new precursors can be developed and effective CVD chemistries designed. Precursors with suitable properties must be selected and synthesized, and the chemical species involved in their reactions must be identified. The structures, thermodynamics, and gas transport parameters of these species must be evaluated and the rates of possible chemical reactions determined. Finally, the significant reactions are selected and integrated into a model of reactive gas flow in the CVD equipment.

To date, no existing CVD process meets all the requirements described above. For example, of the five principal chemistries used to deposit tin oxide, none have excellent properties in all

the categories evaluated (17 properties in all, ranging from stability, toxicity, and vapor pressure to cost and coating properties). Tin chloride was rated excellent in all categories except corrosion, uniformity, and byproducts. Only tetramethyltin was rated as excellent in corrosion, but it was found to be unsatisfactory in toxicity. The same holds true for the precursors of coatings of silicon dioxide, titanium nitride, and amorphous aluminum oxide.

Table 2-3. Knowledge base needed to develop high-productivity coating processes.

Coating Properties

- Structure
- Mechanical stability and hardness
- Chemical reactivity
- Optical properties
- Electrical properties

Reactants and byproducts

- Equilibrium vapor pressures for precursors
- Rates of vaporization
- Rates of thermal decomposition
- Thermodynamic properties (heat capacity, enthalpy of formation, entropy)
- Methods for chemical analysis

Deposition kinetics

- Gas-phase reactions
- Surface reactions

These examples underscore the need for a knowledge base that is specific to coatings deposited on glass. To date, most CVD research has been driven by the needs of the semiconductor industry, whose requirements are quite different from those of the float-glass coating industry (Table 2-4). For example, while glass is best coated quickly, semiconductor coatings are best deposited slowly. High temperatures and pressures are good for coating glass but not for semiconductors. Thus, rapid advances in glass coating require research directed toward very different goals than in microelectronics.

Table 2-4. .Comparison of requirements for CVD processes in the semiconductor and float-glass industries.

Requirement	Semiconductor	Float glass
Coating speed	Low	High
Deposition time	Minutes	Seconds
Expensive precursors	Yes, if necessary	Not practical
Deposition temperature	Low preferred	High preferred
Deposition pressure	Low	High (atmospheric)
Plasma activation	Commonly used	Avoided, if possible
Step coverage	Critical	Unimportant
Tolerated defect size	< 0.01 µm	< 100 µm

Surface Chemistry of Commercial Glasses
(Carlo Pantano, Pennsylvania State University)

The condition of the substrate surface has a strong effect upon the formation of any coating, and deposition of coatings on glass is no exception. This was made clear in several examples presented by Prof. Carlo Pantano (Pennsylvania State University, Dept. of Materials Science and Engineering), as well as in numerous comments made during the breakout sessions. Glass is a multicomponent system (see Table 2-5) whose composition varies significantly depending on the application and the process used to manufacture it. Unlike silicon wafers used in the microelectronics industry, glass is also a disordered substrate, having significant molecular heterogeneity both on the surface and in depth. Since it represents a nonequilibrium state of matter, this heterogeneity is affected by changes in processing. For example, variations in glass pull rate used on float lines to change the thickness of the glass can change the reactivity of the surface.

From the point of view of surface topography, glass is a relatively good substrate, since it is atomically smooth and clean (in its initially formed state, at least). However, glass is in its most reactive state when it is clean, as in the case immediately following formation. Changes can occur within hours of its formation, which can result in roughening, formation of new phases, and in-depth hydration. In general, these changes alter the surface reactivity, which can actually be reduced, causing problems for offline coating methods. It is thus clear that knowledge of surface properties and the ability to control them is a critical part of developing an effective coating. Unfortunately, as pointed out in Prof. Pantano's lecture and in the breakout sessions, the surface and surface/coating interfaces are among the least understood aspects of glass science.

The glass surface that exists immediately after formation is highly reactive, particularly toward water. Hydroxylation of the glass surface may occur by at least three mechanisms: 1) chemisorption of water by reactions with dangling silicon cations or Si-O anions; 2) hydrolysis of siloxane linkages (Si-O-Si); or 3) ion exchange at nonbridging oxygen sites. In all three cases, silanol (Si-OH) groups are formed. A fresh glass surface has only a few such groups, as well as characteristic surface channels. As water enters the channels, it reacts to form silanols. Sodium and calcium groups adsorbed to silicon oxides on the surface can break up the glass network and allow water to react, thereby displacing calcium, sodium, and hydroxyl ions. Defects such as Group II elements (Mg, Ca, etc.) can react to form alkaline-earth hydroxides. They can then react with CO_2 to ultimately yield insoluble carbonates. These permanent defects can compromise the mechanical properties of the glass and affect coating. Silanols are also very reactive toward organic compounds, which can physisorb and even condense. Boranols (B-OH) and aluminols (Al-OH) share this reactivity.

It is known that the elemental composition of the glass surface is quite different from the bulk. Thus, in actuality the glass surface is really a layer of varying composition that may range from 10- to 100-µm thick. Species such as calcium and iron are segregated at the surface, often with concentrations from 2 to 3 times higher than in the bulk. Three examples clearly illustrate how processing conditions affect surface composition. In container glass, the high processing temperatures used produce alkali chlorides, which can react with coatings and cause pinhole defects. In the manufacture of fiberglass, flame-attenuated fiber shows greater adsorption of glycine than continuously drawn fiber, indicating that this fiber has substantial Lewis-acid character. Finally, it is well known that the surface of float glass exposed to the tin bath has significant concentrations of adsorbed tin and is thus unusable for many coating applications without modification.

At least four potential solutions exist to the problem of obtaining reproducible surfaces. Etching or cleaning techniques can be used to remove surface deposits. Alternatively, new glass compositions could be developed that are less sensitive to surface contamination. Surface passivation using in situ thermal or chemical treatment may be appropriate for some

applications. Finally, temporary or permanent coatings could be used to passivate the surface. To effect any of these solutions, however, requires a better understanding of reactive sites on multicomponent glasses and how they are affected by process parameters. In addition to information of a fundamental nature, surface-sensitive techniques that can monitor the condition of the glass surface are needed for industrial online monitoring. While it is now possible to characterize glass surfaces with respect to the concentration of terminal hydroxyls and organics, in-depth composition gradients and hydration, overlayer coverage and thickness, and for chemical structure and bonding, few of these methods, if any, are sufficiently robust to be employed routinely in a manufacturing environment. Ultimately, it may be impossible to maintain a pristine, "clean" surface (note that the definition of a "clean" glass surface is not even clear) in a manufacturing environment, mandating that new processes for surface treatment and cleaning be developed.

Table 2-5. Commercial glass compositions.

	Container Glass	Flat "Float"	E-Textile Fiber	Insulation Wool Fiber	Oven Ware USP Type I	Pyrex	TV Funnel	TV Panel	Lead "Crystal" Tableware	Lighting	S Textile Fiber	AR Textile Fiber
SiO_2	72.5	70.7	55.0	57.0	74.0	81.0	54.4	64.0	55.6	77.7	65.0	68.0
B_2O_3			7.0	5.2	11.8	13.0				14.6		
Al_2O_3	1.8	1.3	14.8	8.0	4.7	2.0	1.9	2.0	0.8	2.0	25.0	3.0
CaO	10.0	9.8	20.5	8.1	0.8		2.9					
MgO	0.5	3.5	0.5	4.2			2.0	1.0			10.0	
PbO							24.5	2.1	30.2			
BaO					2.2		0.05	2.0				
SrO							0.05	10.0				
Na_2O	14.5	13.3	1.0	14.5	6.0	4.0	6.5	8.0	8.0	5.4		9.0
K_2O	0.5	0.9	1.0	2.1	0.4		7.5	8.0	3.8			5.0
TiO_2	0.0						0.04	0.4				
ZrO_2	0.0						0.03	2.0				14.0
Fe_2O_3	0.05	0.10	0.08				0.04	0.05		0.05		0.25
Sb_2O_3							0.17	0.41				
SO_3	0.20	0.26										

Characterization of Glass Surfaces, Coatings, and Interfaces (Scott Misture, Alfred University)

To advance the understanding of glass coating and develop new coating processes, researchers must be able to characterize substrate surfaces, interfaces, and coatings, not only in the laboratory, but also online in manufacturing environments. Professor Scott Misture of Alfred University addressed the workshop on the current status of glass surface and thin-film coatings characterization and pointed to some paths for improving X-ray scattering techniques, which show great promise as laboratory and online analytical methods.[1] Although there are

many surface-analytical techniques available, not all are appropriate for analyzing glass surfaces. An ideal method would have several characteristics. First, it should lead to a better understanding of factors affecting the glass surface and any coatings on it. Such factors include thermal history, age, adhesion, organic coupling, and industrial handling. Second, it should be fast and nondestructive. Third, it must have a wide dynamic range of spatial resolutions, from nanometers (for characterizing film structures) to centimeters (for characterizing large substrates). Fourth, it must be adaptable to in situ use under a variety of conditions, such as high-temperature and coating deposition environments. Finally, it should be applicable to as many types of glass as possible, ranging from flat glass to fiber glass.

Many existing surface analytical tools have been applied to glass surfaces, including atomic force microscopy, electron microscopy, infrared spectroscopy, spectroscopic ellipsometry, X-ray and neutron diffraction and reflectivity, and ultrahigh vacuum surface techniques, such as secondary-ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS). In most cases, there have been no attempts to extend these laboratory techniques to online measurements, although all are capable of and have been used to provide real insight into the composition and reactivity of glass surfaces and coatings.

X-ray scattering (XRS), however, stands out as a method that can not only provide useful data concerning a number of important surface parameters, but also one that is currently being used to provide real-time process data in the microelectronics industry. Although processing conditions are quite different in that industry (see discussion of CVD coatings, page 17) the technique does hold promise for glass manufacturing because it does not require a vacuum system. Thus, with the advent of new, compact X-ray sources and improved X-ray optics, synchrotron radiation is no longer necessary, which should allow XRS to be applied to a range of glass manufacturing environments, from float-glass lines operating at atmospheric pressure, to subatmospheric sputtering chambers.

Traditionally considered bulk probes, XRS methods are surface sensitive when the sample surface is aligned at grazing angles (0.2–5 degrees) to the X-ray beam. In these cases, beam penetration depth is a strong function of the grazing angle, photon energy, and the chemistry and physical density of the sample. Penetration depths can thus range from several nanometers to tens of microns. Grazing incidence XRS techniques are rapidly evolving into powerful nondestructive surface characterization tools in the semiconductor industry, which uses thin films extensively. X-ray reflectometry is probably the technique most useful for characterizing coatings, because the thickness of each layer in multilayer coating, its density or density gradient, the top surface roughness, and the interface roughness can all be determined from a single measurement. More detailed information concerning roughness (required for full fractal models and correlation lengths, as well as characterization of graded interfaces), can be obtained from analyzing diffuse reflectance data, although this is more difficult.

An example of the data obtained from a reflectometry measurement is shown in Figure 2-8 for a ZnO coating. By fitting the reflection data to a model of the scattering process, one can obtain coating thickness, surface roughness, and density. Both measurement and analysis are fast and relatively simple. Coating stacks with as many as five layers can be characterized in this manner (Figure 2-9). In addition to post–deposition characterization of coatings, XRS can be used to evaluate the cleanliness of the substrate prior to coating. Comparisons of scattering curves for uncleaned, chemically cleaned, and plasma-etched glass clearly show differences that can be attributed to thickness, roughness, and density of the surface layer (Figure 2-10).

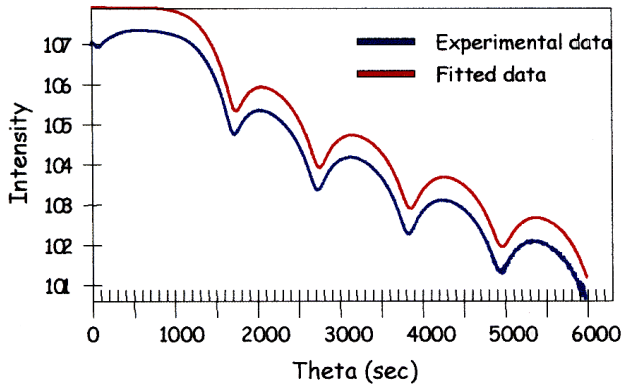

Figure 2-8. Specular X-ray scattering data for a ZnO coating. Data on coating thickness (135 Å in this case) surface roughness (9 Å) and density (5.87 g/cm^3) can be obtained from this measurement.

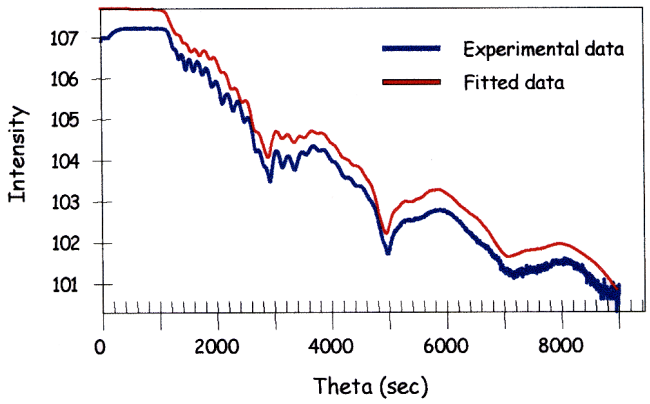

Figure 2-9. X-ray scattering data for a four-layer (ZnO/Ag/Ti/ZnO) coating. Data on coating thickness, roughness, and density of each layer can be obtained from this measurement.

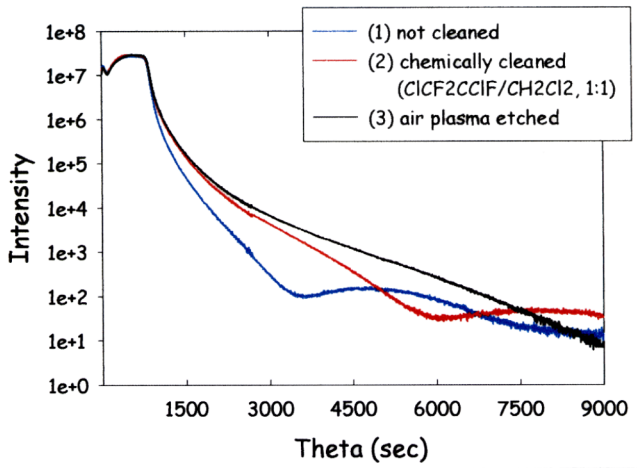

Figure 2-10. X-ray scattering data comparing uncleaned, chemically cleaned, and plasma-etched glass.

Current state-of-the-art laboratory instruments employ multilayer optics and asymmetric crystals or polycapillary optics to give large intensity gains without degrading resolution. These instruments capture a large solid angle of divergent photons from the X-ray source and either collimate the divergent beam or focus it onto the sample. Since the resolution of most of the X-ray techniques improves when a collimated beam is used, most of the next-generation laboratory instruments will employ parallel-beam optics. Coupling parallel-beam collimating optics with asymmetric channel-cut monochromator crystals will provide immense improvements in resolution. For example, in one of Alfred University's multioptic X-ray scattering instruments used to gather specular reflectivity data for coated glass, an improvement of two orders of magnitude in the dynamic range was achieved when multilayer optics were used in the incident and scattered beams instead of a traditional optical arrangement.

With these experimental advances, coupled with increasingly sophisticated computational models, it should be possible to make major strides in the application of XRS to glass surfaces and coatings. In the short term, existing techniques will yield information concerning the origin of defects, providing insight into the underlying causes for "good" and "poor" coating properties. An improved understanding of unintentional surface modifiers, such as organic and other adsorbates that result from handling, should also result. Over the long term, improved and new tools should result in the direct detection of potential defects before processing, direct design of surface coupling agents, and ultimately, high-speed online process monitoring.

References

1. S. T. Misture "X-Ray Scattering Used to Characterize Surfaces and Thin Films," *The Glass Researcher* **1999**, *9*, 5.

Theoretical Approaches to Modeling Glass Coatings and Interfaces (Michael Teter, Cornell University)

The previous three sections indicate that the advancement of coating technology for the glass industry is intimately connected to achieving a better understanding of the interactions between coating materials (both the coatings themselves and the precursors used to make them) and the glass substrate. Complex material and process dependent phenomena control the reactivity of the glass surface. Poorly characterized chemical reactions between precursors and substrates affect the composition, crystalline phase, microstructure, and mechanical, optical, and electrical properties of coatings. Furthermore, the relationship between the molecular, micro, and mesostructures of coatings and the properties important to the coating user (optical absorption properties, electrical resistivity, and adhesion) is unclear. Although extensive experimentation is definitely needed to shed light in these areas, it is clear that adequate time and resources are not available to make rapid progress.

Furthermore, there is a critical need to rapidly screen potential materials for new coatings and determine their properties. Experimental methods for doing this are, at present, extremely time-consuming and expensive. The design of a new coating process often begins with scientific intuition and is followed by extensive experimentation; development times of 10 years or more are not unusual. Thus, new coatings are often derivatives of existing ones, since the range of potential materials is so large. Naturally, this path can miss many promising materials. A new approach is needed that can provide at least a qualitative indication of a given (uncharacterized) material's properties, so that a wider range of possibilities can be accessed, and the number of experiments required to reach key go/no-go decision points can be reduced.

The lecture presented by Prof. Michael Teter illustrated the potential that a new generation of computational tools has to address many issues relevant to coating science and engineering. The methods with the most promise are based on density functional theory (DFT), an approach to predicting the interactions between electrons in solids developed more than 30 years ago by Walter Cohn, recipient of the Nobel Prize in chemistry in 1998. In contrast with so-called "all-electron" methods, in which the Schrödinger equation is solved, for a molecule, the new methods treat solids or surfaces as periodic slabs rather than large molecules. They also use pseudopotentials to simulate the wavefunctions associated with the most tightly bound electrons, which are the most difficult to model, but are also uninvolved in the chemical bonding. As a result, using commonly available desktop computers (such as SGI workstations), materials with up to 100 atoms in the unit cell are accessible to DFT methods. In contrast, all-electron codes can typically treat no more than 20 atoms and are thus forced to simulate solids as clusters.

DFT and the associated techniques for describing extended surfaces and solids are now capable of predicting many properties of materials with good to excellent accuracy. Properties that are accessible to prediction include crystal structures, vibrational frequencies, thermochemistry (e.g., adsorption energies), defects, optical properties, and chemical reactions. For example, Table 2-6 lists the advertised capabilities of the CASTEP code, a commercially available DFT code available from Molecular Simulations Inc. An example of the accuracy of such codes relevant to modeling glass is given in Table 2-7, and rutile.[1] Other examples in which DFT codes have been used to predict properties of materials related to glass include: predictions of silver adhesion to magnesium oxide surfaces;[2] effects of defects on the electrical and optical properties of silica;[3] and predictions of band gaps and optical spectra of tin oxide,[4,5] indium tin oxide,[6] and zinc oxide.[4]

Table 2-6. Selected capabilities of the CASTEP DFT code.

Structural properties Crystal structures (packing) Density Defect structures Surface structures Interface structures	**Thermodynamic properties** ΔU, ΔH, ΔS, ΔG, C_p, C_v Binding energies Surface and interface energies (a measure of adhesion) Phase diagrams
Mechanical properties Compressibility Elastic moduli Thermal expansion coefficients Vibrational frequencies	**Electrical, optical, and magnetic properties** Energy band structure Band gaps Optical spectra Electrical moments Dielectric response

Table 2-7. Comparison between theory and experiment for lattice parameters of various oxides.

Material	**Lattice parameters**	**Theory (nm)**	**Experiment (nm)**	**Δ (%)**
α–cristobalite	a	0.495	0.49570	0.04
	c	0.6906	0.68903	0.23
α–quartz	a	0.4880	0.49134	-0.68
	c	0.5370	0.54052	-0.65
Rutile (TiO_2)	a	0.4584	0.4594	-0.22
	c	0.2961	0.2958	0.10

DFT codes are now commercially available and can be purchased or licensed from several vendors. “Share-ware” codes exist as well. The code one chooses depends upon the nature of the problem of interest, as well as financial resources (since the commercial codes can be quite expensive). Some of the codes now available are listed in Table 2-8. Briefly, CASTEP (for Cambride Serial Total Energy Package) is a commercially available code with wide capabilities. Originally written by M. C. Payne of Cambridge University, it is now marketed by Molecular Simulations Inc. (San Diego, CA). It employs a sophisticated graphical user interface, allowing 3D visualization of model systems. The code was optimized for speed and thus sacrifices some accuracy. The PlaneWave code was develop to provide high accuracy and thus provide a reference against which other codes can be benchmarked. It thus sacrifices speed for accuracy, but in general reproduces predictions of all-electron codes with high fidelity. The VASP code was developed by Jürgen Hafner and is very fast and accurate. It uses Vanderbilt ultrasoft psuedopotentials that are quite acceptable for normal (i.e., not very high-pressure) chemistry. It is available under license from Hafner for a fee and an agreement to add his name to the first publication that uses code results. Finally, ABINIT represents an extension of the PlaneWave code and is nearly as fast as VASP. It uses pseudopotentials that are more transferable. It also has a built-in ability to calculate response functions, so that prediction of phonons or dielectric response (i.e., optical spectra) is routine. This code is free and available over the Internet along with compiled code for common platforms.

Table 2-8. Summary of available DFT codes.

Code Name	Authors	Comments
CASTEP	M. C. Payne	Commercially available; extensive graphics; optimized for speed.
PlaneWave	M. P. Teter and D. C. Allan	Reference code; speed sacrificed for accuracy.
ABINIT	X. Gonze	Facile calculation of phonons or dielectric response. Available free over the Internet.
VASP	J. Hafner	Very fast and accurate. Available under license for a fee.

In summary, DFT codes are at the point where they can be readily applied to problems relevant to the coating of glass. At the present time, all codes that are available should be considered "expert" systems, in that substantial knowledge of solid-state physics/chemistry is needed to achieve meaningful results. However, the interfaces between these codes and the user have improved dramatically, and speeds/accuracy/robustness are now at much higher levels than they have been in the past. It is thus feasible to apply DFT to relatively large-scale systems (up to 100 atoms/unit cell) using commonly available computer technology. These methods hold great promise for addressing complex issues related to glass coating that have been difficult or impossible to solve in the past but that are essential for the development of next-generation materials.

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3. Flat Glass Breakout Group

Performance Targets

The flat glass breakout group organized its performance targets into four general categories: Economics / Market share; Material Performance; New Products; and Customer Needs. Many targets are viewed as ongoing activities because of their technical complexity and the lack of understanding of the underlying problems. The primary targets identified are summarized in Table 3-1.

Economics/Market Share

A major goal in this sector is to increase the market share of coated glass by over 50% within 10 years. For low-E glass in architectural applications, saturation probably means 50% at the present time, since only one of the two pieces of glass in a dual-pane window is coated. However, additional coatings that can provide functions other than solar rejection or control of emissivity (e.g., self-cleaning, electrochromic, or other "smart" window technology) could increase this percentage. A related objective is to reduce the cost and increase the ease of handling to the point where coated glass is comparable to that of uncoated glass. Currently, coated glass requires special handling because coating materials are not sufficiently scratch resistant. Losses in the bending process as well as scratch losses can increase the price of coated automotive glass by as much as 10%, which limits the use of these materials.

A second goal, one that was also identified by the Specialty Coatings group, is to greatly reduce the manufacturing cost of electrochromic glass. Prices currently range from $\$1000/m^2$ to $\$100/m^2$, which is considerably higher than typical low-E glass. Significant reductions in manufacturing cost for the major coated flat-glass product, low-E glass, are unlikely, however. Manufacturing of these materials is fairly mature, at least for the most widely used materials (tin oxide and silver); so it is hard to further reduce the cost of coating.

It is also desirable to improve the economics of using solar-controlled glass in automotive markets. Automotive glass and architectural glass are the two largest markets for flat glass. In addition to esthetic considerations (i.e., the trend toward increasing amounts of glass in automobiles), vehicle heat loads must be reduced to accommodate the smaller climate-control systems needed to further reduce vehicle weight and increase fuel economy. Thus, development of economical solar control coatings may be essential for achieving high-mpg vehicles. Tinting the glass using iron oxide cannot be used to further reduce heat loads, since addition of higher amounts of the iron oxide colorant reduces the visible transmittance to less than the minimum 70% required for vehicles.

Material Performance

Some of the factors that limit the market share for coated glass are directly linked to its performance and properties relative to uncoated glass. Several performance objectives were identified. First, it is necessary to achieve consistency in product quality by reducing variations in the optical properties of low-E and solar-control glass that can occur over time on a given coating production line. Second, storage time and durability must be increased to allow facile storage for three months for both coated glass and assembled dual-pane windows (also known as integrated glass units, or IGUs). Existing offline coating materials, such as silver multilayers, cannot be exposed to air or water without serious degradation. Leakage in an IGU thus leads to nonuniformities in coating optical properties. Third, reducing the cost and ease of handling coated glass is also a performance target here, since these factors are clearly related to the properties (e.g., scratch resistance) of the coatings.

There is also a desire to optimize coatings and their manufacturing processes to minimize environmental impact over the life of product. Examples include: increasing deposition efficiency to minimize effluent; recycling unreacted vapors; using reactants that do not contain chlorine; and developing coatings that do not adversely affect glass properties if they are recycled as cullet in a float-glass operation. Existing sputtered coatings cannot be used as cullet, which inhibits post-consumer recycling.

Table 3-1. Performance targets for coatings on flat glass.

Economics/Market Share Increase market share of coated glass to over 50% within 10 years. Greatly reduce the cost of manufacturing electrochromic glass. Improve economics of solar-controlled glass in automotive markets.	**New Products** Develop novel coatings and materials with unique features. Increase the range of materials available to designers. Develop self-cleaning (or stay-clean) surfaces.
Material Performance Achieve consistency in optical quality over time. Increase storage time and durability of sputtered coatings & total product. Bring cost and ease of handling of coated glass to be comparable to uncoated glass. Optimize coatings to minimize lifecycle environment impact.	**Customer Needs** Increase understanding of end-user needs. Simplify performance information for consumers.

New Products

Clearly, the development of new products is key to the survival and well being of any industry. In the case of flat glass, the industry has been extremely successful in exploiting technologies that are now relatively mature (for example, the earliest online processes for coating float glass were patented in the mid 1970s). Today, however, there is a clear need to advance beyond these older technologies to meet demands that are now on the horizon, e.g., the

need to reduce emissions of greenhouse gases by improving the efficiency of energy utilization. Since glass is found in virtually every building in the nation as well as every automobile, it is clear that developing manufacturing processes that can produce more energy-efficient materials can have a major impact on the energy economy of the U.S. Below are listed three performance targets, in order of decreasing priority, for the development of new materials:

1. Develop new coatings and materials with unique features. The industry must advance beyond the standard materials (silver and tin oxide) currently used for low-E and solar-control window glass. Novel materials with the following properties are needed: coatings with the durability of CVD (pyrolytic) coatings but with the energy efficiency of sputtered silver; coatings that redirect light; holographic coatings; coatings to inhibit electronic communication or enhance it.

2. Increase the range of coated glass that can be used in automotive applications. In particular, bendable coatings that can be used as automotive windscreens and low-cost, durable solar-control glass to reduce the heat load in vehicles are necessary to reach performance targets for high-fuel-efficiency vehicles. Because of the many design constraints on vehicles, however, successful materials must be low cost, easy to handle, and durable.
3. Develop self-cleaning (or stay-clean) surfaces. Such materials have potential applications not only for architectural and automotive applications, but also for use in hospitals and other environments where maintaining cleanliness or sterility is important.

Customer Needs

The definition of customer for purposes of this discussion includes not only the consumer, but also original equipment manufacturers. Examples include window and automobile manufacturers, suppliers (e.g., distributors, hardware stores), and users/installers (e.g. contractors). The group identified two targets for improvement with respect to customer needs:

First, the industry must increase its understanding of end-user needs. In general, the highest concern of end users appears to be the handling and durability of coated glass, which, as pointed out in previous sections, is not yet comparable to uncoated glass. This factor contributes to a substantial increase in the final cost of coated products, to which the cost of the coating itself is not really a factor (cents/ft^2). Coated glass impacts distributors and end users through increased packaging costs; limited shelf life of IGUs; higher susceptibility to damage, scratching, etc.; increased bending costs; increased expertise/complexity in downstream handling; and the lack of coated replacement glass stocked at local hardware stores.

The second target is to simplify coated-glass performance information for consumers so they can more easily make educated choices among available products. Customers need an easy way to evaluate window performance with respect to energy efficiency, solar rejection, shading, color, etc. It was suggested that performance standards analogous to those supplied with refrigerators need to be developed (see for example the Efficient Windows Collaborative web site at www.efficientwindows.org).

Technology Barriers

The flat glass breakout group identified many technical barriers inhibiting the industry from reaching the performance targets just described. These range from very fundamental issues concerning the science of coating glass to institutional and educational issues involving companies and their customers. The large number identified may seem surprising given the relative maturity of the products produced. However, the number of barriers also indicates that the industry is facing major challenges in developing the next generation of coatings, which must perform better in all respects than existing ones while also being considerably cheaper in many instances. The diversity of barriers also reflects the diversity of the industry, which serves customers including window manufacturers, automobile companies, and the computer industry. In all respects, however, the breakout discussions reflected the increasing sophistication of the flat-glass industry as well as its direct customers and end users. Technical barriers are summarized in Table 3-2.

Coating Materials

A number of technical barriers inhibit the development of new coating materials as well as the improvement and wider use of existing ones. They include barriers connected with the properties of the coating material itself, barriers associated with its deposition (e.g., lack of economical CVD precursors), and lack of materials that can perform a specific function. Barriers identified as the most critical to surmount were categorized in this section:

- Lack of durability in active and passive coatings. Coatings on glass typically have poor scratch, oxidation, and hydrolysis resistance, requiring them to be protected in some way (lamination, location on inboard side of glass, secondary protective coatings, etc.). This adds steps to the manufacturing process and increases costs. It also raises the costs of end users, which must implement special storage, packaging, and handling procedures for coated glass.
- Lack of precursor materials (in particular, CVD precursors) with appropriate properties**.** For many materials, the choice of precursors available to use in a CVD process is limited to one or two, and these often do not have the properties of an ideal source material (high volatility, low toxicity, low cost, etc.). This barrier is second only to the previous one in its level of priority.
- High cost of film precursors. Often, the best choice for a CVD precursor is an organometallic compound, since these more often have the required volatility than corresponding halide compounds. Unfortunately, long development times and poor overall yields for the processes used to synthesize these compounds make many of them quite expensive. The cost of high-purity metals used in sputtering processes is also a barrier.
- Lack of transparent barrier to water and oxygen to protect a monolithic electrochromic product. A major reason for the high cost of electrochromics is the need to use two pieces of coated glass. If protective coatings existed, this could be eliminated.
- Relatively poor quality of online CVD coatings. The low-E and solar-control properties of materials deposited by online (typically CVD) methods need to reach the levels achieved in sputtered materials and continue to be recyclable.

In general, the ability to recycle and dispose of most coating materials was not viewed as a serious environmental problem. One reason for this view is that toxic coating materials simply would not be of interest (the industry wouldn't consider sputtering lead oxide, for example). An exception to this is CdTe, which is used for solar cells. However, electrochromic materials may be more of a problem, since these may make use of some potentially hazardous compounds.

Table 3-2. Technical barriers to achieving performance targets for coating of flat glass.

Process Control	Modeling	Institutional Issues
Lack of online process control and poor understanding of how to automate the coating process. ●●●●●●	Lack of computational tools and understanding to predict film properties. ●●●●●●●	Too much focus on technology-driven solutions rather than market-driven solutions.
Lack of measurement tools to characterize the state of the glass substrate. ●	Lack of reliable, user-friendly predictive models for use in process control. ✪●●	Very competitive and secretive community.
Need better measurement systems for quality control. ●	Don't fully understand the underlying fundamentals of material prediction. ●	Lack of outside manufacturer of CVD equipment.
Poor understanding of defects and their level of criticality.		

Coating Materials	Downstream Processing	Industry Product Standards
Lack of durability of active & passive coatings. ✪✪✪✪●●	Supply chain issues - number of handlers affects cost & quality. ●	Lack of an industry standard to define "color neutral". ●●
Lack of precursor materials (especially for CVD). ✪✪✪✪	Lack of understanding of the effects of subsequent manufacturing processes & environmental exposure on coatings. ●	Need to define "clean" glass. ●●
Cost-effective source material (needed in unique formats) difficult to obtain. ●●		
Lack of transparent barrier to water & O_2 to protect monolithic electrochromic products. ●●		
Poor quality of CVD coatings. Non-metallic materials when deposited need to have optical properties comparable to sputtered materials (e.q. silver) and be recylable.		

Legend

✪ =Top Priority ●= High Priority

Table 3-2. Technical barriers to achieving performance targets for coating of flat glass. (continued)

End User Education	Coating Process Capability	Fundamental Understanding
Poor end-user education inhibits intelligent choices. ✪●●●●●●●	Process limitations, yields not as good as they need to be. Effective use of all materials for maximum yield + high uptime required. ●●●	Lack of diverse material knowledge. ●●●●
Explain benefits of coated glass better. Quantitative data on glazing benefits required. No comprehendible standards for consumers to use in judging coating performance. ●●	Limitations in technologies for coating large surfaces with uniformity. ●	Limitations of tools to analyze microstructure of very thin films. ●●●
Lack of effective life cycle cost analysis. Too much focus on initial product cost	Need to improve deposition efficiency. ✪	Lack of understanding of CVD reactions. ●●
	Consistency in sputtering technology.	Lack of technical understanding of optical defects.

Manufacturing New Products
Large cost & risk of development for new coating processes: – No good small-scale screening tools. – Loss of production during online testing. – Focus on production, not testing, etc. ●●●
Manufacturing costs too high.
High impact of coatings on base-glass processing
Manufacturing complexity adds risk & costs.

Legend
✪ =Top Priority ●= High Priority

Modeling (Includes materials design, process simulation, and prediction of materials properties)

The barriers described in this section include not only traditional process modeling but also design of materials and prediction of materials properties. It was recognized by the discussion group that modeling must play a much greater role than it has because of the practical limitations on time and capital resources available for experimental investigations. Sophisticated models must be developed and used to narrow the scope of experiments and provide insight into the effects of processing variables on material properties. Barriers identified in this category area were:

- Lack of computational tools (and understanding) needed to predict film properties. Sophisticated codes exist, but they must be benchmarked to determine their effectiveness. The industry has little experience with these tools. Surmounting this barrier is viewed as a very high priority.
- Lack of reliable, user-friendly predictive models for use in process control. The emphasis here is on process models. Currently, there is little or no connection between process models and online process control because of a lack of control algorithms based on sophisticated process models.
- The fundamental process for material prediction is not well understood. It is very difficult to define a set of performance characteristics for a coating and then develop a completely new material that has those properties (a field now being defined as “design of materials”). How does one get from defining the properties of a desired material to designing a new material that has those properties? The industry is reaching the limits of existing codes, which use nineteenth-century physics and are predicated on ideal materials (no defects, bulk properties, and no impurities). New codes are needed that can deal with real-world materials.

Fundamental Understanding of Coating Processes of All Types

Fundamental science will play a very important role in determining what new products are developed in this segment of the industry and the extent to which performance characteristics can be improved relative to present-day products. Lack of knowledge in areas of physical and inorganic chemistry, solid-state physics, experimental techniques, and computational modeling are all factors inhibiting the advancement of coating manufacturing. The barriers identified are briefly summarized below:

- Lack of diverse material knowledge. More information concerning properties of materials (optical, electronic, mechanical, and magnetic) is needed to design new coatings. Removing this barrier is a relatively high priority.

- Limitations of tools to analyze microstructure of very thin films. Sputtered films can be as thin as 100 Å (typically silver). Models used to design multilayer coating structures indicate that thickness sometimes must be controlled to within 2%; however, it is not clear what this physically means, since 2 Å is essentially a monolayer of material. In addition, at present there is no way to know whether the substrate surface is contaminated. The industry is pushing the limits of existing analytical techniques with such thin films. Both improved models for very thin films and new analytical techniques of characterizing them are needed.
- Lack of understanding of CVD reactions (both in the gas phase and on the surface). This is the major reason for the difficulty in scaling CVD processes from the laboratory to manufacturing.
- Lack of technical understanding of optical defects. What causes them, what are their effects, how can they be eliminated?

Process Control

- Lack of online process control. "Push-button" operation desirable, if possible, to reduce the frequency of errors and increase productivity. In general, however, the understanding of how to automate a given coating process is too poor to even approach this. This is a high-priority barrier.
- Lack of measurement tools to characterize both the glass substrate prior to deposition and the coating itself following deposition.
- Better measurement systems are needed for quality control.
- Defect-detection capabilities are needed to assess the criticality of defects. Defects can go undetected until, for example, an electrochromic coating is deposited on top of the coating, at which point it is too late to fix the problem. Defect-detection capabilities or improvements in process technologies are needed to eliminate or reduce the number of defects.

Coating Process Capability

The focus in this section is on existing manufacturing technologies, principally CVD and sputtering.

- Process yields and flexibility are not as good as they need to be. Manufacturers want to make more effective use of all reactants to maximize yield and maintain equipment productivity.
- Limitations in technologies for coating large surfaces with high uniformity. Some models specify ± 2% uniformity in coating thickness, which can be very difficult to achieve over sheets of glass several square meters in size.
- Sputtering and CVD deposition efficiency need to improve. In sputtering processes, this means more atoms deposited in the film per unit power on the target. In CVD processes, it equates to improved utilization of (probably expensive) precursors.
- Lack of consistency in product characteristics produced by sputtering. Run-to-run and manufacturer-to-manufacturer variability for a given materials leads to variations in optical properties that may make it difficult to, for example, match existing glass qualities when repairs/replacement must be made.

Downstream Processing

These topics are related to post processing by original equipment manufacturers, end users, etc.

- The large number of handlers in the supply chain affects both cost and quality, and increases the likelihood that coatings will become damaged.

- Lack of understanding of subsequent manufacturing processes (e.g., glass bending or tempering) and their effect on coating properties, as well as effects of exposing coating to the environment. For example, a coating may be pristine when it emerges from the float bath, but what happens when it is exposed to air?

Manufacturing New Products

Management barriers to developing new coatings and processes are listed below. The next generation of products will almost certainly use more complex materials, multilayers, etc. Processing technologies must advance ahead of this development if these materials are to be produced economically. Historically, development times for new materials processes have been in the 10–15 year range. Severe downsizing of industrial technical organizations will make it very hard to do this in the future.

- Large cost and risk of developing new coatings. The lack of good, small-scale screening tools (both pilot-scale experimental facilities and theoretical tools) means that production time will be lost in order to scale-up experiments. This amounts to thousands of dollars per day in lost production during testing of a coating process on a manufacturing line.
- The impact on the base glass process leads to a conflict between those involved in coating development and manufacturing personnel, whose focus is on plant productivity.
- Manufacturing costs for new materials are too high. The required capital investment is very large (multimillion-dollar machines), requiring large, high-volume markets. Niche markets are not an economical target for a float line or large-scale vacuum deposition facility.
- The complexity of coating manufacturing operations adds risk and cost.

Industry Product Standards

Barriers listed below include both measured values and the measurement techniques themselves.

- No industry standard for “color neutral”. Lack of this standard is a barrier to replacement and retrofitting of architectural glass.
- The definition of “clean” glass, i.e., the optimal condition for deposition of a given material, is unclear.

Institutional Issues

- Too much focus on technology-driven solutions rather than market-driven solutions.
- Highly competitive and secretive community. The flat-glass industry is composed of a small number of players that compete vigorously. Individual efforts by companies hamper progress of the overall industry, since little of this information makes its way to the broader manufacturing community.
- Lack of an outside manufacturer of CVD equipment, as in the case of sputtering equipment. A supplier of this equipment is needed to amortize development costs over entire industry rather than having all development done in-house.

End-User Education

In general, the industry needs to increase its efforts to educate the consumer with regard to the benefits associated with coated glass, which include factors such as greater interior comfort, reduction of drafts, reduced fading of fabrics, as well as the more obvious ones associated with reduced energy usage. Even with respect to the improved insulating properties associated with glass, it is clear that the consumer needs more information to make intelligent choices. Barriers identified in this category are listed below:

- Poor end-user education inhibits intelligent choices. The industry needs to better define and explain the benefits of coated glass, then translate them into information that decision makers (consumers, architects, builders) can use. This is viewed as a very-high-priority barrier.
- The consumer lacks clearly understandable standards that can be used to judge the performance of a given coating.
- Lack of effective life cycle cost analysis. Too much emphasis by decision makers on initial cost of product without looking at downstream savings due to better energy usage.

Research Needs

Research needs in the flat-glass segment of the industry are numerous and diverse. Topics requiring work range from fundamental issues to institutional problems. The needs identified were divided into seven separate areas, with the "Fundamental Understanding" area subdivided into Theoretical and Experimental needs. Most of the highest-priority needs fell into the area of Fundamental Understanding, which includes seven of the highest priority needs. Coating Materials, Process Control, and Process Development each include one high-priority research need.

The primary concern in the fundamental area is the lack of understanding of the properties of very thin layers (< 100 Å thick), which are becoming increasingly commonplace. The difficulty in understanding how the composition and microstructure of such layers affect their optical, electrical, and mechanical properties is a major impediment to the development of new coating processes. In addition, the rates of reactions used to deposit thin films are poorly understood, which greatly complicates the scaleup of laboratory processes to a full manufacturing capability. Finally, most analytical tools were not developed with the analysis of very thin films in mind. Consequently, there are major needs for research in the experimental, theoretical / modeling, and analytical areas. It should be noted that, although a great deal of this work falls into the mid- to long-term time frames, several important needs were felt to be attainable in the near term (0–5 years).

High priorities outside of Fundamental Understanding include the need for improved online monitoring techniques for detection of coating defects. In the Process Development area, the need for a pilot-scale facility for testing new coating materials and processes is a high priority. Finally, the need to establish a rapid screening method for evaluating the potential of new coating materials was given high priority in the Coating Materials area.

Each of the research needs identified is listed below with some brief clarifying comments. These are also listed in Table 3-3, which includes the level of prioritization received by each need.

Fundamental Understanding

Theoretical Needs

- Benchmark available computer programs on known materials (before creating new ones). Sophisticated first-principles codes are now available to predict, for example, the optical properties of films, stability of interfaces, etc. These have not been thoroughly tested on materials well known to the glass industry (e.g., tin oxide or silver). The performance of these codes needs to be tested to establish their accuracy and usefulness.
- Perform a critical assessment of what we know about CVD reactions**.** What is good science; what's junk? By analogy with the fields of atmospheric chemistry and combustion, evaluate the available literature, select best values, and compile a database.
- Obtain a basic understanding of the factors controlling the volatility of a material and how to control it. This information is key to developing new CVD precursors.

- Develop an understanding of the factors controlling the optical and mechanical properties of very thin layers**.** Existing coating-design codes sometimes predict the need for films with thicknesses ≤ 100 Å with high tolerances (± 1% is equivalent to about one atomic layer, requiring virtually atomic-level control over the deposition process.) Films with a thickness of 20 Å occur in many real-world cases. At this point, there is a significant conflict between models based on continuous bulk films and the real-world films.
- Develop second-generation optical models that relate the microstructure of multilayer films to detailed optical properties**.** If more were known about the microstructure of thin films, then a "second-generation" model could be developed that would incorporate the microstructure into the coating design. Relating film microstructure to optical properties would allow the design of coatings based upon more realistic operating parameters.
- Develop improved optical models that can handle nonideal (i.e., real-world) films**.** Most commercial optical modeling programs come out of the geometric optics world and deal with either nonabsorbing films or with completely reflecting films (i.e., lenses or laser mirrors). These codes usually assume pure, bulk, defect-free materials and were not designed to deal with coatings on glass, where films are multilayer, both absorbing and nonabsorbing, have multiple surface reflections (the front and back side of glass must be taken into account), and multiple substrates (the effects of laminating a coated glass are becoming increasingly important for architectural and automotive applications). Existing codes have been tested against standard products and do not accurately predict optical performance of multilayer films that include absorbing materials (such as silver). Few, if any, commercially available programs can handle combinations of multiple substrates, as in the case of laminated products. An ability to handle interfaces, graded indices, etc. is probably needed to model actual performance. The dependence of optical properties on actual deposition conditions is a severe constraint; optical properties are often determined by the nucleation modes of the film, which are very different from bulk properties.
- Understand the deposition process (both CVD and sputtering); in particular, how does the substrate affect the properties of the resulting film?
- Improve understanding of the physical properties of thin films. More knowledge of the factors controlling mechanical/chemical abrasion and deterioration is needed, so that novel coating designs can be developed (e.g., softer undercoat with a harder, abrasion-resistant, overcoat).
- Develop models that perform simulations over multiple length scales. Process parameters affect microstructure (for example, surface roughness, grain size/orientation, etc.) in ways that affect final macroscopic film properties (absorption, durability, etc.). Thus, models connecting either the molecular or macroscopic scales with the meso- or microscale are required to design better materials and understand their performance.

Experimental

- Measurements of the rates of chemical reactions important in CVD are needed to improve process models and better understanding of scaling issues.
- The effects of thermal cycling on thin films need to be better understood. For example, annealing and tempering operations can affect film properties.
- Chemical interfaces must be better characterized and modeled, so that rates of chemical reactions on these surfaces can be determined. The history of the glass substrate affects chemical reactions involved in deposition of coatings on the surface. An improved understanding of how surface cleanliness affects reaction rates and how to modify the surface is desirable.

Process Control

The following are research needs in process control (Table 3-4):

- Tools for online monitoring of coating defects (size and density).
- Chemical sensors to detect and monitor precursor and effluent concentrations.
- Rugged online sensors for monitoring optical and electrical properties of films.
- Techniques to perform online measurement of surface cleanliness.
- Cognitive algorithms for process controls. “Smart” algorithms that can control a number of process parameters simultaneously to achieve better film quality would simplify operation of the coating process.
- Process controls that take advantage of recent advances in process modeling, sensor hardware, and control theory. Create synergies by combining these three technologies.
- Need inexpensive online measurement of optical absorption properties to 0.1–0.2% absolute.

Table 3-3. Research needs for fundamental understanding of flat glass coating.

	Theoretical	**Experimental**
Near Term < 3 years	Benchmark available computer programs on known materials. ●●○	Measure speed of reactions important to CVD. ✪●○○
	Perform Chemistry CVD reaction – Critical Assessment. ●●●○	Understand compatibility of thin films with thermal cycling (annealing, tempering). ○○○○
Mid-Term 3-10 years	Basic understanding of material volatility ⇒ How to control it. ○	Characterization and modeling of chemical interfaces and effects on deposition kinetics.
	Develop understanding of optical & mechanical properties of very thin layers. ✪✪●○○	
	Second generation of optical models that relate microstructure of multilayer films to detailed optical properties. ✪●○○	
	Improved optical models that handle real-world, nonideal films. ✪✪✪✪○○○	
	Need fundamental understanding of the effects of substrats on film properties. ✪✪●	
	Develop better understanding of physical properties of thin films:Mechanical/chemical abrasion & deterioration. ✪○○	
Long Term > 10 years	Multiscale/multipurpose (including meso scale models to design new matls and understand performance. ✪	

Legend

✪ =Top Priority ●= High Priority ○=Medium Priority

Analytic and Testing Tools (Table 3-4)

- Examine existing analytical technologies and optimize them for thin-film coatings on glass. Extend these technologies to perform multidimensional analyses (i.e., analyze more than one film property at a time). Most analytical tools were not optimized for the examination of very thin films, in range of 20–400 Å. Substrates are often very thick relative to the coating, making samples difficult to handle.
- Develop analytical and modeling tools for determining coating durability then standardize these methods. There is a need to be able to infer at least the qualitative performance of a coating from basic materials properties (stress, indentation hardness, scratch resistance, etc), without having to resort to extensive wear or aging tests.
- Develop modeling tools that can simulate the effects of downstream processing (i.e., post manufacturing of the coated glass) on coating properties. In particular, address forming, bending, and annealing operations.
- Develop coating service-life models based on a standardized durability test. There are no industry-agreed-on standard test methods to compare or evaluate the durability of coated products and their expected lifetimes. Although there are a variety of tests available, such as accelerated weathering and laboratory solar simulation, no standardized models exist for predicting the lifetime of new coatings. Current durability tests are better at making relative comparisons between films than they are at predicting service life.
- Develop improved analytical tools for very thin films (50 Å) deposited by sputtering.

Coating Materials (Table 3-4)

- Benchmark high-performance coatings for aerospace applications (primarily windshields), particularly for durability.
- Develop a small-scale method for rapid screening of potential new coating materials. (Doesn't have to be a CVD-based method).
- Communicate needs/requirements for new materials and precursors to synthetic inorganic chemists.
- Explore new materials that haven't been used to date as thin films on glass. Ideally, examine materials that are already available and are inexpensive.

Process Development (Table 3-4)

- Design and construct an industrial pilot-scale facility to test and evaluate materials and coatings.
- Improve fluid-dynamic modeling tools to control gas-flow uniformity over large areas.
- Create a "virtual coating laboratory" that can be use to relate materials and process variables to optical and other properties. Get theory to the point that it can be used to design coatings with a minimum of experimental work. Develop a simulation capability that can relate process variables to the properties of individual materials and the final combined film stack.
- Develop new or improved ways of cleaning glass.
- Explore the possibility of modifying the glass surface to change its properties rather than applying a coating.
- Invent radically different film-deposition methods.
- Develop a screening tool that can be used to design new coatings, results of which can be extended to large-scale manufacturing processes.

Table 3-4. R&D needed to overcome technical barriers for flat glass coatings.

	Process Control	**End-User Education & Needs**	**Process Development**	**Coating Materials**	**Analytic & Testing Tools**	**Institutional**
Near Term < 3	Online monitoring of coating defects (and sizing / density). ●●○○○○	Simple dollars & cents rating systems for consumer for all products. ○○○	Industrial pilot-scale facility to test materials & coatings. ●●●●○	Benchmark high-performance coatings for aerospace and durability. ○	Examine analytical technologies and optimize for needs of thin-film coatings for glass. ●○	Establish a logic path for R&D activity.
	Chemical sensors for precursors & effluents. ●○	Identify future "wants to stimulate customer pull for new products.	Improve fluid dynamic tools to control gas flow uniformity over large areas.		Testing & modeling for determining coating durability & then develop standardized test. ●○	Launch a broad, industry-supported mass media campaign. ○
	Develop rugged optical & electrical on-line sensors. ○○○○○	Develop set of performance standards / benchmarks, metrics for energy, non-energy, fading, and optical. ●○	Scalable screening tool for design. ●○		Analyze failure modes & affects on equipment, process, & material interaction.	
Mid-Term 3-10 years	Technique to read the glass surface, in-line, to determine cleanliness. ○○○	Determine customer wants and cost / benefit.	Create a "virtual coating laboratory".	Develop small-scale quick-screening method for new material. ●●●○○	Develop service-life models based on standardized durability test. ○	Include requirements for building Low-E coatings in bldg codes. ○
	Cognitive algorithms for process controls. ○	Develop marketing description of non-economic benefits of coated flat glass.	Develop new improved ways of cleaning glass.	Communicate coating needs to inorganic chemists.	Better analysis tools for very thin films. ●●○	
	Develop process controls that take advantage of advances in modeling, sensors, algorithms.		Modify glass surface to change properties rather than applying coating.			
	Inexpensive online optical monitoring to 0.1 - 0.2% absolute. ●●●					
Long Term > 10 years			Invent radically different deposition processes. ○	Evaluate novel materials that haven't been used for thin films. ○○○○		

Legend

● = High Priority ○ = Medium Priority

- Characterize the compatibility of coated glass with adhesives, finishes, etc. applied off line by end users. Use this information to make coatings more robust to end-use. Materials of interest here include sealants used by the construction industry; such as polysulfides, polysilicones, and polyisobutyl; water; and structural seals used in the manufacture of insulated glass units.

Institutional Issues

- Establish a logic path for R&D activities: show how to map and fund these activities. Identify industry-wide fundamental problems or areas for noncompetitive research that can be funded by broad group of companies.
- Launch a broad, industry-supported mass-media campaign ("Got Low-E?").
- Push the incorporation of low-E coatings in building codes.

End-User Education and Needs

- Establish a simple "dollars and cents" rating system for consumer to evaluate all products.
- Identify future "wants" to stimulate customer pull for new products.
- Develop a set of performance standards / benchmarks / metrics for 1) energy performance and 2) nonenergy-related factors, such as fading, appearance, etc.
- Develop a simple explanation of the noneconomic benefits (such as interior comfort, architectural esthetics, etc.) of coated products. Standardize the "comfort factor" or the "fade factor" etc. Develop a simple marketing system based on labels that provide the final customer with a clear statement of the benefits obtained from the new product.
- Perform consumer research to determine what they value and the associated cost / benefit.

4. Container Glass Breakout Group

Performance Targets

Background

Containers include bottles, jars, vases, envelopes, gas tanks, perfume bottles, etc. The glass-container industry is mature and highly competitive. Companies compete not only among themselves, but against other materials, such as plastics and cans made from steel and aluminum. As such, cost is a key, perhaps overriding, factor in the evaluation of any new technology. The consumer is probably unwilling to pay more for an improved container; if anything, they want more performance at lower cost.

Glass containers enjoy several important advantages over competing materials:

- They are impermeable to the environment. This is a critical characteristic that distinguishes glass from plastic.
- Glass does not affect the taste of the material it contains.
- It is nonreactive.
- It enjoys consumer appeal in many applications.
- Because it is clear, the consumer can see what it contains.
- Some consumers find it pleasant to the touch.
- It is flexible with regard to shaping.
- It is 100% recyclable.
- It can withstand high temperatures, e.g., those used for pasteurizing.

There are several "givens" that must be kept in mind with regard to development of any new coating process for containers:

- The container must continue to be 100% recyclable, regardless of the coating used.
- Coating processes must be 100% environmentally friendly.
- The cost of the container must be cheaper than plastic with all the advantages of glass (see above).
- The glass-container industry wants to be a thriving, competitive industry in the future.

The performance targets described (Table 4-1) in this section probably cannot be fully achieved through the development of coatings alone. For example, it may be necessary to increase the strength of uncoated glass to permit the desired reduction in weight and increase in break resistance.

Performance Targets (0-5 years)

Many of the targets in this near-term (0-5 years) time range could be achieved with existing technology. Unfortunately, most of these technologies are not cost effective.

- Reduce container weight by 25% over average current weight (glass weight / volume). Technology and theory exist to do this today.
- Increase container resistance to breakage by using 1) new self-healing coatings that are cost effective and maintain their attributes, 2) coatings that apply a compressive strength to the bottle, and 3) energy-absorbing coatings that increase resistance to mechanical impact. It is difficult to make this target quantitative due to the lack of a quantitative measure of container strength / resistance to breakage.

- Develop coatings that retain fragments in the event of breakage.
- Monitor the coating process online to obtain information concerning deposition rate and coverage.
- Reduce / eliminate UV transmission to minimize damage to product. This is especially important for flint glass and glass used for beer containers. The coatings used must be transparent.
- Increase the uncoated strength of the container through optimization of current system parameters.
- Manipulate color using coatings.
- Protect printing on containers using coatings.
- Increase deposition rates / efficiency.

Table 4-1. Performance targets for container glass.

0 – 5 years	Reduce weight by 25% over today's average
	Increase break resistance using: ▪ Self healing coating that maintains cost-effective attributes over time ▪ Coatings to add compressive strength ▪ Energy-absorbing mechanical impact strength
	Coatings for fragment retention
	Monitor coating process online
	Reduce / eliminate UV transmission using coatings
	Increase uncoated container strength
	Manipulate color thru coating
	Protect printing on glass
	Understand chemistry / kinetics of coating deposition to increase yield
5 – 10 years	Develop one coating with all required properties
	Permanent mold coatings
	Break-resistant glass container – increase strength

Performance Targets (5-10) years

- Use one coating to achieve all desired properties.
- Use alternative (preferably permanent) mold coatings. This is a critical technology to weight reduction and has more impact than the final coating on the ability to decrease weight it also changes the characteristics of container surface.
- Market a break-resistant container.

Technology Barriers

There appear to be no technical barriers to achieving some of the goals just discussed (e.g., improved break resistance, fragment retention, higher strength, energy absorption), even within five years. Much of the technology already exists. However, its cost is prohibitive. Cost and market size are the major barriers to improving container performance (and hence, utilization of advanced coatings). Overcoming these "market-pull" issues as well as the problem of imparting new attributes to a container without increasing its cost were given the highest priorities (see Table 4-2).

The fact that this group did not identify any kind of intermediate goal for strength, for example, is an indication of a mature industry. Materials available today appear to be sufficient, unless a major breakthrough can be achieved, such as an unbreakable container. Achieving a breakthrough of this magnitude will require out-of-the-box thinking; it can't be done with existing technology.

Technology barriers to progress in the container-glass industry are divided into three categories, Knowledge Base, Technical Issues, and Market Issues. As in all other segments of the industry, the lack of basic knowledge concerning coating processes and the materials themselves is a key barrier, as indicated in the Knowledge Base section by law.

Knowledge Base

This area includes barriers of a fundamental science / engineering nature.

- Container firms lack the facilities to develop new coating ideas / concepts.
- A comprehensive view of the integrated glass+coatings system and how the two affect each other is lacking.
- State-of-the-art knowledge with respect to coatings is proprietary and inhibits progress.
- Diagnostics to perform real-time surface characterization to establish film thickness, surface cleanliness, etc. are unavailable.
- No baseline values have been established for container properties such as strength. Thus, it is impossible to benchmark a coating to determine whether it is truly an improvement.
- Lack of interest in the general area of container science / engineering in academia has lead to a dearth of next-generation technology and glass research.
- The following three items are grouped under the heading of container / coating characteristics:
    1. It is not possible to know all sources of flaws in a glass container that contribute to lack of fracture toughness.
    2. Knowledge of the properties of the glass and coating surfaces is incomplete. This information is needed at all stages of manufacturing: from the gob to the mold to the final annealing.
    3. Adequate tools to characterize the surface are not available.

Technical Issues

These barriers are concerned with specific coatings and manufacturing technologies. Also included several barriers are related to "mold doping," in which an organic compound is swabbed on the interior of the mold used to form a container. (The purpose of this coating is to promote facile release of the hot container after it is initially formed).

- No single coating exists that has all of the desired attributes (currently, two coatings are typically used).
- The best mold-coating materials are not available commercially (these have been reported in the technical literature but not marketed).

Table 4-2. Technical barriers to reaching performance targets for glass containers.

Knowledge Base	Technical Issues	Market Issues
Lack of facilities to develop new coating concepts. ●●●▲▲	Lack of single coating that has all desired attributes. ☆	Difficulty adding attributes while maintaining costs. ✪✪☆●●▲
Lack of comprehensive view of integrated glass + coatings system. ●▲▲	Best mold coating materials are not available commercially. ●▲	Market-pull issues
Knowledge on coatings state-of-art not shared. ●●▲	Too much waste from doping molds. ●▲	Reducing cost for manufacturer is primary goal, not better bottle for consumer. ☆
No real-time surface-characterization diagnostics. ●▲	Difficulty adding impact strength from outside the bottle. ●	Lack of understanding of market drivers for enhanced container attributes. ✪●▲▲
Lack of baseline data for container strength.	Lack of color availability at desired intensity. ●	No vision of what a better product would look like.
Lack of next-generation technology & glass research.	Mold doping produces fumes and surface contamination.	Customer preference for non-recyclable products. Consumers don't recognize positive attribute of recyclable products.
Knowledge of characteristics	No organic coating available that imparts compressive strength.	Bottle manufacturers not investing in declining, mature industry.
- Poor knowledge of flaw sources. ●●▲▲	Economical functional coatings not available.	Lack of knowledge of coating processes that have no environmental impact.
- Incomplete knowledge of surface properties. ●●▲	Lack of knowledge concerning performance of hybrid, composite coatings on glass containers.	Reducing container weight impacts entire production line, from manufacturing to transport.
- Inadequate surface-characterization tools. ●▲	Some coatings are a source of contamination.	Bottle manufacturers also manufacture plastics. No incentive to improve.
	Containers are designed by artists without considering strength.	

Legend

Nonmanufacturer committee members ✪ = Top Priority ● = High Priority ○ = Medium Priority ◎ = Low Priority
Manufacturer committee members ☆ = Top Priority ▲ = High Priority ◆ = Medium Priority ▼ = Low Priority

- Doping molds create major waste (1–2% of containers must be rejected after mold swabbing). This process is also very labor intensive.
- Adding impact strength to a bottle by putting a coating on the outside is difficult.
- Coatings that can be used to change container color are not available at the desired intensity.
- Mold dopings are also an environmental hazard. They burn when applied initially, create noxious fumes and particulates. These can affect the surface of the container and the properties of any coatings that are applied.
- No organic coatings exist that will apply a compressive stress on the bottle (which tends to increase strength).
- Functional coatings that might indicate, for example, the temperature of the product or whether or not it has become contaminated or spoiled, either do not exist or are too expensive.

- Complex coatings, such as hybrids, micro-/nano- composites for crack termination/deflection, multilayers, or "skins", have not been tested to determine their effects on container performance (the industry has no knowledge of these).
- Coatings themselves can be a source of contamination, whether they are applied inside or outside. For example, silicones interfere with the foaming of beer.
- Containers are typically designed by artists with little or no consideration of strength. Their designs can be quite old and are thus marketing tools. This makes it very difficult to alter their appearance.

Market Issues

Barriers described here concern institutional characteristics as well as limitations imposed by what consumers want and will pay for.

- It is difficult to add new properties to a container or improve the existing ones without increasing its cost.
- Market-pull issues:
  1. Reducing cost while maintaining quality is the primary goal of manufacturers, not providing the consumer with a better bottle. Essentially, there is no market pull for a glass container with improved characteristics.
  2. There is also a lack of understanding of market drivers for various attributes.
- The industry does not have a vision of what a better product might look like.
- Consumers prefer nonrecyclable products and don't seem to recognize the benefits of a recyclable container. Only 37% of all containers are recycled, and only a small portion of these are glass.
- Container manufacturers are not investing in what is viewed as a declining, mature industry. There are now fewer container lines which run faster (i.e., have higher productivity). Adding a new or improved coating will increase capital costs on the line.
- A given is that any new coating process must have no environmental impact (although current ones are not impact-free). The industry lacks knowledge of coating processes that are environmentally benign. Some of the compounds used today (tin compounds in particular) are quite toxic.
- Reducing the weight of a container ("lightweighting") has a major impact on production: the container dimensions change, so fill requirements or handling equipment must also change; transportation (secondary packaging) and marketing (e.g., soft-drink machines) are also affected. These are major barriers to improving both strength and weight of a glass container.
- Glass-container manufacturers also make plastic containers, so they are in competition with themselves. Thus, there is little incentive to improve the product.

Research Needs

Research needs for coatings in the container sector are divided into four areas (see list below). Within these, several research needs stand out in terms of the high priority assigned to them. Like other segments examined in the workshop, obtaining more and better data to expand the knowledge base received great emphasis; four of the nine top-rated needs fall into this category (see Table 4-3). All four are viewed as being capable of having an impact on the industry in the near term (0–5 years). Three of the four deal with surface processes (topographical effects, real-time surface monitoring, and research to understand the molding process). The remaining item, development of an interactive data base for coatings information, could impact the industry within significantly less than five years.

Two of the top priorities fall into the Technology Development category: (1) the need for a pilot-scale facility for testing coating technologies and (2) the need to explore nontraditional coatings and/or processes that can place the container surface under compression. Ultimately, development of an unbreakable bottle would be a revolutionary advance for the industry, so an assessment of the theoretical requirements to achieve this was also given very high priority. In the short term, however, evaluation of existing and potentially inexpensive coatings (such as the hybrid coatings known as "planomers") could provide some intermediate improvements in container properties without increasing costs.

Clearly, market drivers have a strong impact on the manufacturing direction in the container industry. Thus, emphasis was placed on conducting a marketing study to understand the needs of both consumers and producers before attempting to design next-generation containers (in which coatings will likely be an important part).

The complete list of research needs is given below with a short explanation in most cases of the thinking behind them.

Market

Near Term (0-5 years)

To assist in establishing appropriate directions for R&D, a market study should be conducted to understand the needs of both producers and end users. The following should be addressed:

- Determine the marketability of glass with specific characteristics.
- Determine the effect that a given change in container and/or coating design would have on the entire cycle (manufacturers, end users, etc.).
- Establish the cost and production volume likely for the new technology.
- Identify barriers to market penetration, such as handling, storage, transportation.
- Identify barriers to increased recycling by consumers.

Mid Term (5-10 years)

Study future uses of glass (technology-based development).

Table 4-3. Research needed to overcome technical barriers in the coating of glass containers.

	Market	Expanding the Knowledge Base	Assessing/Bench-marking Existing Technologies	Identification of Requirements for New Technology	Technology Development
0-5 years	Conduct market study to understand needs before starting R&D ✪ ☆ ▲○	Determine the effects of surface topography on current coating performance (glass & mold). ☆○○○ ◆◆◆	Test existing inexpensive hybrid coatings. ✪	Determine theoretical requirements to achieving break-resistant glass. Quantify additional strength requirements ☆●● ▲◆	Explore options for online testing of coating technologies (e.g., pilot-scale facility). ● ○○ ◆◆
	Survey consumers to determine barriers to increased recycling ● ○	Examine surface evolution & coating formation in real-time. ✪ ▲○	Assess current state-of-art for: - light-weighting - energy absorbing - fragment retention coatings. ● ▲	Establish requirements & definitions to increase mold performance (life).	Explore avenues for surface treatment prior to coating. ○ ◆
		Identify sources of defects in both coatings and in the container itself.	Benchmark currently available color coatings - testing - prices (producing). ●	Utilize finite element analysis to identify stress deficiencies.	Develop ion-exchange coatings for improved strength.
		Conduct research to understand effects of surface molding process on glass. ●● ▲ ◆	Benchmark existing materials as possible mold-release coatings. ●		Develop simple quality control measurement for cold-end coverage.
		Evaluate effects of internal surface treatments on strength ● ▲◆	Assess present state of online coating measurement technology & recommend future possibilities / needs. ◆		Explore solid mechanics of laminated containers.
		Explore fundamentals of interactions between coatings, glass surface, and glass structure. ● ○○			
		Develop interactive database to collect & store information on coating material & deposition options. ○○ ◆◆			
		Evaluate effects of glass composition on coating performance. ○			

Legend

Nonmanufacturer committee members ✪ = Top Priority ● = High Priority ○ = Medium Priority
Manufacturer committee members ☆ = Top Priority ▲ = High Priority ◆ = Medium Priority

Table 4-3. Research needed to overcome technical barriers in the coating of glass containers. (continued)

	Market	Expanding the Knowledge Base	Assessing/Bench-marking Existing Technologies	Identification of Requirements for New Technology	Technology Development
0-5 years		Study chemistry & kinetics of present coating processes to improve yield & homogenity.			
		Determine the influence of minor glass components on coatings.			
5-10 years	Conduct study for future uses of glass (technology-based) develop. ▲	Explore alternative forming processes & technologies to increase integration of coating-glass forming.			Explore non-traditional coatings & coating processes that provide surface with compression. ✪ ▲○○○ ◆◆
		Develop coatings to facilitate nondestructive evaluation.			Develop "intelligent" coatings as temperature sensors, internal pressure detectors, UV sensors, etc. ○○
		Feasibility requirement study of completely new bottle.			Explore alternatives to mold doping . ◆

Legend

Nonmanufacturer committee members ✪=Top Priority ● =High Priority ○=Medium Priority ◎=Low Priority
Manufacturer committee members ☆=Top Priority ▲=High Priority ◆ = Medium Priority ▼ = Low Priority

Expanding the Knowledge Base

Near Term (0-5 years)

- Determine the effects of surface topography on current coating performance. Consider both the coatings on the glass and the mold coating.
- Examine the evolution of the glass surface and coating formation in real time.
- Identify sources of defects in both coatings and in the container itself.
- Understand the glass-mold interaction.
- Evaluate effects of internal surface treatments on strength.
- Explore fundamental aspects of coating-glass structure interactions.
- Develop an interactive database containing information on coating materials, their uses, and deposition methods.
- Identify the effects of glass composition on coating performance; determine how impurities and minor constituents in the glass affect the coating.
- Investigate the chemistry and kinetics of the coating process to improve its yield and the uniformity of the coating.
- Determine the influence of minor glass components on coatings.

Mid Term (5-10 years)

- Explore alternative processes that can integrate forming and coating.
- Develop coatings that facilitate nondestructive evaluation. Could be volatile materials, but they must also be either environmentally friendly or permanent.
- Determine what research is needed to develop a completely new glass container.

Assessing/Benchmarking Existing Technologies

Near Term (0-5 years)

- Evaluate existing inexpensive hybrid coatings, such as the "planomer" coating for potential application to container glass.
- Assess current state of-the-art for: 1) light-weighting, 2) energy absorbing, and 3) fragment-retaining coatings.
- Benchmark available coatings for imparting color to the glass to determine 1) performance and 2) cost of production. Compare results with industry needs.
- Benchmark existing coatings for their ability to function as mold-release coatings. Determine how they perform when coated on the mold.
- Assess the state of online coating-measurement technology to 1) identify currently applicable technologies and 2) determine future needs / directions for research.

Requirements for New Technologies

Near Term (0-5 years)

- Determine theoretical requirements for break-resistant glass. Quantify how much additional strength (beyond present containers) is required.
- Establish requirements to increase the lifetime of mold coatings.
- Apply finite-element analysis to identify stress deficiencies in containers. Develop models that can simulate the effects of an impact on a container and identify where the stresses are located.

Technology Development

Near Term (0–5 years)

- Explore options for online testing of coating technologies. Establish a pilot-scale facility for doing this.
- Explore surface-treatment technologies that could be used prior to coating to improve coating performance.
- Develop ion-exchange coatings for improved strength.
- Develop a simple, quantitative quality-control measurement for cold-end coating coverage.
- Explore the solid mechanics of laminated containers. Assess whether this technology can be used to replace monolithic glass and achieve improved strength and break resistance.

Mid Term (5–10 years)

- Explore nontraditional coatings and deposition methods that can provide compressive stresses to the container.
- Attempt to develop "intelligent" coatings that can serve as temperature sensors, internal pressure detectors, UV sensors, etc.
- Explore alternatives to mold doping.

5. Coatings on Glass Fiber Breakout Group

Background

Glass fibers are used to make a wide range of products, including composites, shingles, automotive parts (fiberglass), fiberglass insulation, and optical fiber. Representatives of the textile fiber (used for making composite materials) and the fiberglass insulation industries were present; a representative from the optical fiber industry was unable to attend the workshop.

The glass used to make textile fibers and insulation is typically E glass (see Table 2-5), which is a borosilicate glass containing high concentrations of alumina and calcium oxide. Coatings are an essential part of the manufacturing of these products; without them, it would be impossible to manufacture products such as fiberglass insulation. Coatings used today are multifunctional, but their primary purpose is to protect the fiber surface and provide lubrication. They are also used to impart strength and to tailor the mechanical properties of composite materials.

Coatings are deposited by aqueous solution chemistry. Precursors consist of highly dilute organic compounds in water, which limits the kinds of coatings that can be applied to the glass. Fiber-coating technology has not progressed significantly over the last several decades with respect to solving problems related to fiber wetting, adhesion, and aging. It is largely a mature technology in terms of performance and need. New manufacturing methods and materials are required before improvements in product performance can be significantly improved.

One of the major problems with glass fibers is that they do not maintain their theoretical strength (around 10^6 psi) after manufacturing. Typically, fiber strengths are a factor of 10 or more weaker than the theoretical value, even with strength-enhancing coatings. Coatings are designed to maintain fiber strength as much as possible; in fact, without coatings, cracking is instantaneous. This is evidently due to preexisting surface flaws, which lead to stress-corrosion cracking. Solving this problem is becoming increasingly important, since many fiberglass composites, particularly those used in the automotive industry, are now being put under continuous loads, which adversely affects their tensile fatigue and creep.

The glass fiber industry faces many technical challenges. There is a strong desire to increase the performance of standard resins (e.g., polyimides). However, the complexity of the problem and lack of underlying knowledge, particularly with regard to the fiber surface and how it interacts with the coating, make it difficult to know where to begin. In fact, the answer to a very basic question—what percentage of the fiber is coated? —is not known with certainty. Although techniques such X-ray photoelectron spectroscopy can be used to determine this, they are time-consuming and cannot be implemented online where they are needed. Research is needed to explore the latest in analytical technologies, such as field-emission Auger, atomic force microscopy, and X-ray scattering, to characterize the fiber surface more accurately. Knowledge of surface coverage is particularly important, since it affects fiber properties and aging behavior. In addition, increasing production rates (i.e., higher fiber draw rates) affects coating coverage and fiber surface properties.

Many environmental issues are associated with the manufacturing of fiber coatings and the resulting products. Because of recent regulations, it is no longer possible to use many of the raw materials (typically solvents) that were formerly commonly used. Pressure to reduce the use of hazardous materials goes beyond organic compounds and now extends to usage of compounds such as ammonium hydroxide. This makes it very difficult for coating designers to develop new technologies that can improve the performance of fiber-based products. Unfortunately, the least expensive resins, formaldehyde and pheno-formaldehyde resins, are also the least environment-friendly. Regulation of these resins is becoming increasingly stringent.

In addition to these manufacturing issues, there is a disposal problem with respect to glass-fiber waste. This material, which includes defective scrapped material, insulation trim, and edge cuts, is usually coated with organics that must be removed before disposal. Currently, incineration is the only viable technology. As a result, more material than is desirable is going to landfills. Industry is reluctant to build a market for scrap, since this could compete with newly manufactured products. However, the industry does want to minimize waste and convert these materials to useful products.

Finally, the high concentrations of binder (i.e., organic coatings) on some products have implications for air quality inside the home. Low-density products such as fiberglass insulation contain only about 3% binder, but some products contain as much as 20% binder. It is known that binder aging leads to undesirable outgassing of formaldehyde; long-term exposure to this compound may have health implications.

Technology Targets and Objectives

Technology targets for coatings on glass fibers are summarized below and include several objectives common with other segments of the glass industry. For example they include the need for a database containing information on interactions between coatings and the fiber substrate, the desire to have greater coordination among companies to develop important fundamental science, and the need to employ rapid screening techniques to improve the economics of developing new coatings. Environmental issues are more of a concern in this industry than in other segments. Consequently, several targets deal with recycling and recovery of waste products associated with fiber coatings. A summary of the targets is found in Table 5-1.

Near Term (0–5 years)

- Improve coating coverage, i.e., wetting behavior of fiber.
- Incorporate state-of-the-art modeling capabilities to design fiber coatings.
- Improve coordination among manufacturers concerning existing science and data.
- Expand market for fiberglass composites in the auto industry.
- Improve understanding of surface-coating interface.
- Establish a database of information concerning fiber / coating interactions for use by manufacturers.

Mid Term (5–10 years)

- Use rapid screening techniques to evaluate new coating formulations.

Long Term (> 10 years)

- Use process control to measure and control coverage.
- Develop alternative coating systems (perhaps based on nonaqueous chemistries) while maintaining low cost.
- Produce fiber coatings that don't loose their strength over time.

Table 5-1. Performance targets for coating fiberglass.

0-5 years	5-10 years	Over 10 years
Improved "coverage" quality.	Rapid screening of new potential coating formulations.	Use process control to measure and control coverage.
Utilize state-of-the-art modeling capabilities.		Develop alternative coating systems (i.e., non-aqueous) at equivalent or lower cost.
Improve coordination with manufacturers on existing science & data.		Develop fiber-coating systems that don't lose strength with time.
Expand fiberglass composite use in auto industry.		100% VOC recovery in processing.
Improve understanding of surface-coating interface.		Develop applications for scrap or recycle fiberglass.
Create Database for interactions for manufacturers (start with silanes).		Develop non incineration–based process to recover cured fiberglass.
		Improve tensile fatigue & creep properties for composites.
		Develop coatings that increase R value with fewer air-quality issues (migration) insulation.

- Recover 100% of VOCs used in processing. Although the industry uses raw materials that contain low amounts of VOCs whenever possible, substantial quantities of these compounds are still exhausted to the atmosphere.
- Recycle scrap fiberglass into usable products. Currently, 10–40% of various fiberglass products are recycled.
- Use nonincineration-based methods to recover cured fiberglass.
- Improve tensile, fatigue, and creep properties, with the ultimate objective of increasing long-term performance (i.e., reduce aging effects).
- Develop coatings that yield higher R values (for insulation) with reduced air-emissions (i.e., migration of gases such as formaldehyde) and improved compression response.

Technical Barriers

Technical barriers in the glass-fiber industry were subdivided into four categories. In common with the other segments, the need to know more about the underlying physical and chemical processes that control coating formation and performance is a high priority. It is clear the industry suffers from a major lack of fundamental knowledge about its coating processes.

Of the eight highest priority barriers, six of them occur in the Fundamental Knowledge category. In particular, lack of understanding of the glass/coating interface and how surface properties of the glass affect coating properties, such as adhesion, are major deficiencies. Fiber coating processes are very complex, usually involving multiple components to achieve a

multifunctional coating. Interactions between these components lead to variable properties and great difficulty in process optimization.

Barriers identified are listed below with a brief summary. Table 5-2 indicates the priorities assigned to each.

Fundamental Knowledge

- Lack of understanding of the glass/coating interface and how it affects coating and fiber properties as well as the functionality of the fiber.
- Little or no understanding of coating/fiber interactions at the molecular level.
- Not clear what properties a glass surface should have for optimal coating (don't know what's desirable).
- Inability to understand the origin of defects. Fibers clearly lack the theoretical strength they should have, but the origin of defects and how they lead to strength reduction, as well as the effect of coatings on them, are unclear.
- Lack of understanding of wetting behavior. Coatings are applied by solution techniques. Reactants must stick to the surface.
- Inability to predict how the rate of coating formation affects properties and how this changes when coating processes are scaled from the lab to production.
- Little is known about the properties of as-deposited, in-use, and aged coatings.
- Aging of fibers leads to serious degradation of some products. For example, blown-fiber insulation collapses over time, evidently because of strength degradation.
- Inability to develop higher molecular-weight materials as emulsions. If this could be done, it might allow composite properties to be increased beyond present levels. This is particularly important for automotive applications, where having a high strength/weight ratio is critical.

Process Technology

- Lack of enabling technologies for coatings. The glass-fiber industry has been using basically the same technology for decades. "Use what you know" is the underlying tendency. The reluctance to invest in capital equipment further limits the use of new and potentially superior (more efficient, higher-quality coatings, etc.) technologies.
- The coating system is overly complex. Too many components are interacting, making process optimization extremely difficult.
- The cost of innovative coatings is prohibitive. In addition, it can be difficult to "uncoat" fibers coated with these materials (even by incineration) so they can be recycled.
- Coating technology isn't keeping pace with increases in the number of filaments in a bundle. Current fiber bundles contain several thousand fibers.
- Lack of nonincineration-based processes for recycling fiberglass insulation.
- High energy use in dewatering phase. Primarily an issue for insulation, not in the textile or chopped-fiber business. Between 250 and 500 Btu/lb. of insulation is expended to cure and dry the coatings.
- Lack of integration techniques for process control.
- Limits on how much coated fiber can be recycled through the melt, due to contamination problems. Currently, only a few percent of so-called "basement scrap" can be recycled into the melt, since the melt is extremely sensitive to formation of defects. Most scrap is simply landfilled.

Table 5.2 Fiberglass technology barriers to achieving performance targets for coating fiberglass.

Institutional Issues	Process Technology	Fundamental Knowledge	Analytical Tools	Process Technology	Fundamental Knowledge
Lack of cross-disciplinary interaction ●	Lack of enabling technologies for coatings ●▲▲	Lack of coating / glass interface understanding of properties and functionality ✪☆☆☆●	Lack of spacially resolved tool for coverage measurement ●▲▲▲	Unable to utilize most recycled fiber in melt (contamination)	R values degrade over time in blown-fiber insulation
High cost & unavailable infrastructure for fiberglass insulation recycling	Coating system is overly complex ▲▲	Lack of understanding of (molecular)level interactions in coatings ✪☆●	Unable to measure coating efficiency & coverage in real time, online ●●		Unable to develop higher molecular-weight materials as emulsions
Lack of adequate technical staff (from downsizing)	High materials cost for innovative coatings ● Lack ability to "uncoat" for recycling ▲	Lack of understanding of glass surface ✪●▲▲▲	Unable to measure mechanical properties online, real time ●▲		
Lack of knowledge vis-à-vis other industries' coating experience	Ability to keep up with increases in number of filaments in bundle	Inability to understand origin of defects ●●▲▲	Unable to determine silanol concentration on multi-component glass ▲		
	Lack of non-incineration based processes for fiberglass insulation recycling	Lack of understanding of wetting behavior ▲▲▲	Inability to measure glass surface defects ●		
	High energy use in dewatering phase	Unable to predict how forming rate affects behavior from lab-scale to production ●▲▲			
	Lack of integration techniques for process control	Lack of understanding of coating properties (as deposited, (in use, aged) ▲			

Legend

Nonmanufacturer committee members ✪ = Top Priority ● = High Priority
Manufacturers committee members ☆ = Top Priority ▲ = High Priority

Analytical Tools

- No technique available that can provide quantitative spatially resolved information concerning coating coverage.
- Unable to measure deposition efficiency and coverage in real time (i.e., online).
- No way to measure mechanical properties of fibers, such as tensile strength, online. If this could be done, it might provide clues as to where the loss of strength occurs.
- For multicomponent glasses, the silanol (Si-OH) concentration on the surface cannot be determined (with the possible exception of silica). Silanol groups are the active chemical constituents on the fiber surface that bind to the coating and thus strongly affect adhesion.
- No way to measure surface defects on the glass.

Institutional Issues

- Lack of cross-disciplinary interactions. For example, the industry could benefit from extensive science and engineering done to improve ceramic composites (particularly in the area of continuous fiber ceramic composites).
- High cost and lack of infrastructure needed to recycle fiberglass insulation.
- Lack of adequate technical staff due to corporate downsizing.
- No communication among companies and thus ability to benefit from the knowledge/mistakes made by others.

Research Needs

Research needs in the glass fiber segment are divided into five categories. The overriding concern is to obtain a better understanding of the fiber surface and how it interacts with the various coatings applied to it. To this end, the highest priority needs are found in the Tools Development and Tools Application categories. In particular, there is a strong need to both develop new technologies that can be used to characterize fiber surfaces and interfaces and to apply existing analytical methods to this task. Closely related to this need is the requirement for online sensors capable of determining coating thickness, coverage, and properties such as fiber strength at the high drawing speeds used today. There is also a recognition that theory can make a significant contribution to this effort, but that new tools may need to be developed to address the issues unique to glass fibers.

The complexity of existing coating processes and the consequent difficulty in optimizing their performance points to the high-priority need for new high-speed coating technologies. Such methods may involve technologies that are well developed in other areas, such as CVD. In fact, it is also recongnized that fiber-coating technology might benefit from knowledge gained in the development of non-fiber-based coating technologies, in particular those used to coat particles.

Other high-priority research needs include: the need to develop rapid screening and prototyping methods; the need to obtain a better understanding of wetting phenomena; and the desire for a pilot-scale facility for testing new coating concepts and processing technologies.

A detailed list of the research needs identified for fiber coatings along with a brief description of each is given below. Relative priorities for these needs can be found in Table 5-3.

Tool Development

- Develop new technologies for surface and interface characterization. Reflects the lack of knowledge of the coating/glass interface. However, efforts should also be directed at characterizing so-called “triple junctions,” which are locations where air, glass, and coating

intersect due to inadequate coverage. Presumably, slet fiber degrades at these places because of attack by water and other air-born reactants, resulting ultimately in delamination.

- Characterize existing methods and develop new ones for measuring coating coverage. Examples include AFM, X-ray scattering, AES, TOF SIMS, etc.
- Develop an improved method for measuring wetting behavior. Currently, dynamic contact-angle analysis is used, which is an old technique that produces very noisy data.
- Develop sensors for online measurement of coverage, strength, thickness at high speed. No such devices exist today.
- Develop / apply theoretical modeling tools to provide insight into a wide range of fiber-coating issues. This is an area that has seen little or no work and needs to be explored.
- Develop rapid screening and prototype methods for evaluating new coating strategies.

Process Technology

- Develop new, high-speed coating technologies that are less complex, nonaqueous (to eliminate drying and curing), and yield fibers with improved tensile strength. CVD is one possibility; evaluate others as well. Explore innovative coating chemistries, since existing technologies can't seem to improve strength. A higher-melting glass could be used, but this has major energy and processing speed penalties.
- Explore option of applying a glass with high-temperature attributes (or other positive features) as a coating. For example: use CVD to deposit silica on the fiber, instead of using a higher-melting glass fiber and incurring the energy cost, etc.
- Investigate coating technologies developed in their industries (e.g., particle-based).
- Develop fiber-coating system for higher tensile strength.

Tool Application

- Study the interface and surface of glass fibers. In particular, what influences silanol formation and reaction? How do these sites "age"?
- Conduct pilot-scale testing of new fiber-coating technologies.

Environment

- Develop methods to recycle fiber as it exists (i.e., in whatever form: coated, uncoated, in a matrix). Competitive issue for fiber vs. metals, which are readily recyclable.
- Develop coating technologies that minimize discharge of waste water that must be treated. Essentially, move toward nonaqueous technologies.
- Develop improved VOC emission control technologies.
- Develop low- or VOC-free coatings, especially for fiber insulation, in which the coating (binder) is a much larger component of the fiber (as much as 20%).
- Develop technologies to recycle composites.
- Investigate potential for incorporating fiberglass composites in asphalt. This could be especially important for automotive composites, for which there is a high volume and no recycling alternative to landfill.

New Markets

- Investigate potential for partnering with the building industry to develop new fiber-reinforced products. Examples include fiber-reinforced subflooring and artificial lumber.

Evaluate potential uses of glass fiber to reinforce metals (metal-matrix composites).

Table 5-3. R&D required to overcome the technical barriers for fiberglass coatings.

	Tool Application	Tool Development	Process Technology	Environment	New Markets/Products
Near Term 0 – 5 years	Perform surface & interface studies on fibers. ✪●▲▲	Develop new technologies for surface & interface characterization. ✪☆☆☆☆●			
		Perform studies on coverage measurement (e.g., AFM, X-ray scatt., AES, TOF SIMS, etc.). ●▲▲▲▲			
		Develop better technique to measure wetting behavior. ○◆◆			
Mid Term 5 – 10 years	Fund pilot-scale testing by industry	Develop new sensors (online) for high speed, to determine coverage, and determine strength & thickness. ●▲▲○◆◆	Investigate coating technologies developed in other industries (e.g., particle-based). ○◆◆◆◆	Develop methods to recycle fiber as it exists. ◆◆	Investigate partnering with building products industry. ○◆
		Develop theoretical modeling tools (for fiber as well as coating). ●○◆◆◆		Utilize materials that produce less discharge. ◆	
		Develop rapid screening & prototype methods for coating strategie. ▲▲○		Develop improved VOC emission control technology.	
Long Term >10 years			Develop new high-speed coating technologies: Process - CVD - Less complex - Unknown other Coating - Innovative coating chemistry - Nonaqueous ●▲○◆	Develop low VOC or VOC-free coatings (especially for insulation).	Evaluate glass fiber application with metal matrices. ○
			Develop fiber-coating system for higher tensile strength. ◆◆	Develop technology to recycle composites.	
			Develop technologies to coat glass on glass (for improved properties). ○	Evaluate application of recycled fiberglass in asphalt.	

Legend

Nonmanufacturer committee members ✪ = Top Priority ● = High Priority ○ = Medium Priority

Manufacturer committee members ☆ = Top Priority ▲ = High Priority ◆ = Medium Priority

6. Specialty Coatings on Glass Breakout Group

Background

The Specialty Coatings working group agreed early in its discussions that, although this was the "none-of-the-above group," i.e., it covered coatings applications outside of flat, container, and fiber glass, that the correct topic for the group is specialty coatings on glass, not coatings on specialty glass. The former includes coatings on large-area substrates, such as those produced by a float line, while the latter generally represents niche markets, such as optical components (by one person's definition, however, "specialty glass" means everything except soda-lime and float glass, which would include some rather large markets, such as television tubes and optical fiber). It was also agreed that low-E coatings would not be an area of discussion, since the group expected that this would be covered by the flat-glass working group.

Specialty coatings include many value-added products that are essential for the survival of the glass industry; however, this is clearly a broad and diffuse area. As a result, the group chose to focus its discussions by defining specific functionalities for coatings. These are:

- Electrochromics
- Conductive coatings
- Optical applications
- Semiconducting coatings
- Catalytic coatings
- Coatings to modify surface energies
- Nanodevices

The last three were included for purposes of long-term, "out-of-the-box" thinking that goes beyond the more traditional optical applications.

A general conclusion reached is that for any of these materials to become widely used, their cost needs to come down substantially. This probably means some form of online processing, e.g., CVD on a float line. In fact, economical manufacturing methods limit the markets for virtually all specialty coatings.

A second important point evident throughout the discussions is that, although many of the materials discussed are exotic and have only niche markets (if any) today, the challenges faced in making/manufacturing them now will also be faced in the near future by the flat glass (and possibly other segments) of the industry as they try to mass-produce these materials. As U.S. industry moves from low-value commodities to high-value-added, high-tech materials, the future of the glass industry may be linked to successful development of these materials.

The technical goals outline by the Specialty Coatings working group are summarized in Table 6-1.

Electrochromics

This is perhaps the most obvious specialty coating and enjoys relatively high commercial and research interest. Electrochromic (EC) glass (also known as "smart glass" or "smart windows") is glass that can be darkened or lightened electronically. A small voltage applied to it will cause the glass to darken; reversing the voltage causes it to lighten. This capability

Table 6-1. Performance targets for specialty coatings on glass**.**

	Electrochromics	**Conductive**	**Optical**	**Semi-conducting**	**Catalytic**	**Modified Surface Energies**	**Nano Devices**
0 – 5	Solid state device (not laminated).	Mid-wavelength IR transmission. (3–5 μm)	0.1% Measurement & control over small areas.				
	Lifetime of 20–30 years (or appropriate to application.		High-rate deposition of TiO_2.				
	Improved IR-reflecting properties (auto glass).						
	Low cost ($10 / ft^2).						
5 – 10	Ability to make coatings online using CVD.	1Ω / square at low cost & transparent.	0.1% Measurement & control over large areas.	Good polycrystalline films (for display).		Controlled deposition of organics.	
			Transmit 70% visible and reflect 100% IR and UV.				
> 10	$2 / ft^2		New material sets for greater refractive index spread.		Photo catalytic with high lifetime & wide applications		Ability to deposit coatings on line at the nano scale.

allows for the automatic control of the amount of light and heat that passes through the glass, thereby presenting an opportunity for windows to be used as energy-saving devices. EC coatings could also fall under the category of flat glass, since a principal application for these coatings is for architectural purposes. However, automotive applications are also quite important and represent a current product (electrochromic mirrors, found primarily on higher-end vehicles in the U.S., are fairly common in Europe). In addition, EC coatings cannot yet be deposited on a float line and thus appear to fall more appropriately under the definition of a specialty coating.

Cost reduction is a key short (0–5 year) and mid-term (5–10 years) target for ECs. Within 5 years, it is hoped that the cost of these materials will be reduced to the order of $\$10/ft^2$, which represents an order-of-magnitude reduction from today's cost. A related 10-year target is to reduce the cost to less than $\$2/ft^2$, which would bring ECs into the economic range for widespread architectural use. There was some feeling that cost reduction was a higher priority than increasing the lifetime of the product, in that economics can drive improvements in quality. However, most seemed to feel that performance and cost go hand in hand, and that a sizable market cannot be developed without simultaneous improvements in product performance (in particular, lifetime) and reductions in cost.

Cost reductions of the magnitude contemplated probably require the ability to manufacture coatings on a float line using CVD, rather than the techniques typically used today. The latter include sputtering, electron-beam deposition, and sol-gel techniques, sometimes used in combination.

Key technical problems still must be solved before EC technology can become widely used. Aside from reducing its cost, a key objective for manufacturers is to increase the lifetime of EC coatings, which, if used in architectural applications, would typically be required to perform tens of thousands of switches over their 20–30 year lifetime. For automotive applications, the lifetime can be reduced somewhat, to 10 years / 150,000 miles. Present lifetimes are approximately an order of magnitude away from reaching this goal.

A key goal for automotive applications is the development of solid-state coatings that do not require lamination. Current materials must be protected from the atmosphere, since many of them will react with water or oxygen. Achieving this goal will both simplify the manufacturing process and increase product lifetimes. A second goal in this market is to improve the IR-reflecting properties of ECs in order to reduce the heat load on the vehicle. However, this could be accomplished by a nonswitchable coating and may not require electrochromic technology.

Conductive Coatings

Conductive coatings include materials such as tin oxide, tungsten oxide, and indium-doped tin oxide, which are transparent conductors and can be used for a range of optical and electronic applications. Examples of current and future (long-term) applications include touch screens, display panels (LCD), windshield defrosters, and highly reflective low-E architectural materials.

The two key goals for these materials are, first, to increase the mid-wavelength IR reflectivity (3–5 µm range) to improve the performance of these materials for low-E and related energy-efficiency applications and second, develop a low-cost method of producing transparent films with very low resistivity (< 1 ohm / square) over large areas. The films are needed not only so that these materials can be used in architectural applications, but also to improve the economics of using them in other applications (construction of smart windows, displays, automotive applications, etc.) where cost is a major driver.

Optical Coatings

This area includes reflective and antireflective materials, coatings that provide selective transmission (i.e., filters), and nonlinear optical applications. Here, a key short-term objective is to develop a high-rate, economical deposition method for titanium dioxide (TiO_2), which is a good high-refractive-index material whose principal use is as the dielectric in multilayer coatings. Titanium dioxide is also needed for antireflection coatings, where both a high- and a low-index material are required. Existing deposition methods (principally sputtering) are slow and temperamental, probably because the titanium targets tend to become poisoned. Alternative materials, such as niobium oxide, deposit more quickly, but are much more expensive.

In general, a wider range of materials is needed to expand the range of possible refractive indices. In particular, however, coatings that transmit 70% of visible light (the minimum required for U.S. automobiles), and can also reflect 100% (or nearly) of the IR and UV, must be developed in order to meet the goals set by automakers for the development of high-efficiency vehicles.

Finally, greater control over optical properties is required than is available today. An important short-term goal is to achieve 0.1% measurement and control capabilities over small areas (< 1 ft^2). In the long term, the industry needs to achieve the same standard for large areas by 2010. Current methods are accurate to only 0.4%.

Semiconducting Coatings

The primary applications for these materials are in the electronic-device markets. Here, high-quality films for display applications are needed. The ideal material would be an epitaxial (i.e., single crystal) film, but this is very difficult to achieve. Practically speaking, polycrystalline films would be acceptable, but their quality must improve over what is available currently. This is an area of high commercial importance to the glass industry because of the large volume of the market and high growth potential (see the overview of the specialty coatings segment above).

Novel Applications (Catalytic, Modified Surface Energies, and Nano-devices).

The following three areas go beyond the traditional optical applications just described:

1) Catalytic materials. Photocatalytic materials with long lifetimes and high durability would have a wide range of potential applications. Currently, the only material that has been developed significantly is TiO_2. Applications for TiO_2 include self-cleaning glass, not only for the food and health industries, but possibly for automotive and architectural applications as well. Such materials may also be able to function as sensors.
2) Films that modify surface energies. Organic films that can change the hydrophobicity, lubricity, etc. of glass are of interest. The objective in this area is to develop controlled methods for depositing these coatings.
3) Nanodevices. The ability to deposit coatings online at nm scales is a long-term goal (> 2010). There are many potential applications, including microscopic power sources, keyless entry, and on-window electronic devices.

Technology Barriers

Barriers in the specialty coatings area were broken down into three broad categories: process, measurement and control, and materials. The six barriers with the highest priority are evenly distributed across these three categories. Process barriers include a range of problems

common to the manufacturing of almost all specialty coatings. However, it also includes barriers specific to certain types of materials, such as electrochromics. The top priorities here are to develop the ability to consistently manufacture coatings on large pieces of glass and control the crystalline phase of the materials that are deposited. Measurement and control issues include feedback control, which is highly important because of the need to very tightly control process conditions and remain within the narrow tolerances specified by coating design models. The two highest priority barriers in this area are: 1) the lack of higher-precision intelligent process control and, closely related to this, 2) the inability to measure coating properties reliably and accurately across large substrates. Materials questions generally fall into the field of materials science and concern the difficulty of achieving films with specific properties. Many issues here are related to film defects. The highest priority barriers are the short lifetimes for electrochromic materials and the poor durability and adhesion of coatings.

The complete list of barriers identified is given below with a brief summary. Table 6-2 also indicates the priorities assigned to each.

Process Barriers

General manufacturing

- No consistent manufacturing capability exists to produce conductive coatings on large pieces of glass (> 1 ft^2).
- The uneven quality of glass coming off the float line and its offline treatment (storage, packaging, etc.) yields nonuniform substrate properties for coatings. A related problem is the lack of a high-volume, high-rate cleaning process for substrates.
- It is currently impossible to maintain a “clean-room” environment during mass-production of coatings.
- Many deposition processes require vacuum conditions; need an open-air process (or at least one that operates at atmospheric pressure) that can produce coatings of high optical quality.
- To obtain high-density coatings at extremely high rates, a refined cathodic-arc deposition process is required. This technology is used currently to deposit metallurgical coatings on engine parts and can do so at very high deposition rates. However, it must be filtered because of the production of particles and is thus not sufficiently refined at present to yield coatings for optical applications.
- Existing CVD methods cannot deposit coatings over large areas with adequate control over purity. Process byproducts can cause coatings to deteriorate over time.
- Poor understanding of how to control defects such as pinholes caused by sputtering arc discharges and embedded target metal limit coating performance and quality. This problem is related to the condition of the substrate and its cleanliness.
- Manufacturing processes for specialty coatings are slow and low-yield in general, resulting in high costs.

Table 6-2. Technology barriers to meeting performance goals for specialty coatings on glass.

Process Barriers	Measurement & Control	Materials
Lack of consistent manufacturing capability to produce large pieces. ✪✪ ●●	No high-precision feedback process-control mechanisms. ✪✪ ●●●● ▲▲	Lack of good high-temp glass with correct chemical expansion for semiconducting films. ●
Inability to produce electrochromics at high yield ●● ▲	Lack of reliable, precise measurement tools for large substrates (product characteristics, process characteristics, real time, online (moving) x,y,z).	Short lifetime of electrochromics. ✪✪ ● ▲
Can't maintain quality of virgin glass coming off float line. ▲	Lack of analytical tools for quality control of film & surface properties. ●● ▲	Inferior quality of flexible coatings.
Don't know how to sputter MgF_2.		Inferior quality of bendable coating s.
Inability to maintain "clean room" in mass production.		CVD material set too small. ●●●
Inability to control TiO_2 phase, refractive index. ●●●●		
Refined cathodic-arc deposition process is needed.		Poor durability & adhesion of coatings. ● ▲▲
Lack of high optical quality open air process at ambient conditions (atmospheric P). ☆ ▲		High cost of silver.
Lack of understanding of ITO deposition processes. ●●		Lack of modeling capabilities for complex systems. ●
Poor control of uniformity & purity in CVD processes. ●		Response time too slow for electrochromics, especially for automotive applications.
Lack of high-volume, high-rate cleaning method for substrates.		Lack of phase control in optical coatings.
Improved defect control for sputtered coatings needed. ●●●●		Limitations in present set of conductive materials.
No high-rate deposition process for thick coatings of electrochromics over large areas. ●●		
Slow, low-yield manufacturing speed. ●		
Lack of nano-pump to deliver a few molecules on demand.		

Legend

Nonmanufacturer committee members ✪ = Top Priority ● = High

Manufacturer committee members ☆ = Top Priority ▲ = High Priority

Electrochromics

- Yields for manufacturing electrochromics are ≤ 20%, which limits their market penetration and applications.
- Deposition techniques for electrochromics and conducting coatings are limited to small areas and can't always deposit coatings of required thickness (0.5 µm) over large areas.

Other specific materials/processes

- Attractive high-index materials such as MgF_2 have no good manufacturing route (in particular, there is no method for sputtering fluorides).
- Inability to shift deposition processes to different regions of the material-properties phase space. For example, TiO_2 cannot be deposited at high rate with a given phase and index of refraction. This is probably because the process is not at equilibrium.
- The understanding of the sputter deposition process for indium tin oxide (the most common transparent conducting coating) is poor and inhibits effective process control and defect reduction. This is also true for optical coatings.

Measurement and Control

- Tolerances in specialty coatings can be extremely tight (e.g., ± 1–2 % on something already only 100–Å thick). Process control technologies don't have the requisite precision. More automation, on-board process intelligence to solve problems before they occur, turn-key operation (processes are too complex), active feedback control, and dependability are needed.
- Reliable and precise measurements of both product characteristics (surface quality, color, reflectivity, durability) and process parameters (temperatures, pressure, flow rate, gas concentration) for deposition on large substrates, which are common, are difficult. These measurements must be made in real time, online (i.e., while the substrate is moving), in three different directions, and in vacuum.
- Once coatings are manufactured, analytical tools for analyzing film and surface properties across a large substrate are lacking (quality-control issue).

Materials

Electrochromics

- The short lifetime of electrochromics limits their application. Parasitic electrochemical reactions, interfacial reactions (e.g., between electrolyte and oxide), and poor seal integrity are responsible for the short lifetimes.
- Response time for electrochromics is too slow for them to be widely used in automotive window applications.

Other materials

- For semiconducting coatings, there is no high-temperature glass whose thermal expansion closely matches that of silicon. This is a very important problem for displays.

- Flexible coatings used for touch panels on electronic devices such as personal digital assistants ("palm pilots") do not have the requisite flexibility. Deposition methods must be able to deposit on very thin glass ("microglass") and result in coatings that can flex in service.
- Bendable coatings (i.e., those that can be deposited, then bent into a desired shape, as for an automobile windshield) are inferior because of poor adhesion.
- Although CVD is perhaps the method of choice for high-volume, economical coating, the accessible material set is much too small.
- Coating durability and adhesion limits the use of many specialty coatings. For example, silver has poor durability to the environment and must be protected in some way, either by lamination, or preferably, by a second coating layer (yet to be developed). Photocatalytic coatings suffer poor adhesion, limiting their useful lifetime.
- The cost of silver, the most widely used (16 Mm^2 coated / year) IR reflector, is high relative to other materials that might be used. Silver is the most expensive transparent sputtering target material. Its present cost is $6 / oz, while other materials, such as aluminum, are much cheaper ($0.01 / oz). However, no material that can match the properties of silver has yet been found.
- Modeling capabilities for predicting materials properties are insufficient, although rapidly advancing DFT / pseudopotential methods are making it possible to predict materials properties with much higher precision. It is now possible to model systems with up to 200 atoms / unit cell with 1% accuracy and up to 10,000 atoms / unit cell with 20% accuracy, suggesting that theory and computational power are reaching the point that extension of this science to simulation of coatings is feasible.
- Control over material phase in optical coatings currently does not exist. The optical properties of, for example, anatase vs. rutile TiO_2 are different, but controlling the relative amounts of these materials that are deposited is not yet possible.
- The present set of conductive materials that could replace indium tin oxide is limited. A greater range of electron mobility and carrier density is needed.

Research Needs

Research needs in the specialty coatings segment of the industry are divided into five areas, three of which are strongly process related: Information, Manufacturing Processes, and Measurement and Control Standards. Research in the Information section addresses the need for more and better data concerning the properties of materials that either are now or may become of interest for possible coatings. The top research priority here is the need for a computational tool to rapidly screen possible new coating materials, a need shared by other industries. Research described in the Manufacturing Process section deals with problems associated with specific manufacturing processes. Two high-priorities for research are found here: the need to improve understanding of the titanium dioxide deposition process and the desire for a flexible, atmospheric-pressure deposition process. Measurement and control standards concern not only the development of new methods for measuring film properties, but also the definition of standards for both coatings and virgin glass that can be used to evaluate materials.

In addition to these areas, research needs specific to certain material types were also identified. Electrochromics contains three of the highest priority research needs: development of improved kinetic and thermodynamic models for simulating the formation and operation of these materials, the need for an online (probably CVD) method for manufacturing ECs, and the need for studies of the interface between ion conductors and the electrochromic layer. Under Conducting Materials, the need for improved solar-control films that can be bent and tempered

(for automotive windshields primarily) and lower cost conducting transparent films was highlighted.

A detailed list of the research needs identified for specialty coatings along with a brief description of each is given below. Relative priorities for these needs can be found in Table 6.3, as well as an indication of the time frame required to have an impact on the industry (near-, mid-, long-term, and ongoing).

Information

Modeling of materials properties

- Develop simpler software for predicting properties of materials. The thrust of this comment is a directive to academia to develop potent computer programs that nonexperts can use to predict properties of complex materials.

Databases

- Conduct a systematic research program and develop a tool to computationally screen possible materials. Models used or developed must work for real-world materials, i.e., those with defects, dopants, very thin layers, etc.
- Develop a website as a repository for key materials properties.
- Establish a virtual thin-film coating center (characterization and database management) to provide a central location where information concerning materials properties, literature references, deposition process, etc. can be obtained. There may be a role for professional societies in this activity, since they might be a good repository and could maintain the database.
- Conduct a round-robin exercise including manufacturers and suppliers to compare measured values for film properties obtained by various methods. Use this information in establishing standards. Encourage communication between companies.

Manufacturing Processes

- Develop a fundamental understanding of how to economically sputter TiO_2 with desired refractive index and clarity. This is a short-term goal that industry is already close to reaching.
- Develop next-generation large-area glass-cleaning tools. Very thin “microglass” is a particular problem. This is not a matter of fundamental understanding, but rather of practical (engineering) implementation.
- Develop better stain-inhibiting materials to protect glass.
- Develop patterning methods for deposition at the micro- and nanoscales.
- Develop an atmospheric pressure online or continuous batch coating process analogous to CVD processes used to coat float glass. This process must be flexible so that it can be easily modified to deposit a wide range of materials and thicknesses.

Table 6-3. Research needs to overcome barriers in specialty coatings on glass.

	Electrochromics	Information	Manufacturing Processes	Measurement & Control Standards	Conducting Materials
Near Term	Develop improved kinetic & thermodynamic, and electrochemical models for electrochromics. ✪✪✪✪✪	Simpler software that nonexperts can use to predict materials properties ● ○○	Economical sputtering methods for TiO_2 with desired index & clarity (fundamental understanding). ✪ ● ○	Standards for multilayer films ○○○ ◆	Modified ITO with alternative dopants. ○
	Reliable accelerated durability testing method for electrochromics. ○	Round robin to compare film data among glass manufacturers & suppliers	Next-generation large-area glass cleaning tools. ● ○○ ◆	Online grazing incidence x-ray analysis for process control ●	
	Interfacial studies between ion conductors / electro-chromics. ✪○		Improved stain inhibiting materials for glass protection. ◆	In situ optical full – width monitor to control process & monitor defects ●● ○ ◆	
				Simple, fast method for characterizing coatings composition to 0.1% ●	
				In-situ technique for measuring coating conductivity & other non-optical properties ○○ ◆◆	
				Determine properties of a clean room	
Mid-Term	Electrochromic switching methodologies to improve speed, lifetime. ○ ◆		Develop patterning methods for deposition at micro- & nano-scale. ○○	Understand factors affecting "aging" of glass & how changes in surface affect coating ▲▲	Reliable, stable, low cost, high-utilization sputtering source for ITO. ●
	Electrochromics with higher contrast ratios . ○○		Develop flexible atmospheric pressure deposition processes. ✪ ● ▲	Establish a "standard" glass surface ○	Screen potential new transparent conducting materials. ● ○ ◆◆
			Liquid to gas phase delivery equipment for lg. areas (in CVD) (Pilot scale facility?). ●	Quantifiable, consistent adhesion tests and standards ○○○	Bendable & heatable solar-load reduction films (<2Ω / square). ✪ ●●

Legend

Nonmanufacturer committee members ✪ = Top Priority ● = High Priority ○ = Medium Priority
Manufacturer committee members ☆ = Top Priority ▲ = High Priority ◆ = Medium Priority

Table 6-3. Research needs to overcome barriers in specialty coatings on glass. (continued)

	Electrochromics	Information	Manufacturing Processes	Measurement & Control Standards	Conducting Materials
Mid-Term			Develop electrochemical understanding of silver passivation interface. ○	Fuzzy logic development for process control.	
				Unified PLC-based system for measurement/control of flows. ●●	
				Improved glass substrate characterization and surface quality. ▲	
Long Term	Develop a CVD-deposited electrochromic film. ✪● ○				ITO replacements. ●●●
Ongoing		Systematic program to computationally screen possible materials. ✪ ○○	Alternatives to existing coating methods. ● ○○		Low-cost transparent conducting films. ☆○ ◆
		Website of key materials properties. ○○	Energy adders to deposition process. ●		
		Virtual thin-films coating center. ●			

Legend

Nonmanufacturer committee members ✪ = Top Priority ● = High Priority ○ = Medium Priority
Manufacturer committee members ☆ = Top Priority ▲ = High Priority ◆ = Medium Priority

- Develop reproducible and durable equipment to vaporize liquid precursors that can be used in large-area deposition. A pilot-scale facility may be needed here.
- Develop an understanding of the electrochemistry of the silver/passivation-layer interface (low-E coatings).
- Explore alternative coating technologies to replace existing methods (sputtering and CVD). Examples include sol gel, plasma spray, arc deposition, and laser ablation.
- Investigate energy adders to the deposition process (i.e., ways to pump energy into the process while the film is being formed). An example of this is plasma-enhanced CVD, which can speed up surface reactions. Another is the use of ion bombardment during e-beam evaporation to produce air-stable coatings.

Measurement and Control Standards

Standards

- Design standards for multilayer films: thickness, shading coefficient, optical properties (*n* and *k* values of the index of refraction).
- Define a "standard" glass surface for use as a baseline substrate.
- Develop quantifiable, consistent adhesion tests and standards.

Measurement techniques/process control

- Develop online grazing-incidence X-ray analysis. This is being done now, but the technique needs to be made robust for the manufacturing environment.
- Develop an in situ optical full-width monitor to control the deposition process and obtain information on defects. Must be able to process multiple sheets of glass at a rate of two 144 in. _ 100 in. sheets / minute or one 3.2 m _ 6 m sheet every 45 s.
- Develop a simple, fast method to characterize the chemical composition of coating to ± 0.1%. The method needs to cost less than present ones (such as fluorescence) and be capable of online measurement. It is possible to do this now, but the available techniques are too expensive.
- Develop an in situ technique for measuring coating conductivity and other nonoptical properties.
- Determine the properties of a clean room: what is a clean room as far as coatings manufacturing is concerned (not the same as in IC manufacturing)? What level of cleanliness is needed to significantly reduce defects?
- Develop / implement fuzzy logic for process control.
- Develop a standard (PLC-based) measurement and control system for flow control.

Quality control

- Understand the factors that influence "aging" of glass and how changes in the surface affect coatings.
- Develop improved methods for characterizing glass substrates and determine how to clean and characterize them.

Electrochromics

- Develop improved kinetic and thermodynamic models for electrochromics to understand both performance and processing. A detailed electrochemical model is also needed.
- Develop a reliable accelerated durability testing method. Standards for calibrating this method are now under development.
- Understand the processes occurring at the interface between ion conductors and the electrochromic layer.
- Develop new switching methodologies to improve speed and lifetime of these materials.
- Develop electrochromic materials with higher contrast ratios (< 1% transmission). Make the material dark enough that mechanical shading devices (drapes, etc.) are no longer necessary. The primary application here is for architectural uses in which night / back-illuminated situations occur.

- Develop an atmospheric-pressure, online CVD method for economical production of electrochromics.

Conducting Materials

- Modify indium tin oxide (ITO) deposition processes to substitute different dopants for indium.
- Develop a reliable, stable, low-cost, high-utilization sputtering source for ITO.
- Screen materials for their potential as transparent conducting materials.
- Develop improved solar-load reduction films that can be bent and heated. Need sheet resistances less than 2 Ω/square.
- Develop low-cost replacements for ITO, which is comparable in price to silver. In addition, its transparency is highly dependent on the sheet resistance (for example, 80% transmission can be achieved from 20 Ω/square material, while only 70% transmission is possible if the resistance is 5 Ωs/square).
- Develop lower-cost conducting transparent films, including manufacturing and processing.

Appendix A: Coatings on Glass Workshop Agenda

Monday evening, January 17.

6 p.m. Reception at Wente's Sparkling Wine Cellars

Tuesday, January 18.

7:30 a.m. Registration. Juice and coffee available. *Combustion Research Facility Lobby*.

8:00 Introductions: Mark Allendorf (Sandia National Laboratories). *Auditorium*
Background of the workshop / Statement of objectives: Vince Henry
Workshop format and roles: Jack Eisenhauer (Energetics Inc.)

8:20 Overview presentations / Industry representatives:

Flat glass (Rick McCurdy, Libbey-Owens-Ford Co.)
Container glass (Clem McKown, Elf-Atochem)
Fiberglass (Les Campbell, Owens-Corning Inc.)
Specialty glass (Carl Lampert, Star Science)

10:20 Break (juice, coffee, pastries). *Auditorium Lobby*

10:30 Status of coating science and technology

CVD chemistry (Roy Gordon, Harvard)
Surface / interface interactions (Carlo Pantano, Penn State)
Characterization (Scott Misture, Alfred Univ.)
Theoretical / modeling approaches (Mike Teter, Cornell Univ.)

12:30 Lunch. *Mezzanine.*

1:45 Breakout session 1: Breakdown along industry sectors. Where does industry want to be in 0-5, 5-10, >10 years; identification of barriers to progress and ranking of relative importance. *Conference rooms 117, 210, 217, 229.*

3:15 Break. *Mezzanine.*

5:15 Wrap up comments; dinner logistics. *Auditorium.*

6 p.m. Dinner at Wente's Restaurant

Wednesday. January 19.

7:45 a.m. Juice and coffee available in the Auditorium Lobby.

8:00	Opening remarks, Theo Johnson (DOE / OIT). *Auditorium*
	Summary presentations by working-group leaders
9:10	Breakout sessions 2. Roadmapping exercise. Determine R&D required to achieve goals; prioritize. Identify stakeholder roles. *Conference rooms 117, 210, 217, 229*
10:30	Break. Juice, coffee, pastries. *CRF Mezzanine*
Noon	Lunch. *Mezzanine.*
1:00	Breakout sessions 2 (continued). Session to continue discussions initiated during morning session. *Conference rooms 117, 210, 217, 229*
2:00	Break. *Auditorium lobby.*
2:15	Plenary summaries; refreshments. *Auditorium.*
	Closing remarks
4:00	Adjourn

Appendix B: Attendees

Dr. Mark Allendorf
Sandia National Laboratories

Dr. Jon Bauer
Johns Manville Technical Center

Dr. Ted Besmann
Oak Ridge National Laboratory

Dr. Edward Boulos
Visteon Glass Division

Mr. Les E. Campbell
Owens Corning

Dr. James J. Finley
PPG Industries

Dr. Donald Foster
Lawrence Berkeley National Laboratory

Dr. Robert J. Gallagher
Sandia National Laboratories

Prof. Roy Gordon
Harvard University

Mr. Michael Greenman
GMIC

Dr. Marvin Gridley
Ball-Foster Glass Container Co.

Dr. James Hamilton
Johns Manville

Dr. Don Hardesty
Sandia National Laboratories

Dr. Vincent Henry
Henry Technology Solutions

Dr. Russell Hill
BOC Coating Technology

Mr. Theodore Johnson
US Department of Energy

Dr. Moe Khaleel
Battelle, Pacific Northwest National Lab.

Dr. Carl Lampert
Star Science

Dr. James Lingscheit
BIRL / Northwestern University

Mr. Joseph Loibl
Visteon
Fairlane Business Park

Dr. Peter Martin
Battelle, Pacific Northwest National Lab.

Dr. Richard J. McCurdy
Pilkington LOF

Dr. Anthony McDaniel
Sandia National Laboratories

Mr. Clem McKown
Elf Atochem North America, Inc.

Mr. Darryl Middleton
Visteon
Fairlane Business Park

Dr. Scott T. Misture
Alfred University

Mr. Tyler L. Moersch
Aspen Research

Mr. Steve Nadel
BOC Coating Technology

Prof. Carlo G. Pantano
Penn State University

Mr. Greg Piserchia
3M

Dr. Denis Postupack
Coca Cola Co.

Dr. Michael Rubin
Lawrence Berkeley National Laboratory

Dr. David Russo

Elf Atochem

Dr. Steve Sapers
Optical Coating Laboratory, Inc. (OCLI)

Dr. Steve Selkowitz
Lawrence Berkeley National Laboratory

Mr. R.P. Shimshock
Southwall Technologies

Dr. Charles Sorrell
US Department of Energy

Dr. Karel Spee
TNO Institute of Applied Physics

Prof. Michael Teter
Cornell University
LASSP, Clark Hall

Dr. Peter Walsh
Sandia National Laboratories

Dr. Xingwu Wang
Alfred University

Dr. Sicco Westra
Southwall Technologies